The Studies of Fullerenes and Metallofullerenes in Geometry, Electron Transfer, Chromatography and Characterization

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> Doctor of Philosophy In Chemistry

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ABSTRACT

Since their discovery, fullerenes and metallofullerenes have been investigated regarding their structures, synthesis, isolations, and applications. The highly symmetric structures of fullerenes and metallofullerenes lead to extraordinary physical properties, such as electron transfers, and attract major attention from the science community. It has been well established that the stabilities of fullerenes and metallofullerenes can be estimated by recognizing structural patterns. Recently, we developed a generalized spiral program and additional codes and believe they are useful for fullerene/metallofullerene researchers. The higher fullerenes, those with more than 90 carbon atoms, also follow certain structural patterns. In our studies, we have shown that the higher fullerenes with tubular structures are stable in thermodynamics and can survive the aminopropanol reaction, but other spherical fullerenes cannot. For the past three decades, great efforts have been devoted to applying fullerenes and metallofullerenes as electronic materials. In our studies, we find the ground state electron transfer properties endow metallofullerenes as an ideal material for perovskite solar cells to enhance the stabilities. It has been shown in our investigations that common metallofullerenes, such as $Sc_3N@C_{80}$, are capable to be as the electron transfer layers in perovskite solar cells, and the test demonstrates that our

novel perovskite solar cells may achieve high stability and high efficiency. The electron transfer abilities of metallofullerenes are studied with the $M_2(a)C_{79}N$ since electron densities located in between the two metal atoms convert between a single electron bond and a double electron bond. The huge spherical electron delocalized structures of fullerenes and metallofullerenes lead to strong interactions with other delocalized systems, such as graphene. Previous studies have shown that graphene has a unique ability in molecular adsorptions. However, the graphene surface is not always flat and the rippled areas have effects on the packing styles. Therefore, we examined the behavior of fullerenes on the rippled graphene surface and then compared with another flat molecule, PTCDA. The results show that the effect of rippled areas varies due to molecular structures. This study gives instructions for electronic device manufacturing using graphene and fullerenes. In our studies, polarizability is a key factor of fullerenes and metallofullerenes. It has been shown that the chromatographic retention behavior has a strong relationship with the average polarizability of a molecule. Based on the experimental data, we built a model for the prediction of chromatographic retention times using computational polarizabilities. After that, we validated the model by two series of chromatographic data. The characterization of carbon-based materials has been long investigated. In the last chapter, we introduce a dynamic nuclear polarization-based method to characterize the structures of chars and studied the adsorption of oxygen on the activated radical sites. Overall, the dissertation reports my Ph. D. studies in the areas including theoretical studies of fullerene geometries, chromatographic models, applications and also experimental studies of the applications of fullerenes/metallofullerenes and characterization.

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GENERAL AUDIENCE ABSTRACT

Fullerenes and metallofullerenes are important materials for engineering and science. In general, a fullerene cage contains only carbon atoms and has a closed spherical structure. Theoretically, for a given number of carbon atoms, there are thousands of different ways to assemble a fullerene structure, just like assembling Lego. However, just a limited number of fullerene molecules have been discovered. In the past four decades, several theories have been proposed to explain the fact. For example, an isolated pentagon rule shows that the fullerene structures should not have any conjugated pentagons, which will decrease the stabilities of fullerene molecules. In this dissertation, I would like to show our results, which demonstrate fullerenes that can be synthesized follow certain patterns. We apply experimental and theoretical methods to discover the patterns and explain the reason. The application of fullerenes/metallofullerenes is another hot topic. We consider the structures of fullerenes endow them extraordinary abilities of electron transfers. Therefore, we use metallofullerenes as electron transfer material in a solar cell, and we have a good solar cell with high efficiency. We also inspect the interactions between fullerenes and rippled graphene surface. The results are also extended to understand the chromatographic behavior of fullerenes. By considering the physical properties of fullerenes, we build up simple models to simulate the chromatographic retention behaviors of fullerene inside the chromatographic column. The characterization of carbon-based material is a big challenge and in this dissertation, we demonstrate our contributions of a novel method for characterization, which can detect activated carbons.

ATTRIBUTIONS

The dissertation reports my progress in fullerene/metallofullerene studies and is written mainly based on the following published or submitted papers, in which I am listed as the first author or co-first author:

1. Liu, X.; Zuo, T.; Dorn, H. Polarizability effects dominate the chromatographic retention behavior of spheroidal and ellipsoidal metallofullerene nanospheres, *J. Phys. Chem. C* 2017, 121, 7, 4045-4049

2. Liu, X.; Zuo, T.; Dorn, H. DFT prediction of chromatographic retention behavior for a trimetallic nitride metallofullerene series, *Inorg. Chim. Acta* 2017, 468, 316-320

3. Li, Y.; Liu, X. (co-first author); Chen, C.; Duchamp, J.; Huang, R.; Chung, T.; Young,
M.; et, al. Differences in self-assembly of spherical C₆₀ and planar PTCDA on rippled graphene surfaces, *Carbon*, 2019, 145, 549-555

4. Liu, X.; Koenig, R.; Seeler, T, Tepper, K.; Franklin, H.; Wang, X.; Huang, R.; Shanaiah, M.; Dorn, H.; Stevenson, S. Tubular Allotropes of Carbon: A New Series of Five-Fold Symmetry C₉₀, C₁₀₀, C₁₂₀, C₁₅₀, C₁₈₀, and C₂₀₀ Fullerenes or [5,5] End-Capped Carbon Nanotubes? *under review*, 2019

5. Wang, K.; Liu, X. (co-first author); Huang, R.; Wu, C.; Yang, D.; Hu, X.; Jiang, X.; Dorn, H.; Priya, S. Endohedral Metallofullerenes Doped Spiro-OMeTAD for Efficient and Stable Halide Perovskite Solar Cells. *ACS Energy Lett.*, 2019

6. Liu, X.; Gu, J.; Wightman, J.; Dorn, H. Elucidation of Oxygen Chemisorption Sites on Activated Carbons by Flow Dynamic Nuclear Polarization. *under review*, 2019

A small portion of data and discussion is from the following partially completed manuscripts:

Liu, X.; Li, Y. (co-first author), Huang, R.; Duchamp, J.; Kirkpatrick, K.; Tao, C.;
 Dorn, H. Computational and TEM studies of Gd₃N@C₈₀ on the graphene surface.

2. Liu, X.; Huang, R.; Kirkpatrick, J.; Duchamp, J.; Dorn, H. The preparation of $Sc_2@C_{79}N$ and $La_2@C_{79}N$ reveals the nature of single electron bond.

3. Velkos, G., D. S. Krylov, K. Kirkpatrick, **X. Liu**, L. Spree, A. U. B. Wolter, B. Büchner, H. C. Dorn, and A. A. Popov. "Giant exchange coupling and field-induced slow relaxation of magnetization in $Gd_2@C_{79}N$ with a single-electron Gd–Gd bond." *Chem. Commun.*, 2018, 54, 2902-2905.

Any published or submitted paper, in which I am not a major contributor, is not included in the dissertation.

A brief summary of my work on the generalized spiral programs is introduced as a part of the background for the geometry studies. The key part of the generalized spiral program code and the manual is available in my master thesis at Virginia Tech:

Liu, X. Generation of heptagon-containing fullerene structures by computational methods. Diss. Virginia Tech, 2016, https://vtechworks.lib.vt.edu/handle/10919/83480

Other program codes are included in the thesis are available upon request.

Results from the above papers, thesis and projects have been reorganized due to the subjects and the chronological order. **Chapter 1** introduces the fullerene geometry studies and the separation of a series of tubular fullerenes from C_{60} to C_{100} . The separation is understood based on the molecular polarizability distributions, which dominate the reactivity of fullerenes. The polarizability is a dominant factor for chromatographic retention behavior. The chromatographic retention behavior studies and models are introduced in **Chapter 3**. **Chapter 2** demonstrates our fundamental studies in the electron transfers between fullerenes/metallofullerenes have been shown as ideal materials for perovskite solar cell electron transfer layers to enhance the stabilities and obtain high efficiency at the same time. **Chapter 4** is a summary of the application of dynamic nuclear polarization on carbon-based material characterizations.

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Life is a long journey to collect beautiful memories.

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Chapter 1 Geometry Studies of Fullerenes/Metallofullerenes and Applications

Since their discovery, the highly symmetric spherical structures of fullerenes and metallofullerenes have attracted major attention from the science community.¹ For the past three decades, great efforts have been devoted to obtaining fundamental understandings as well as to exploring applications.²⁻⁴ It has been shown that the physical properties of fullerenes/metallofullerenes may be estimated by decoding the structural patterns.^{5–8} Shortly after the synthesis of the first several fullerene isomers, it has been realized that the arrangements of fullerene faces dominate the stabilities of isomers, and the observation is summarized as the isolated pentagon rule (IPR).⁹ Then the relationship between geometric structures and stabilities is extensively investigated and related computer algorithms and programs were developed.^{10,11} Currently, quantitative models are reported to estimate the energies of fullerenes and metallofullerenes mainly based on the geometric motifs.¹² These investigations regarding the fullerene geometries provide not only convenient tools for fullerenes research but also a novel view for understanding fundamental questions of fullerenes, such as the formation mechanisms.¹³ In the classical definition, fullerenes contain only pentagonal and hexagonal faces. However, it has been suggested by experimental observations and theoretical studies that fullerenes with heptagonal faces are essential intermediates connecting fullerenes of different sizes.^{14–16}. The first heptagon-containing metallofullerene has been synthesized and reported.¹⁷ In this chapter, I would like to give a brief summary of fullerene geometric studies and introduce our results related to fullerene geometries. Recently, we discovered a series of high fullerenes with the pattern of D_{5h} and D_{5d} symmetries. In this chapter, the synthesis, isolation and theoretical explanations are reported.

1.1 Fullerene Geometry Study

A fullerene is a carbon allotrope in the form of a spherical shape. C₆₀-I_h is the first discovered fullerene molecule with a soccer ball structure. C₆₀ is named as Buckminsterfullerene after the famous architect, Buckminster Fuller. The hollow structure endows fullerenes as ideal containers for various inner clusters, and fullerenes with other species encapsulated in the cages are known as endohedral fullerenes.^{2,18} Nowadays, a large family of metallofullerenes with different metal clusters have been reported.² Among these known isomers, trimetallic nitride template (TNT) endohedral metallofullerenes (EMFs) are one of the most important families due to the high yield and the potentials for applications.¹⁹ In the meantime, the development of chromatographic techniques also provides more possibilities to obtain new fullerenes isomers.²⁰ On the other hand, fullerene isomers, because of their uniform spherical shapes, are ideal probes to study mechanisms of chromatography to improve the chromatography instruments and methods.²¹

Significant progress has been achieved in both fundamental and applied research of fullerenes/EMFs for the past three decades. Previous studies demonstrate that EMFs are potential materials for photovoltaic,^{22,23} biomedical²⁴ and electronic applications.^{25,26} Especially, Gadolinium-based metallofullerenes have been utilized as the contrast agents for diagnostic magnetic resonance imaging (MRI), and several articles have been published reporting the current progress.^{24,27} In a seminal study, Dorn and co-workers demonstrated that Gd₃N@C₈₀ derivatives had advanced ability for cancer detection. Another essential topic of fullerenes and metallofullerenes is the formation mechanism,

and it is still an open question. The formation mechanism is closely related to fullerenes geometries since structure transformations are inevitable and critical for the formations.²⁸ Generally, there are two major categories of models for fullerene formation mechanisms, which involve a top-down approach and a bottom-up approach, respectively. Several versions of "bottom-up" theories have been proposed suggesting a pathway starting from C₂ unit to carbon chains, rings and eventually fullerene cages. In recent years, evidence in laboratory and in interstellar observations suggest a quite different mechanism, which suggests the formation starts from graphene and involves a "top-down" approach.²⁹⁻³¹ One of the strong support arguments for the top-down mechanism is the transmission electron microscopy (TEM) observation that graphene can roll up and produce semifullerene species.²⁹ Recent astronomical studies report that graphene and fullerenes, especially C₆₀, exist in interstellar space.³¹ Since the interstellar condition is too cold to provide the required condition for bottom-up formation, fullerenes in interstellar space are possibly formed through a top-down mechanism. Although the discussion is still going on, these studies help people obtain fundamental understandings of fullerenes and metallofullerenes. There are many common assumptions in both bottom-up and top-down mechanisms, which are supported by experimental observations and theoretical studies.

Although it was proposed that fullerene may transform among different isomers, direct evidence was absent until recently. Zhang et al. demonstrated that asymmetric metallofullerenes $Y_2C_2@C_1(51383)-C_{84}$ and $Gd_2C_2@C_1(51383)-C_{84}$ are able to shrink to highly symmetric C_{80} cages.³² The results validate the assumption that fullerenes may convert to other isomers to achieve energy minima. The transformation details are still not clear, and a possible way includes a Stone-Wales (SW) rearrangement and via

heptagon-containing fullerene intermediates. The molecular level evidence not only validates the transformation process but also provides strong evidence for a top-down mechanism. Based on the experimental observation, Zhang et al. proposed a fullerene transformation map involving heptagon-containing fullerenes, and the transformation includes C_2 loss and the SW rearrangements.³³ Shortly after that, the first heptagon-containing fullerene isomer, LaSc₂N@C_s(hept)-C₈₀ was synthesized in the laboratory utilizing an arc-discharge technique.¹⁷ Two classical isomers, LaSc₂N@I_h-C₈₀ and LaSc₂N@D_{5h}-C₈₀ are found at the same time and just a tiny fraction is the heptagon-containing fullerene, although all these three metallofullerenes are at almost the same energy level. The results indicate that the heptagon-containing fullerenes are kinetically unstable and may prefer to converting to stable classical fullerenes if possible.

As demonstrated in the formation mechanism studies, the structural studies of fullerenes/EMFs remain one of the most essential topics in fullerene research. It has been recognized that there is a relationship between the fullerene structures and their physical properties. Shortly after the discovery of the first fullerene, it has been recognized that the distribution of pentagons on fullerene cages has a major effect on fullerenes' stabilities. It is from the observation that for each given number of carbons atoms, thousands of hundreds of isomers are possible, however, only a tiny fraction of these isomers have been isolated. The experimental results and theoretical computations suggest that conjugated pentagons decrease stabilities of fullerenes dramatically. The result has been summarized as the isolated pentagon rule (IPR), which at the first time connects the structural patterns with a physical property, stability. The IPR is a qualitative and empirical rule, and although none of empty-cage fullerene violates the IPR, non-IPR

been synthesized and reported.^{34,35} Two metallofullerenes have non-IPR metallofullerenes, $Sc_3N@C_{68}$ and $Sc_2C_2@C_{66}$, were reported by Dorn group and Shinohara group independently at almost the same time in 2000.^{36–38} After that, several other non-IPR metallofullerenes were produced and reported.^{39,40} Nowadays, it has been realized that the encapsulated clusters may change the electron density distributions on the fullerene cage and therefore the IPR is not strictly obeyed by metallofullerenes.^{41,42} Although the details of the inner cluster effect are still unclear, several results are very instructive and lead to better understandings of the fullerene stabilities. In previous studies, it has been proposed that the transferred electrons from the inner clusters are located on the pentagon-pentagon edges and then increase the stabilities of fused pentagon on metallofullerene cages.² After that, Zettergren et al. proposed that the structure of fullerene may be represented as several motifs and the stabilities of fullerene isomers are able to be estimated by counting motifs.⁵ As a brief summary, they believe that the stabilities of charged fullerenes or metallofullerenes are controlled by two key motifs, the electrophilic pentalene motif and the electrophobic pyrene motif. The distribution of these two kinds of motifs dominates the stabilities of the fullerenes and metallofullerenes. Uniformly distributed pentalene and pyrene motifs may dramatically decrease the Coulomb repulsion between charges and then stabilize the fullerene cages. Another key factor is the amount of charge on the fullerene cages, and normally a cage with six negative charges are ideal and have high stabilities.¹² In 2014, Wang et al. reported the first quantitative model using motifs for metallofullerenee energy estimations. They believe the energy of a metallofullerene is dominated by the numbers of seven motifs and a linear regression utilizing the seven motifs as variables can ideally estimate the energies. They compared the estimated energy data from their model with those from quantum chemistry computations and observed a good agreement between the two datasets. The linear regression model is rather simple to provide high accuracy results.

1.2 Generalized Spiral Algorithm and Program

In our previous work, we developed a program based on a modified spiral algorithm and added numbers of functions to the program to obtain useful information of fullerene structures, such as Hamiltonian cycles and conjugation tables. The background knowledge of the program and the algorithm are also interesting and I would like to give a brief summary.⁴³

Fullerenes are molecules with spherical structures. A fullerene cage is a polyhedron in a mathematics perspective. All fullerene cages are convex polyhedral and Euler's polyhedral formula is applied to figure out the relations among numbers of edges, vertices, and faces. Each vertex of the fullerene polyhedron is a carbon atom and each carbon atom has three bonds connecting its neighbors due to the sp² hybridization. Therefore, we may build two formula using three variables, which are numbers of edges, faces, and vertices. For classical fullerenes, this calculation is available in most articles regarding the fullerene structures and is also included in my previous thesis. The generalized spiral program is designed to calculate not only classical fullerene structures but also non-classical fullerene structures. Here, I would like to use one heptagon-containing fullerene as an example and other non-classical fullerenes are calculated in the same way with minor changes of the formula.

If we use p, h and hp represent the numbers of pentagon, hexagon, and heptagon, respectively, then the following two equations are true:

$$\begin{cases} \text{Relation between faces and edges:} \\ \frac{(5p+6h+7hp)}{3} = n \\ \text{Euler's polyhedron formula:} \\ hp+p+h-\frac{n}{2} = 2 \end{cases}$$
(1.1)

Obviously, the values of p, h, and hp depend on each other. Then we can solve the equation system and get the result:

$$\begin{cases} hp = p - 12 \\ h + 2hp = \frac{n}{2} - 10 \\ 2p + h = \frac{n}{2} + 14 \end{cases}$$
(1.2)

Similarly, if a fullerene contains other polygonal faces, the relations of different polygons are calculated based on Euler's polyhedral formula.

Adjacency matrices are used in the program during the calculation to record the fullerene structures and remove any possible duplicates. An algorithm is also designed to check the validation of representation and find out different representations belonging to the structure of the same fullerenes. A quick idea is to convert the 3-dimensional fullerene structures to 2-dimensional graph using Schlegel projection, which is a one-to-one operation. It is also straightforward to implement a function to convert the projection graph back to a 3-dimensional cage. A spiral strip is applied to reach the faces on the projection with a specific order and then use the order sequence to represent the structure when we follow a certain rule for the spiral strip. This algorithm simplifies the checking step and it is also able to remove all duplicates. More detail about the spiral algorithm

and its generalized version is available in my previous thesis for a master degree. Although the algorithm has not been strictly proven mathematically, it has been shown that all fullerene isomers smaller than C_{380} has at least one possible spiral.^{44,45} Currently, the largest fullerene isolated is C_{100} by the Stevenson Group and Dorn Group, and they also reported the observation of C_{120} on spectra. As we know the brute-force algorithm to generate all possible structures is in exponential time, and the spiral algorithm reduce the time dramatically and is a polynomial time algorithm. The time complexity is estimated in the following way. The number of all possible structures with **n** atoms is calculated using the following equation:

$$\frac{\left(\frac{n}{2}+2\right)!}{12!\left(\frac{n}{2}-10\right)!}$$
(1.3)

If we assume each isomer requires one unit time to do the calculation, then the time is $O(\frac{\left(\frac{n}{2}+2\right)!}{12!\left(\frac{n}{2}-10\right)!}) \sim O(n^{12})$, which is also acceptable if the fullerene cage is not extremely
large. Normally, it takes around a week to calculate all possible structures of C₁₂₀ running
the clusters. The symmetry can also be calculated at the same time when we calculate
possible structures.

Nowadays, experimental observation and computational results have shown that fullerene structures not only control fullerene stabilities but also affect other physical properties. Zhang et al. reported that non-IPR fullerenes, which contain fused pentagon motifs (pentalene), always show significant dipole moments and enhanced solubilities in polar solvents.⁴⁶ It has been validated by measuring a series of Yttrium based TNT EMFs and by DFT computations. As we know, chromatographic retention behaviors of fullerenes

and metallofullerenes are primarily controlled by polarizabilities and dipole moments.⁴⁷ It has been well known that fullerenes and metallofullerenes with significant dipole moments have stronger dipole-dipole interactions with stationary phases that lead to longer chromatographic retention times.⁴⁷

1.3 Structural Patterns of Fullerenes/Metallofullerenes

Note: In the following section, I thank our collaborator Dr. Stevenson and his coworkers for providing the experimental separations and aminopropanol reactivity studies the for tubular fullerenes. I also thank Dr. Wang and her coworkers for running ¹³C NMR and analyzing the experimental data at the National Magnet Laboratory at Florida State. I did all the DFT calculations and prepared all the structural figures for this section.

Publications are ubiquitous for C_{60} and C_{70} fullerenes; yet few studies exist for pristine samples of higher fullerenes (*e.g.*, C_{90} and higher). Reasons for this paucity of literature include (1) typical yields less than 0.5%, (2) inefficient separation methods, and (3) only trace amounts of pristine and isomerically pure samples. Because the number of possible structural isomers increases with cage size, the complexity of fullerene extracts increases as well. Whereas $C_{60}(I_h)$ and $C_{70}(D_{5h})$ each have one structural isomer that obeys the isolated pentagon (IPR) rule, there are 46 and 450 candidate IPR structural isomers for C_{90} and C_{100} , respectively.¹⁰ If only HPLC is used, the co-elution of fullerenes and their structural isomers is often a very difficult obstacle to overcome. For example, multiple isomers of C_{90} have been chromatographically isolated^{48–51} and their structures determined by X-ray crystallography.^{49–51} The similarity of retention times among various C_{90} isomers on various HPLC columns is problematic. In the work of Xu *et al.*,⁴⁸ three unique stationary phases were needed. Their initial fullerene and metallofullerenes mixture first used a PYE column, then a Buckyprep column, and finally a Buckyprep-M column to finally resolve and isolate C_{90} isomers I and II. Subsequently, three structural isomers of C_{90} were isolated using a three-stage HPLC process of Buckyprep-M, Buckyprep, and PBB columns by Yang *et al.*^{49,50} Their crystallographic analysis indicated purified C_{90} samples of $C_1(30)$ - C_{90} , $C_1(32)$ - C_{90} , and the $D_{5h}(1)$ - C_{90} nanotube.^{49–51}

The rationale for using aminopropanol is the high reactivity of amines toward fullerene cages.^{52,53} The amination reaction with fullerenes has previously been leveraged into a separation method by immobilizing the amine moiety onto a solid support.^{54,55} Alternatively, the reaction can be done in solution by using the hydrophilic group (*e.g.*, – OH) of aminoalkanols to render fullerene contaminants water-soluble for subsequent removal with a separatory funnel.^{56,57}

In this work, the Stevenson laboratory has developed a new isolation method for purifying pristine samples of nanotubular fullerenes. In a single step with aminopropanol, we reduce the myriad of species to a simplified sample of predominantly two spheroidal fullerenes, C_{60} and C_{70} , and two tubular species, $D_{5h}(1)$ - C_{90} and $D_{5d}(1)$ - C_{100} . In addition, even though C_{120} or higher series members were not isolated in this study, mass spectral data clearly shows our methodology separates adjacent fullerenes. We also demonstrate DFT computations and the polarizability of carbon bonds to support the chemical separation protocol. We report UV-vis spectra and ¹³C NMR characterization for pristine samples of $D_{5h}(1)$ - C_{90} and $D_{5d}(1)$ - C_{100} . X-ray crystal structures have been obtained for chlorinated derivatives^{58,59} of these tubular species. The prior crystallographic work on $D_{5h}(1)$ - $C_{90}^{50,58}$ and the chlorination derivative of $D_{5d}(1)$ - C_{100}^{59} support their existence.

Our results suggest that isolated C_{90} and C_{100} are members of a larger [5,5] singlewalled carbon nanotube family. Scheme 1.1 shows that adding 10 belt carbons permits increasingly longer tubes with alternating D_{5h} and D_{5d} symmetry. The $D_{5h}(1)$ -C₉₀ and $D_{5d}(1)$ - C_{100} species represent just two of these family members. There is a unique feature of this [5,5] nanotubular family that involves the successive insertion of the five-hexagon (remove torus) rings between the caps. If an even number of rings is inserted between the upper and lower halve-C₆₀ caps, the caps remain spatially intact at the same positions, for example, $D_{5d}(1)$ - C_{100} . However, insertion of an odd number of five-hexagon (remove torus) rings requires rotation of the upper cap by $\pi/10$, $D_{5h}(1)$ - C_{90} .⁶⁰ The Fowler and Manolopoulos spiral program clearly shows the final subtle change in this spiral assembly from D_{5h} to D_{5d} symmetry.¹



Scheme 1.1 Family of nanotubular fullerenes created by the sequential addition of 10 belt carbons to elongate the tube length.

There is literature precedence by Achiba *et al*⁶¹ who suggest a transition from spherical fullerenes to tubular species as the number of carbons increases. A recent theoretical study by Bodner *et al*⁶⁰ discusses the growth of multiple units of 10 carbon increments in the progression of C₆₀ to C₇₀, to the polytopes of C₈₀, C₉₀, and beyond. These two literature sources, combined with the resistance of C₁₀₀ to the chemical attack described herein, suggest that C₁₀₀, like the D_{5h}(1)-C₉₀ structure, should also be considered a nanotube with fullerene hemispherical endcaps. Our ¹³C NMR experiments are consistent with D_{5d}(1)-C₁₀₀ having a tubular structure.

Scheme 1.2 describes an overview of our chemical approach to obtain samples enriched in $D_{5h}(1)$ - C_{90} and $D_{5d}(1)$ - C_{100} . The carbon cages of C_{60} and C_{70} become more watersoluble upon reaction with aminopropanol. The tubular $D_{5h}(1)$ - C_{90} and $D_{5d}(1)$ - C_{100} resist chemical attack and remain in the solvent. When the reaction is stopped, a separatory funnel removes the functionalized fullerenes in the aqueous layer (*e.g.*, aminated C_{60} and C_{70}). Not only do the $D_{5h}(1)$ - C_{90} and $D_{5d}(1)$ - C_{100} remain unreacted in the organic layer, *e.g.*, toluene, but the larger species of C_{120} , C_{150} , C_{180} , and C_{200} survive the chemical reaction as well, *vide infra*.



Scheme 1.2 Selective chemical reaction to isolate $D_{5h}(1)$ -C₉₀ and $D_{5d}(1)$ -C₁₀₀.

To test our hypothesis of increased reactivity for C_{60} and C_{70} fullerenes relative to the tubular $D_{5h}(1)$ - C_{90} and $D_{5d}(1)$ - C_{100} , 500 mg of fullerene extract (Alfa Aesar) was dissolved in 500 mL of toluene and soaked overnight. While stirring, 15 mL of aminopropanol was added. Aliquots were taken at 0.5, 1, 2, and 4 hours and analyzed by HPLC. As shown in **Figure 1.1**, the log of peak area versus reaction time suggests that C_{60} is the most reactive, followed by C_{70} , $D_{5h}(1)$ - C_{90} , and $D_{5d}(1)$ - C_{100} , which is the least reactive. The larger negative slopes for C_{60} and C_{70} indicate their greater reactivity toward aminopropanol.



Figure 1.1 Plot showing a reactivity trend of $C_{60} > C_{70} > D_{5h}(1) - C_{90} > D_{5d}(1) - C_{100}$.

To further understand the reactivity of $D_{5h}(1)$ - C_{90} and $D_{5d}(1)$ - C_{100} , four separate experiments were designed with 500 mg of extract, 500 mL toluene, and 15 mL of aminopropanol. The HPLC trace for the extract prior to reaction is shown in **Figure 1.2a**. **Figure 1.2b-1.2e** represent HPLC analyses of experiments with reaction times of 0.5 h, 5 h, 12 h, and 24 h, respectively. Clearly, the ratio of $D_{5d}(1)$ - C_{100} to $D_{5h}(1)$ - C_{90} improves as a function of reaction time. The more horizontal slope of the $D_{5d}(1)$ - C_{100} (**Figure 1.1**) and persistence of unreactive $D_{5d}(1)$ - C_{100} in solution (**Figure 1.2**) suggest a $D_{5d}(1)$ - C_{100} species that is the more chemically inert of these two species.

Wanting to leverage the reactivity differences of C_{60} and C_{70} versus $D_{5h}(1)$ - C_{90} and $D_{5d}(1)$ - C_{100} , we developed a two-stage process. In stage 1, we used aminopropanol to obtain a sample enriched in $D_{5h}(1)$ - C_{90} and $D_{5d}(1)$ - C_{100} . This first stage improves the percent abundance for $D_{5h}(1)$ - C_{90} and $D_{5d}(1)$ - C_{100} and solves the problem of contaminant structural isomers, which readily react and removed. Stage 2 is a fraction collection with a single HPLC column to isolate $D_{5h}(1)$ - C_{90} and $D_{5d}(1)$ - C_{100} nanotubes.

The enrichment levels for $D_{5h}(1)$ - C_{90} and $D_{5d}(1)$ - C_{100} at various reaction times can be compared. **Figure 1.3a-1.3c** show chromatograms wherein the percentage of $D_{5h}(1)$ - C_{90} improves from <0.05% (extract) to 4% (5 h) and to 6% (12 h). This increase from 0.05% to 6% is better than two orders of magnitude. Also in **Figure 1.3a-1.3c**, the percentage of $D_{5d}(1)$ - C_{100} improves from less than 0.01% in the extract to 4% after 5 hours of reaction time to 11% $D_{5d}(1)$ - C_{100} after 12 hours. This $D_{5d}(1)$ - C_{100} enrichment factor approaches three orders of magnitude. The use of HPLC fraction collection now becomes feasible and practical.

Samples corresponding to **Figure 1.2b-1.2e**, were injected into a PYE column (4.6 x 250 mm, SES Research) and fractions corresponding to the $D_{5h}(1)$ - C_{90} peak (11 min) and $D_{5d}(1)$ - C_{100} (19.2 min) were collected until a single HPLC peak (**Figure 1.3d**, **1.3e**) and single mass spectral peaks (**Figure 1.4d**, **1.4e**) were obtained. This data indicate a high purity (99.5+ %) for both $D_{5h}(1)$ - C_{90} and $D_{5d}(1)$ - C_{100} . Chromatographic conditions were 1 mL/min xylenes for the mobile phase and 360 nm detection.



Figure 1.2 HPLC chromatograms for (a) carbon soot extract and samples corresponding to reaction times of (b) 0.5 h, (c) 5 h, (d) 12 h, and (e) 24 h.



Figure 1.3 HPLC chromatograms for (a) carbon soot extract, species remaining in solution after (b) 5 h and (c) 12 h, and purified (d) $D_{5h}(1)$ - C_{90} and (e) $D_{5d}(1)$ - C_{100} .

The mass spectral data in **Figure 1.4** correspond to the samples shown in **Figure 1.3**. **Figure 1.4a** shows the miniscule abundance of $D_{5h}(1)$ - C_{90} and $D_{5d}(1)$ - C_{100} in the carbon soot extract. As the aminopropanol reaction proceeds, the percentage of $D_{5h}(1)$ - C_{90} and $D_{5d}(1)$ - C_{100} clearly increases.



Figure 1.4 LDI mass spectra for (a) carbon soot extract, (b-c) species remaining in solution after 5 h and 12 h, purified (d) $D_{5h}(1)$ -C₉₀ and (e) $D_{5d}(1)$ -C₁₀₀.

The chemical separation protocol provides a new avenue for isolating and purifying a new five-fold symmetry series of D_{5d} - and D_{5h} - C_{2n} (n=35, 40, 45, 50, 55, and 60) fullerenes. The chromatographic and mass spectral data show no evidence for the D_{5h} - C_{80} and D_{5h} - C_{110} species *vide supra*. The HOMO-LUMO gap has been extensively employed in describing the stability of fullerenes and metallofullerenes. As shown in **Figure 1.5**, the computational DFT HOMO-LUMO gaps roughly correspond to the relative abundances of D_{5h} - C_{70} , D_{5h} - C_{90} , D_{5d} - C_{100} and even D_{5d} - C_{120} . More importantly, the HOMO-LUMO gaps for the D_{5d} - C_{80} and D_{5h} - C_{110} species are ≤ 1 eV indicating the relative instability of these two fullerenes in this series.



Figure 1.5 The D_{5d} - and D_{5h} - C_{2n} (n=35, 40, 45, 50, 55, and 60) nanotubular fullerene series and DFT HOMO-LUMO gaps.



Figure 1.6 Color samples in vials. The samples from left to right are C_{60} (purple), C_{70} (reddish-orange), C_{90} (orange) and C_{100} (purple).

The colors of the five-fold symmetry fullerenes I_h -C₆₀ and D_{5h} -C₇₀ are compared with the pristine D_{5h} (1)-C₉₀ and D_{5d} (1)-C₁₀₀ samples in **Figure 1.6**. The UV-Vis experimental spectra were obtained for the isolated $D_{5h}(1)$ -C₉₀ and $D_{5d}(1)$ -C₁₀₀ species and compared to the DFT computationally predicted spectra as shown in **Figure 1.7**. The $D_{5h}(1)$ -C₉₀ spectrum in **Figure 1.7a** is a match for the $D_{5h}(1)$ -C₉₀ nanotube structure that was

previously published by Yang *et al.*⁵⁰ In that work, three C₉₀ isomers were characterized by UV-Vis with corresponding X-ray crystal structures.⁴ To our knowledge, our report is the first UV-vis for pristine $D_{5d}(1)$ -C₁₀₀, with no corresponding matching spectrum in the literature. Of note in **Figure 1.6** is the purplish color of $D_{5d}(1)$ -C₁₀₀ in solution. Dissolved in carbon disulfide, $D_{5d}(1)$ -C₁₀₀ has peak maxima at 410 nm, 661 nm, and a large peak at 574 nm that dominates the UV-vis spectrum. It should be noted that C₆₀ also has peaks at 540, 560, and 600 nm consistent with the complimentary purplish color of Ih-C₆₀ and D_{5d}(1)-C₁₀₀.⁶²



Figure 1.7 Experimental and DFT UV-Vis spectra for samples, in CS_2 , of (a) $D_{5h}(1)$ - C_{90} and (b) $D_{5d}(1)$ - C_{100} .

As previously indicated, there are 46 and 450 possible isolated pentagon rule (IPR) isomers for the C₉₀ and C₁₀₀ fullerenes, respectively.¹ A surprising feature of this large array of isomers is the absence of IPR isomers with high symmetry and correspondingly limited spectral ¹³C NMR lines. There is only one five-fold high symmetry IPR isomer for C₉₀, a D_{5h}(1)-C₉₀ isomer with expected 6 lines, (3 x10, 3 x 20).

The 125 MHz ¹³C NMR for isolated C₉₀ fullerene is shown in **Figure 1.8a** and consists of only 6 observed lines. This C₉₀ isomer has 4 pyracylene 6,6,5 carbon sites that range in chemical shifts from 153.6 to 133.7 ppm for the end-capped carbons to the belt carbons. The poor S/N ratio limits the predicted intensity ratios with the aberrant intensity peak at 153.6 ppm, but the other 6,6,5 peaks are in qualitative agreement. The 6,6,6 junction belt carbons exhibit ¹³C NMR chemical shifts of 132.2 and 128.5 ppm with the expected intensities of 10, 20, respectively. In addition, the DFT computational results for D_{5d}(1)-C₉₀ are in agreement with the experimental data and all predicted values are within ~2.5 ppm.



Figure 1.8 Experimental versus theoretically calculated NMR spectra for samples, in CS_2 , of (a) $D_{5h}(1)$ - C_{90} and (b) $D_{5d}(1)$ - C_{100} .

The C₁₀₀ fullerene has only 3 high symmetry isomers with fewer than 10 spectral lines, D_{5d}(1)-C₁₀₀ (2 x 10, 4 x 20), T(321)-C₁₀₀, (1 x 4, 8 x 12), and D₅(450)-C₁₀₀ (10 x 10). The isolated C₁₀₀ sample was limited by poor solubility in most solvents, but a ¹³C 200 MHz (18.8 T) NMR spectrum was obtained in *o*-d₄-dichlorobenzene and required 77 hours of scan time (**Figure 1.8b**). The C₁₀₀ isomer has 4 pyracylene 6,6,5 carbon sites that range in chemical shifts from 153.2 to 138.0 ppm for the end-capped carbons to the belt
carbons with approximately correct intensity ratios of 10, 10, 20, 20, and 20, respectively. The DFT 6,6,6 junction belt carbons have predicted ¹³C NMR chemical shifts of 124.9 and 126.8 ppm, but only a peak at 124.4 was observable in agreement with the most shielded carbon. However, the remaining ¹³C NMR signal is most likely concealed under the *o*-d₄-dichlorobenzene solvent. It should be noted that the ¹³C NMR experimental and computational data are only consistent for the $D_{5d}(1)$ -C₁₀₀ isomer since, 1) 5 out of the expected 6 ¹³C NMR experimental peaks are within 0.5-1.2 ppm of the DFT computational values, and 2) only the 6,6,5 carbon sites have the correct intensity ratios of 10, 10, 20, and 20, respectively for the D_{5d} isomer *vide supra*.

Of particular relevance to this study is the lower chemical reactivity of pristine $D_{5h}(1)$ -C₉₀ and $D_{5d}(1)$ -C₁₀₀ and C₁₂₀ toward amination with aminopropanol. In earlier reported DFT studies for the amination of [5,5] and [10,0] endcap nanotube carbons with methylamine, both 6,6 bonds paracyclene and 6,5 pentagon carbons exhibit exothermic formation energies in [5,5] and [10,0] nanotubes.⁶³ Later studies clearly show that the mono-addition of methylamine occurs at a specific 6,6 C-C junction (a-b bond, **Figure 1.9**) of the pyracylene unit in C₆₀ and the endcap of [5,5] caps of C₁₂₀ are significantly more energetically favorable in comparison with the addition to other 6,6 and 5,6 C-C junctions.⁶⁴

Sabirov has shown that a polarization model is useful for understanding the modes of ozone and diazomethane addition to higher fullerenes $C_{70}(D_{5h})$, $C_{76}(D_2)$, and $C_{78}(C_{2v})$, which have inequivalent double bonds.^{65,66} This polarizability model predicts the same 6,6 C-C junction as found for the earlier amination studies as illustrated in **Figure 1.9**, *vide supra*. The Sabirov approach considers the fullerene molecule as a polarizable

ellipsoid in a polar coordinate system (origin is at the center of mass of the molecule) and assigns each reaction center a point (different carbon atom) belonging to the polarizability ellipsoid and characterized by the polarizability ξ which is in the direction of the reaction center. The polarizability index Ξ was determined as the average between two adjacent sites (bond).

$$\xi = \left(\frac{\sin^2\psi\cos^2\varphi}{\alpha_{xx}^2} + \frac{\sin^2\psi\sin^2\varphi}{\alpha_{yy}^2} + \frac{\cos^2\psi}{\alpha_{zz}^2}\right)^{-0.5}$$
(1.4)

$$\Xi = 0.5 \left(\xi_1 + \xi_2\right) \tag{1.5}$$

As illustrated in **Figure 1.10**, a specific 6,6 C-C junction (a-b) exhibits a much larger polarizability index than any other carbon bond for the endcaps of $D_{5h}(1)$ - C_{70} , $D_{5h}(1)$ - C_{90} , $D_{5d}(1)$ - C_{100} , and $D_{5d}(1)$ - C_{120} . Although a second bond (b-c) slightly exceeds the Sabirov criteria for low reactivity ($\Xi < \alpha_{av}$), the earlier DFT amination studies and the significantly greater reactivity predicted by the polarizability index for the a-b bond suggest greater reactivity for the a-b bond. Thus, the polarizability index predicts high chemical reactivity for only one type of 6,6 bond (10 bonds total) in the endcap of these [5,5] tubular fullerenes. Since the trend for the five-fold symmetry series $D_{5h}(1)$ - C_{70} , $D_{5h}(1)$ - C_{90} , $D_{5d}(1)$ - C_{100} , and $D_{5d}(1)$ - C_{120} has an increasing number of non-reactive bonds ($\Xi < \alpha_{av}$) relative to the more reactive 6,6 bond, the reaction rate should decrease as found experimentally with aminopropanol, (**Figure 1.1**). In addition, lower symmetry ellipsoidal and spherical isomers for C_{90} , C_{100} , and C_{120} should exhibit higher reactivity toward amination *vide infra*.

Strength for this argument is based on the three experimentally isolated and characterized

isomers of C₉₀, C₁(30)-C₉₀, C₁(32)-C₉₀, and D_{5h}(1)-C₉₀ reported by Yang and coworkers.⁶⁷ They have also reported longer chromatographic retention times for the C₁(32)-C₉₀ and D_{5h}(1)-C₉₀ isomers relative to the D_{5h}(1)-C₉₀ isomer with a PBB column.⁶⁸ Fullerene chromatographic retention is known to be sensitive to fullerene and metallofullerene solute polarizability.²¹ The higher number of reactive bonds ($\Xi > \alpha_{av}$) for the C₁(30)-C₉₀ and C₁(32)-C₉₀ isomers (see SI), in comparison with the D_{5h}(1)-C₉₀ isomer (**Figure 1.9**), indicates more sites of reaction. The D_{5h}(1)-C₉₀ isomer has only 10 reactive 6,6 C-C junctions; whereas, the C₁(30)-C₉₀ and C₁(32)-C₉₀ isomers each have significantly more chemically reactive, $\Xi > \alpha_{av}$, C-C bonds. The latter two lower symmetry isomers have a more ellipsoidal shape in comparison with the tubular [5,5] D_{5h}(1)-C₉₀ isomer.



Figure 1.9 Polarizability indices for carbon bonds for $D_{5h}(1)$ - C_{70} , $D_{5h}(1)$ - C_{90} , $D_{5d}(1)$ - C_{100} , and $D_{5d}(1)$ - C_{120} .

It is also noteworthy that a stable C_{120} species persists (**Figure 1.5b** and **1.5c**) and survives the aminopropanol reaction protocol without adjacent fullerenes, C_{2n} (n = 55-65). This is a significant finding. The C_{120} fullerene mass spectral peak elicits conjecture regarding the identity of this C_{120} isomer and whether it is a family member of this alternating D_{5d} and D_{5h} series. There are 10,774 IPR possible C_{120} isomers and only four isomers with five-fold symmetry, (3 D_{5d} and 1 D_{5h} isomers).¹ The D_{5d} (10765)- C_{120} and D_{5h} (10766)- C_{120} fullerenes are also [10,0] nanotubes (**Figure 1.10**) but are expected to be unstable because of the smaller HOMO-LUMO gaps < 1 eV. The D_{5h}(10666)-C₁₂₀ fullerene is predicted to be stable (2.4 eV) but is not expected to survive the aminopropanol procedure with 50% total reactive bonds ($\Xi > \alpha_{av}$), see SI. Only the D_{5d}(1)-C₁₂₀ has the same C₆₀ endcap as D_{5h}(1)-C₉₀ and D_{5d}(1)-C₁₀₀ with only 20% reactive bonds ($\Xi > \alpha_{av}$). This C₁₂₀-D_{5d} isomer has a reasonably predicted stability, HOMO-LUMO gap (1.2 eV) and is the most likely of these four candidate C₁₂₀ structures to survive the aminopropanol reaction protocol, (see **Figure 1.4** and **1.10** and SI). We predict that when isolated and characterized, this species is most likely the D_{5d}(1)-C₁₂₀ isomer within the alternating tubular nanotube [5,5] end-cap series D_{5h}-C₇₀, D_{5d}-C₈₀, D_{5h}-C₉₀, D_{5d}-C₁₀₀, D_{5h}-C₁₁₀, and D_{5d}-C₁₂₀.



Figure 1.10 The D_{5d} - and D_{5h} - C_{120} fullerenes and DFT HOMO-LUMO Gaps.

To provide additional insight regarding this five-fold series of D_{5d} - and D_{5h} - C_{2n} (n=35, 40, 45, 50, 55, and 60) tubular fullerenes, we have obtained individual electrostatic potential maps as illustrated in **Figure 1.11**. As previously described, insertion of an even number of five-hexagon torus rings (D_{5d} - C_{100} and D_{5d} - C_{120}) between the upper and lower

halve- C_{60} caps, allows the caps to remain spatially intact at the same positions. Whereas, insertion of an odd number of five-hexagon torus rings (D_{5h} - C_{70} and D_{5h} - C_{90}) requires rotation of the upper cap by $\pi/10$. This symmetry difference is clearly observable in these surface electrostatic maps. In the end caps, the blue-red transition along each five-fold axis also describes the electrostatic site for the reactive amination a-b bond previously described. Increasing from C_{70} to C_{120} , the central belt of hexagons in each member shows surface electrostatic regions (blue) with progressively more positive potential. This trend is consistent with the lower chemical reactivity toward amination of the carbons in this region.



Figure 1.11 Computational electron density maps for C_{70} - D_{5h} , C_{90} - D_{5h} , C_{100} - D_{5d} and C_{120} - D_{5d} .

To experimentally assess whether an increasing number of non-reactive belt carbon bonds with lower polarizability indices, ($\Xi < \alpha_{av}$) leads to lower reactivity for longer tubular fullerenes, we repeated the experiment described in **Figures 1.3** and **1.4** and changed only the reaction time to a longer period, 48 hours. If correct, then longer tubes should survive. This is exactly what is observed in **Figure 1.12**.

In Figure 1.12a, the extract contains a mixture of spheroidal fullerenes and tubular species. Circled in Figure 1.12b are family members of tubular series that survive 2 days of reaction with aminopropanol. Note the neighboring C_{120} spheroidal fullerenes, Figure 1.12a, in comparison to their absence in Figure 1.12c. For example, adjacent to C_{120} in Figure 1.12c, there are no spheroidal fullerenes at C_{116} , C_{118} , C_{122} , and C_{124} . Likewise, there are no surviving, neighboring spheroidal fullerenes adjacent to C_{90} , C_{100} , C_{150} , C_{180} , or C_{200} . Overall, this experimental finding is consistent with the polarizability and fewer reactive sites for the longer C_{150} , C_{180} , and C_{200} tubular species. This data suggests an overarching discovery of a new chemical-based separation approach to differentiate between tubular and spheroidal allotropes of fullerene carbon.



Figure 1.12 LDI mass spectra comparing (a) extract with (b) the family of tubular fullerenes that survive (c) 48 hours of reaction with aminopropanol.

The results of the current study demonstrate that the isolation of pristine $D_{5h}(1)$ - C_{90} and $D_{5d}(1)$ - C_{100} can be achieved by selective regional reactivity of the endcap nanotube carbons of [5,5] nanotube-like fullerenes. It is clear that it is possible to isolate pristine tubular fullerenes even larger than C_{100} . Since single-walled carbon nanotube (SWNT) samples usually consist of mixtures with variations based on tube diameter, length, and chirality, the availability of pristine [5,5] end-capped nanotubes from C_{100} - C_{180} will provide unique samples for a myriad of single-walled carbon nanotube (SWNT) studies. The chemical reactivity/separation protocol described herein for the separation/mass spectral analysis of the [5,5] nanotube-fullerene family could be an important fingerprint for future studies of fullerene samples from other terrestrial and extraterrestrial sources.⁶⁹

Further, we have developed a new method for separating tubular carbon from spheroidal fullerene allotropes.

1.4 Conclusion

In this chapter, a brief background of fullerene geometry research is introduced. In addition, I describe our contributions and current progress. The generalized spiral program is a powerful tool to calculate fullerene structures and obtain a novel view of fullerene research. Recently, the largest fullerene, C_{100} - D_{5d} is synthesized and isolated. It also encourages us to investigate the series and more interesting results are found. We acknowledge that the mechanism still remains unclear and more efforts are necessary. We believe our contributions are helpful for further studies.

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Chapter 2 Application Studies of Fullerenes/Metallofullerenes as Electronic Device Material

Since the discovery in the 1980s, fullerenes and metallofullerenes open a new era for carbon-based materials. In the past three decades, great efforts have been devoted to investigations regarding fundamental questions as well as applications. Due to the excellent electronic properties, fullerenes and metallofullerenes have been applied as high-performance electronic materials, such as biomedical agents. In this chapter, I would like to review the significant studies of fullerenes and metallofullerenes as electronic devices. In addition, I will present our contributions to both fundamental questions and applications. Graphene, another allotrope of carbon, is an ideal platform to adsorb molecules on the surface. It has been known that fullerenes/metallofullerenes can be organized on the graphene surface, and the complex is potential to build up electronic devices. Recently, a technique has been published showing that C_{60} is able to form a single layer close-packed structure on a graphene surface. However, the graphene surface is not always flat and rippled regions may affect the interactions between C₆₀ molecules and the graphene surface. In this chapter, a brief summary of our research on the effects of ripple regions on graphene adsorption abilities is presented. Among all metallofullerenes, trimetallic nitride template (TNT) endohedral metallofullerenes (EMFs) are mostly applied in fundamental and applied research due to their high stabilities, excellent electronic properties and high yields in synthesis. Nowadays, perovskite solar cells are in the center of energy material investigations and are potential to be commercialized in the near future. However, there are several drawbacks limiting further applications. In this chapter, we introduce our design of the electron transfer layer of a perovskite solar cell to improve the stability of solar cells at the same time achieving high energy conversion efficiency. In addition, I also introduce our current progress in reverse transformations of electrons between EMFs and organic aromatic compounds. Then we utilize endohedral heterofullerenes (EHFs) to investigate the single-electron bond by observing the electron transfers.

2.1 Differences in Self-Assembly of Spherical C₆₀ and Planar PTCDA on Rippled Graphene Surfaces

Note: In this following section, I thank Dr. Chenggang Tao and Yanlong Li for performing STM experiment and taking pictures of molecules on the graphene surface. I did all the computations and worked with the Tao group on data analysis.

Graphene is a unique two-dimensional (2D) material that exhibits fascinating physical and chemical properties and has a wide range of applications.^{1–3} For instance, thanks to its single-atom thickness and flexibility, graphene is an excellent candidate for flexible electronics, textures and gas sensors.^{4–9} To optimize the applications of graphene and other 2D materials, it is essential to investigate how curvature effects and tunes their properties. It has been reported that graphene on rough substrates (e.g. SiO₂) or suspended exhibits nonplanar aberrations.^{10,11} Furthermore, rippling the graphene to induce a curved surface would introduce variability into the properties of graphene and changes interactions with adsorbed molecules, which have not been experimentally examined.

Significant research efforts have recently been devoted to investigating the adsorption and desorption of various molecules on planar graphene and other 2D materials, such as fabricating and tuning molecule/graphene hybrid structures.^{12–16} Among the organic species, C_{60} and perylenetetracarboxylic dianhydride (PTCDA) has attracted a huge amount of research interest partially because they are key components, as effective acceptors, in photovoltaic cells.^{12,16–24} In the past two decades the power conversion efficiency of organic solar cells has rapidly increased, currently beyond 17%.²⁵ To further improve the efficiency of organic cells, it is necessary to understand the interactions between the organic species and other building blocks like graphene, which is an excellent material for transparent electrodes in solar cells.^{26,27} Development and study of hybrid nanostructures based on rippled graphene, C_{60} /rippled graphene, and PTCDA/rippled graphene could provide significant insights for improving the efficiency of organic solar cells.

Previous experimental and computational studies have found that C_{60} and PTCDA on a planar graphene surface form a hexagonal close-packed (hcp) structure and a herringbone structure, respectively.^{12,13,16–19,28,29} The major interaction present in the C_{60} -planar graphene system is a π - π stacking interaction.³⁰ π - π stacking interactions are common in parallel aromatic systems, have distances ranging from 3.0 to 4.0 Å and are mainly based on van der Waals forces.^{31,32} The PTCDA-graphene system also contains π - π stacking interactions, but the dominant interaction that leads to a herringbone pattern is intermolecular hydrogen bonding.¹⁷ We now report significant experimental and computational differences of spherical C_{60} and planar PTCDA self-assembled structures on rippled graphene surfaces. The inherent ability to tune the interactions between rippled graphene and structurally different molecules will undoubtedly open the door to

interesting properties and potential applications of curved 2D materials, such as flexible sensors.^{33–36}

2.1.1 Experimental and computational methods

Experimental: All STM measurements were carried out in an ultra-high vacuum (UHV) scanning tunneling microscope system (Omicron RT-STM). Before C₆₀ deposition, the graphene was grown using chemical vapor deposition (CVD) onto Cu foil37 and annealed for 12 hours at 673K in a preparation chamber with a base pressure of 1 x 10^{-10} torr. PTCDA powder (TCI AMERICA, 99.0% purity) was loaded into the homemade Knudsen cell and mounted in the load lock side A of the STM system. C₆₀ powder (MER Corporation, 99.5% purity) was loaded into the homemade Knudsen cell and mounted in the load lock side B of the STM system. The C₆₀ and PTCDA sources were degassed to 1 x 10^{-6} torr prior to deposition. C₆₀ and PTCDA molecules were then simultaneously deposited onto graphene at a deposition rate of ~ 0.5 monolayer/min with the background pressure below 1.8×10^{-8} torr. During the deposition process, the substrate was kept at 413 K. The sample was subsequently annealed at 423 K for one hour in the preparation chamber of the STM system with a base pressure of 1.0 x 10⁻¹⁰ torr. All of the STM measurements were performed at room temperature with a base pressure of 1.9×10^{-10} torr. The STM used a chemically etched tungsten tip.

Computational: Density functional theory (DFT) based calculations are used to obtain a further understanding of the self-assembled systems. A model containing an adsorbed molecule and a curved graphene surface is used to simulate the attachment of C_{60} and PTCDA on the rippled graphene surface. The structures of C_{60} and PTCDA are fully optimized at B3LYP level with def2-SVP basis set as provided in ORCA 3.0.3. The

curved graphene is constructed based on experimental observation and then is optimized with constraints to maintain the bending angles and size. The energies of the combined system are estimated based on single point calculations.^{38–40} DFT based approaches with D3-correction are used to address the intermolecular interactions between the C₆₀/PTCDA molecules and the graphene.^{41,42} The distances between C₆₀ and the curved graphene surface are changed consistently and system energy for each distance is calculated. The energy of C₆₀-curved graphene complex is sensitive to the orientation of the C₆₀ molecules on graphene. To solve the orientation-related challenge, we employed a detailed minimum potential search on representative orientations.^{43,44} Comparative calculations with molecules adsorbed on planar graphene are also reported. Additional computational details are presented in Appendices.

2.1.2 Results and Discussion

The self-assembled structure of molecules adsorbed on graphene relates to the geometry of graphene underneath. We identified three different patterns of graphene: planar graphene labeled as I (**Figures 2.1a-d**), 2D-rippled graphene labeled as III (**Figures 2.1a-d**), 2D-rippled graphene labeled as III (**Figures 2.1e and 2.1f**). Planar graphene usually forms a Moiré pattern on Cu substrate. **Figure 2.1i** shows a Moiré pattern with a hexagonal Moiré superlattice with a periodicity of 2.0 nm. Besides the planar graphene areas, we also observed 1D-rippled graphene (**Figure 2.1a-c**). **Figure 2.1a** shows the coexistence of planar graphene (I) and 1D-rippled graphene (II). **Figure 2.1d**, a line profile of blue line in **Figure 2.1b**, shows a periodicity of ~5 nm with an amplitude of 0.23 nm. Typically, the peaks of the rippled graphene have heights that range from 0.2 nm to 0.4 nm and periodicities that range from 3 nm to 10 nm. High-

resolution STM images (**Figure 2.1c** and **Figures S2.1d** and **S2.1e** in Appendices) reveal a honeycomb lattice of graphene on the top of each ripple. For 2D-rippled graphene (**Figures 2.1e** and **2.1f**), the ripples are along with two perpendicular directions with the peak height and periodicity similar to 1D-rippled graphene. Considering the heights of the ripples are much higher than the surface smoothness of the underneath Cu(111), Cu(100) or Cu(110) that is in the range of less than 0.1 nm,^{34,35} the line profiles of the ripples (**Figure S2.1. b, c in Appendices**) indicate that the graphene in these areas is quasi-suspended over the Cu substrate.

The formation of rippled graphene is mainly due to the negative thermal expansion coefficient of graphene.^{34,35,45} The rippled graphene always emerges near the boundary of graphene. The planar graphene appears on the Cu (111) facet and the 1D and 2D rippled graphene appear on the Cu (100) and Cu (110) facets. Our measurements lead us to believe the rippled graphene is caused by the negative thermal expansion coefficient of graphene and the interaction between graphene and different Cu facets. As the sample is cooled from the annealing temperature, the graphene expands as the Cu surfaces contract. The excess graphene on Cu surfaces leads to graphene ripples. In the middle domain, the excess graphene diffuses towards planarity, while near the boundaries the spatial constraints cause rippled graphene to form. Since graphene has a stronger interaction with Cu (111) facet, graphene preferentially forms a Moiré pattern on Cu (111) instead of a rippled pattern.



Figure 2.1 (Color online) STM topographical images of planar graphene (labeled as I), 1D-rippled graphene (II) and 2D-rippled graphene (III) on Cu. (a) Large area STM image of planar graphene (I) and 1D-rippled graphene (II) showing the linear periodic modulation and the spatial modulation frequencies ($V_s = -2.340$ V, I = 0.110 nA). (b) High-resolution STM image of 1-D rippled graphene ($V_s = -0.340$ V, I = 1.900 nA). (c) STM image of the 1-D rippled graphene, observed from the square region marked in (b), the schematic model on top of the atomic image shows the ripples along zigzag direction ($V_s = -0.280$ V, I = 1.900 nA). (d) Line profile perpendicular to the 1D-rippled graphene (marked as a blue line in (b)) showing the periodic modulation. (e) STM image of graphene on two different Cu facets, planar graphene (I) and 2D-rippled graphene (III) ($V_s = -2.74$ V, I = 0.045 nA). (f) High-resolution STM image of 2D-rippled graphene,

observed from the dashed square region marked in (e) ($V_s = -2.600 \text{ V}$, I = 0.068 nA). (g) A schematic model shows 1D-rippled graphene sheet. (h) Large area STM image of planar graphene (I) and 1D-rippled graphene (II) ($V_s = -1.850 \text{ V}$, I = 0.340 nA). (i) Atomic STM image showing the Moiré pattern of planar graphene, observed from the dashed squared region marked in (h) ($V_s = -1.850 \text{ V}$, I = 0.450 nA).

We deposited C_{60} molecules on both rippled and planar graphene with low coverage, typically less than 10%. On planar graphene, C₆₀ molecules self-assemble to an hcp arrangement (Figure 2.2e) similar to previous studies.^{12,16,29} Figure 2.2f is the zoomed image of the area marked in Figure 2.2e showing a Moiré pattern. This Moiré pattern originates from the Moiré pattern of graphene and Cu (111) surface as shown in Figure **2.1i**. For C_{60} on rippled graphene, the C_{60} self-assembly is more complicated than that on the planar case. C₆₀ molecules form a quasi-hcp structure as shown in Figures 2.2a-c at various scales. The quasi-hcp structure formed on rippled graphene has a different angle from that formed on the planar area. For example, the angle shown in **Figure 2.2c** is 54.1° instead of 60.0° shown in Figure 2.2f. The angle difference between C₆₀ on rippled graphene and planar graphene is due to the geometric curvature of the rippled graphene. When compared to C₆₀ adsorbed on planar graphene, the hcp structure on rippled graphene is distorted by the curvature of the surface. The difference is also reflected in the corresponding Fast Fourier Transform (FFT) images (the insets in Figures 2.2c and **2.2e**).



Figure 2.2 (Color online) STM images of C_{60} on 1D-rippled graphene (II) and on planar graphene (I). (a) Large area STM topographic image of the C_{60} on 1D-rippled graphene showing well-defined linear periodic modulated ripple ($V_s = -2.00 \text{ V}$, I = 0.060 nA). (b) Zoomed-in STM image (measured from the dashed square of (a)) of C_{60} on a long periodic graphene ripple ($V_s = -2.60 \text{ V}$, I = 0.050 nA). (c) High-resolution image (measured from the dashed square region of (b)) C_{60} on 1D-rippled graphene, shows a lattice angle α of 54.1° with a quasi-hcp pattern ($V_s = -2.60 \text{ V}$, I = 0.040 nA). Inset, the corresponding FFT image of (c). (d) A line profile along the perpendicular direction of the 1D-rippled graphene marked with the blue line in (c) (top), side view and top view showing the quasi-hcp C_{60} on 1D-rippled graphene (bottom). (e) Large area STM image of the C_{60} on planar graphene with a well-defined Moiré pattern on facet I ($V_s = -2.65 \text{ V}$, I = 0.046 nA). (f) High-resolution STM image of C_{60} on planar graphene (measured from the square region of (e)), showing a lattice angle β of 60.0° and a Moiré pattern on facet I ($V_s = -2.65 \text{ V}$, I = 0.046 nA). Inset, the corresponding FFT image of (e), showing a lattice angle β of 60.0° and a Moiré pattern on facet I ($V_s = -2.65 \text{ V}$, I = 0.046 nA). (f) High-resolution STM image of C_{60} on planar graphene (measured from the square region of (e)), showing a lattice angle β of 60.0° and a Moiré pattern on facet I ($V_s = -2.65 \text{ V}$, I = 0.046 nA). Inset, the corresponding FFT image of (f).

The difference between the C_{60} structure formed on planar graphene and rippled graphene is primarily due to the differences of van der Waals forces for peaks and valleys. Based on our DFT calculations, C_{60} will initially deposit in the valleys of rippled graphene. As additional C_{60} is deposited covering the peaks, the quasi-hcp structure is formed. DFT calculations identify the binding energy of a C_{60} -graphene valley site to be 0.34 eV more than the binding energy of a C_{60} -graphene peak site. The high-resolution STM image suggests that adsorbed C_{60} is not continuously deposited in the valleys of the 1D-rippled graphene. The C_{60} molecules are not fully revealed in the STM images because the STM tip is not sharp enough to measure into the narrow valley regions.

In order to better understand the interactions between adsorbed molecules and rippled graphene, we investigated PTCDA on 1D-rippled and planar graphene substrates. Similar to C₆₀ on graphene, the coverage of PTCDA on rippled and planar areas is low, typically less than 8%. The most common arrangement for PTCDA molecules on planar graphene is a herringbone structure (**Figures 2.3c** and **2.3d**). The high resolution STM image (**Figure 2.3d**) reveals a herringbone arrangement with $a_1 = 1.3$ nm, $a_2 = 1.96$ nm, and $\gamma = 90^\circ$, consistent with previous reports.^{13,17,18,28} The inset in **Figure 2.3c** is the FFT image of the herringbone structure obtained from an ordered area shown as the right part of **Figures S2.2c**. On 1D-rippled graphene, the herringbone structure of the adsorbed PTCDA molecules is influenced by the graphene curvature. In **Figure 2.3b**, we see there are a few PTCDA herringbone structures at the top right corner, while other regions show PTCDA molecules forming a distorted herringbone pattern. The FFT images of PTCDA

on rippled and planar graphene (the insets in Figures 2.3b and 2.3c) also show the difference.



Figure 2.3 (Color online) STM images of PTCDA on 1D-rippled graphene and on planar graphene. (a) Large area STM image of PTCDA on 1D-rippled graphene ($V_s = -2.51$ V, I = 0.042 nA). (b) STM image of PTCDA on 1D-rippled graphene showing a distorted herringbone pattern ($V_s = -2.510$ V, I = 0.042 nA). Inset, the corresponding FFT image of (b). (c) Large area STM image of PTCDA on planar graphene ($V_s = 1.800$ V, I = 0.030 nA). Inset, the FFT image of the PTCDA herringbone structure on planar graphene. (d) Zoomed-in STM image of PTCDA on planar graphene; a_1 and a_2 indicate the short and long lattice vectors of a unit cell of the PTCDA herringbone pattern ($V_s = 1.800$ V, I = 0.030 nA). (e) STM images of coexistence of meta-stable PTCDA structure (purple curved region) and normal PTCDA herringbone structure ($V_s = -2.500$ V, I = 0.030 nA). (f) STM image of remaining normal PTCDA structure after the meta-stable PTCDA removed by STM tip ($V_s = -2.500$ V, I = 0.030 nA).

Our results (**Figures 2.3e**, **2.3f**, and **S2.2**) further show that PTCDA sub-monolayer is very easy to disassemble, due to the weak interaction between PTCDA molecule and graphene on a copper substrate. During disassembly, we found a very interesting meta-stable PTCDA structure (purple curved region shown in **Figures 2.3e** and **S2.2**) with a rectangular lattice. This meta-stable structure is formed by the interaction between PTCDA molecules and the STM tip. After growing to a critical size, the meta-stable PTCDA would be moved away by the tip (**Figures S2.2g** and **S2.2h**).

When compared to planar graphene, molecules adsorbed onto 1D-rippled graphene show different patterns. To obtain further understanding of the formation mechanism we calculated the magnitude of the adsorbed molecule/curved graphene interaction. We employed computational approaches based on DFT with van der Waals dispersion corrections to explore the interactions between C₆₀ molecules and the curved graphene surface. As previously noted,⁴⁶ the potential energy of C_{60} -graphene complex is sensitive to C_{60} molecular orientation on the graphene surface. Previous work established that the energy minima of different C₆₀ orientations are similar and are in the range of rotation energy barriers.⁴³ Inspired by previous studies, we inspect typical orientations (described in Appendices). A detailed examination of typical C₆₀ orientations is employed to investigate the effects of orientations and to find the most stable configuration. It has been confirmed that the offset face-to-face alignment (Figure S2.2. b in Appendices) is energetically favored and shows a ~1 kcal/mol lower energy than other orientations.^{47,48} As shown in Figure 2.4 (a,b), there are two archetype locations on curved graphene surface for arranging C_{60} molecules, the peak and the valley. C_{60} molecules located on the peak area may be modeled with a C₆₀ on a convex aromatic surface and C₆₀ molecules located in the valley area may be modeled with a C_{60} on a concave aromatic surface. A previous computational study revealed that C_{60} molecules on a concave aromatic surface have larger intermolecular interactions which provide greater stability.⁴³ As illustrated in **Figure (2.4d)**, a C_{60} molecule located on a graphene peak has relative interaction energy of – 0.92 eV while the interaction energy for C_{60} in a graphene valley is – 1.26 eV. The relative interaction energy for C_{60} and planar graphene falls in between with a value of – 1.07 eV. Calculations reveal an optimized C_{60} molecule – curved graphene distance of 3.1 Å. The energy curves shown in **Figure 2.4.d** show a significant energy difference between C_{60} molecules located on a peak and those located in a valley. **Figure 2.5** shows the results of DFT calculations for adsorbed molecule-graphene interactions. The curved graphene structure increases the stability for C_{60} molecules in valley regions. The additional stability leads to the self-assembled quasi-hcp configurations of C_{60} molecules on the 1D-rippled graphene surface.



Figure 2.4 (Color online) Computational results for C_{60} on 1D-rippled graphene and planar graphene showing energetically favored orientations. (a) C_{60} molecule on a peak site on curved-graphene, (b) C_{60} molecule with a valley site on curved-graphene and (c) C_{60} on planar-graphene. (d) Plot of C_{60} -graphene distance versus relative energy for C_{60} on a graphene peak (pink), C_{60} in a graphene valley (blue) and C_{60} on planar graphene (green).

In contrast to the hcp pattern for C_{60} molecules on a planar graphene surface, it has been shown that PTCDA molecules form herringbone structure on a planar graphene surface. However, on a 1D-rippled graphene surface, we observed disordered herringbone pattern for the PTCDA molecules. The disordered structure implies that the curved graphene

surface has a significant effect on the self-assembly of the PTCDA molecules. We utilized DFT-based calculations to obtain a further understanding of the structures of a PTCDA molecule on a 1D-curved graphene surface. Our calculations show the relative energies between PTCDA and curved graphene on a peak and in a valley are -2.17 eV and -2.61 eV, respectively. This may be compared to relative energy of -2.40 eV for PTCDA on planar graphene. Calculations reveal that PTCDA molecules prefer different orientations on a graphene peak and in a graphene valley as shown in Figure 2.5a, b. A PTCDA molecule in a valley aligns symmetrically while the lowest relative energy for a molecule on a graphene peak makes a 30° angle with the ridge (Figure 2.5c). A possible explanation for the angle is the electronegative oxygens minimizing contact with the graphene while maximizing π - π stacking interactions. The difference in preferred orientations for PTCDA molecules on peaks and in valleys show that curved graphene may be used to help to regulate the orientation of molecules. Compared to the C_{60} /curved graphene interaction, the PTCDA/curved graphene interactions are slightly stronger due to a larger contact area between PTCDA molecules and the curved graphene. In both cases, adsorbed molecules in valley sites show a stronger interaction than the same molecule adsorbed on planar graphene.



Figure 2.5 (Color online) DFT results for adsorbed molecule/graphene interactions. (a) Energy difference of a C_{60} molecule on 1D-rippled graphene surface (b) Energy difference of a PTCDA molecule on a 1D-rippled graphene. (c) Energy curve for a PTCDA molecule rotation on 1D-rippled graphene on a peak location (top); favored PTCDA orientations (bottom). (d) Favored PTCDA orientations at the peak site (left) and at the valley site (right).

2.2 Reversible Electron Transfers Between TNT-Metallofullerenes and Organic Aromatic Donor

Note: In this following section, I thank Dr. Kai Wang and Dr. Shashank Priya for performing and collecting experimental data. I worked with Dr. Kai Wang and did the theoretical part of this project.

Fullerenes, due to their unique electronic properties have been applied to form electron donor-acceptor systems with various organic donor molecules in solution as well as in the solid phase.^{49–52} The rigid structures of fullerenes enhance the charge transfer abilities

because of the small reorganization energies after obtaining extra electrons.53 The fullerene-based donor-bridge-acceptor architectures exhibit efficient electron transfers between donors and acceptors under excitation.^{54–59} Metallofullerenes with metal clusters encapsulated inside fullerene cages are more easily reduced compared to empty cage fullerenes with organic donor molecules.^{60,61} In a seminal study, Akasaka et al. reported the existence of reduced species of La(a)C₈₂ [La(a)C₈₂], when they mixed La(a)C₈₂ and aza- and thiacrown ethers in solution.^{62,63} Recently, it has been reported that La@C₈₂ and an organic donor molecule, N, N, N', N'-tetramethyl-p-phenylenediamine (TMPD) form a stable complex in nitrobenzene. The oxidized species of TMPD and reduced species of La@C₈₂ have been detected by UV/vis spectra and electron paramagnetic resonance (EPR) spectra.⁶⁴ In 2011, a dimetallofullerene with relatively small band gap, La₂@C₈₂ have been confirmed for forming stable complexes and showing ground state charge transfers with TMPD in nitrobenzene.⁵³ The $[La_2@C_{80}]^-$ radical is similar in electronic structures with the recently reported stable single molecule endohedral heterofullerene family $M_2(a_{C_{79}}N)$ (M = Y, La, Gd, Tb) and the stability of these molecules is because the electron spin is stabilized by two metal atoms and protected by the fullerene cage from any attack.^{65–67} The small band gap of $La_2(a)C_{80}$ reduces the stability of the dimetallofullerene molecule, and on the other hand, makes it easy to be reduced and form complex with organic donors.53,68 However, evidence for the ground state charge transfers between highly stable metallofullerenes, such as trimetallic nitride template endohedral metallofullerenes (TNT-EMFs) still remains unknown.


Figure 2.6 UV/vis Spectra of Sc₃N@C₈₀ ($3.6 \times 10^{-5} M$) in (a) nitrobenzene with spiro-OMeTAD (0.2 - 10.0 eq) and (b) toluene with spiro-OMeTAD (1.0 - 11.0 eq).

Recently, metallofullerenes have been utilized in electron transfer layers with 2, 2', 7, 7'tetrakis(N,N-bis(p-methoxyphenyl)amino)-9,9'-spirobifluorene (spiro-OMeTAD) to design efficient perovskite solar cells.^{69–71} The enhanced energy conversion efficiency is due to the facile electron transfer between metallofullerenes and spiro-OMeTAD molecules.^{72,73} In the previous study, it has been confirmed that spiro-OMeTAD has the potential to form stable complexes with electron transfers and has been extensively applied in various kinds of solar cell designs.⁷⁴ The spiro-OMeTAD has been an ideal organic electron donor because of relatively lower oxidized potential. Encouraged by early studies, we propose to build stable reversible electron transfer systems using $M_3N@C_{80}$ (M = Sc, Y, Gd) and spiro-OMeTAD. In this study, we examined the ground state electron transfer between $Y_3N@C_{80}$ and spiro-OMeTAD in various solvents using EPR and UV/vis spectra. The experimental results are then augmented by density functional theory (DFT) based computations to obtain a further understanding of complexation and charge transfer.

The charge transfer between fullerenes and organic donors has long been investigated under photoexcitation. Ground state charge transfer, on the other hand, is quite unusual and very helpful to form efficient charge transfer layers for electronic devices, such as solar cells. As previously reported, the radical species of metallofullerenes and organic donors can be detected by UV/vis and EPR spectra. Currently, we reported a new reversible charge transfer system formed by stable and abundant metallofullerene, $M_3N@C_{80}$ (M = Sc, Tb and Lu) and spiro-OMeTAD molecule, which is widely used in perovskite solar cells.

As illustrated in **Figure 2.6**, we investigate the ground state electron transfer behavior between $Sc_3N@C_{80}$ and an organic electron donor, Spiro-METaD in two common solvents. The cation of spiro-OMeTAD has a characteristic UV/vis peak at 525 nm in nitrobenzene and at around 400 nm in toluene. The crossing point on each spectrum confirms the two species and the electron transfers between the $Sc_3N@C_{80}$ and the spiro-OMeTAD. The anion of the $Sc_3N@C_{80}$ shows no significant absorption peak at the range from 300 to 1200 nm. In **Chapter 2.3**, more details are shown for characterizing the absorption peaks of spiro-OMeTAD and its cation. As we all know that perovskite solar cells, although shows excellent energy conversion efficiency, are not stable in vapor conditions and the efficiency will drop dramatically after the electron transfer layer absorbs water. It is because the materials for the electron transfer layer, which are metal based or metal oxide based crystal, are hydrophilic and may have chemical reactions with water. Nowadays, it is still a challenge for the further development of perovskite solar cells. As shown in this chapter, we find the fullerene cages can act as the hydrophobic layer outside the electron transfer materials and will not decrease the electron transfer ability. Therefore, we propose the metallofullerenes, especially TNT-EMFs are an ideal material to enhance the stabilities of perovskite solar cells and not hurt the energy conversion efficiency.



Figure 2.7 Electron density change after multi-site complexation of one. The red denotes the negative charges and blue denotes the positive charges. Isovalue = 0.003. Carbon atoms are gray, hydrogen atoms are white, scandium atoms are cyan, nitrogen atoms are yellow, oxygen atoms are pink.

The experimental data were augmented by DFT-based computations to further understand the ground state electron transfer system. As illustrated in Figure 2.7, the electron density of $Sc_3N@C_{80}$ increases as a corresponding loss of electron density in the spiro-OMeTAD region after the complexation. The computational results show that the spiro-OMeTAD has the potential to donate electrons to the $Sc_3N@C_{80}$ at ground state without any photoirradiation. Although previous studies confirm that fullerenes, such as C_{60} are efficient electron acceptors, the ground state electron transfer behaviors are quite unusual and just a few investigations were reported. The π structure of each arm of the spiro-OMeTAD and the large delocalized structures of the $M_3N@C_{80}$ suggest that there must be π - π interactions between the two molecules. It was well recognized that the π - π interactions between the spiro-OMeTAD and the $M_3N@C_{80}$ molecules lead to the ground state charge transfer. As shown in the titration, the spiro-OMeTAD was added from 0.2 eq to 5 eq. Although the structures of the complexes still remain unknown, each spiro-OMeTAD molecule can complex more than one $M_3N@C_{80}$ molecule and multi spiro-OMeTAD molecules are capable to form complexes with one spherical $M_3N@C_{80}$ molecules. The average diameter of a $Sc_3N@C_{80}$ is around 0.83 nm, which is the suitable size for the cavity formed by two spiro-OMeTAD molecules as well as for that made by multi spiro-OMeTAD molecules. In addition, as shown in Figure 2.8, a significant result is that the spin density of the oxidized species of spiro-OMeTAD molecule is delocalized. The delocalization of the unpaired electron originates from the spiro-OMeTAD's tetrahedral geometry structures and stabilized the radical [spiro-OMeTAD]⁺⁺.



Figure 2.8 Electron spin density figure of [spiro-OMeTAD]+ radical. The unpaired electron is delocalized over the entire molecule.

2.3 Endohedral Metallofullerenes Dopant for Halide Perovskite Photovoltaic Application

Photovoltaics employing organic-inorganic lead halide perovskite photoactive materials have captured attention owing to their extraordinary device efficiency. A power conversion efficiency (PCE) record of 22.7%⁷⁵ was reported last year. However, the severe moisture sensitivity of the halide perovskite materials drastically limits the device operational lifetime, presenting challenges in their transition to industiralization.^{76,77} In particular, the ionic dopants commonly employed for the hole transport layer (HTL), 2,2',7,7'-tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9'-spirobi-fluorene (spiro-OMeTAD), typically accelerates perovskite performance degradation because of its hygroscopic nature. The intrinsic spiro-OMeTAD is electrically unfavorable for charge transport due to its low hole mobility (μ_h) ~2 × 10⁻⁴ cm² V⁻¹ s⁻¹ and requires complex doping and processing for photovoltaic application. To date, various ionic dopants have been introduced to improve the electrical properties of spiro-OMeTAD. Bach *et al.* carriers into the system.⁷⁸ Henry et al. found that the addition of lithium bis(trifluoromethylsulphonyl)imide (LiTFSI) could significantly boost the charge carrier mobility.⁷⁹ Additionally, ionic dopants such as silver bis(trifluoromethanesulfonyl)imide CuSCN,⁸² CuI,⁸³ and Keggin-type polyoxometalates $SnCl_4$,⁸¹ (AgTFSI).⁸⁰ (POMs)-phosphovanadomolybdate (H₄PMo₁₁V·nH₂O)⁸⁴ have been reported to electrically enhancing the spiro-OMeTAD HTL. Recently, Jeon et al. reported the lithium-ion endohedral fullerene ($Li^+(a)C_{60}$) dopants for the spiro-OMeTAD HTL, which opens the road of using metallofullerene ions as dopants to foster the performance of HTL.⁸⁵ Nevertheless, the hygroscopic nature of these ionic dopants inevitably deteriorates the device stability. Parasitical issues also arise from the LiTFSI doping in spiro-OMeTAD, as LiTFSI itself is not a direct *p*-dopant and additional oxygen is required for the redox reaction. This reaction occurs randomly under the processing environment and becomes reversible during the device operation depending upon ambient conditions. All these behaviors are detrimental towards the long-term stability and reliability of solar cell.

Here, we report the application of endohedral metallofullerenes (EMFs) that can act as the non-ionic dopant for spiro-OMeTAD HTL in halide perovskite solar cells. The EMF consists of a fullerene sp^2 hybridized carbon cage and atoms, ions, or clusters encapsulated in the cage. The variability of the encapsulated species imparts multifunctional properties which have driven the use of EMFs in optoelectronics,⁸⁶ magnetic resonance imaging contrast agents,⁸⁷ electron-spin quantum computer⁸⁸, atomic clock⁸⁹, *etc.* In this study, we employ the trimetallic nitride template (TNT) EMF, *i.e.*, the I_h -(C₈₀)⁶⁻ incarcerating the trimetallic scandium nitride cluster (Sc₃N)⁶⁺ to replace the LiTFSI. The non-ionic and hydrophobic nature of the Sc₃N@C₈₀ TNT EMF delivers stronger moisture resistance and provides higher device stability. In addition, Sc₃N@C₈₀ has been reported to exhibit superb ability to stabilize charge separated states with a low reduction potential,⁹⁰ making it a good *p*-type dopant for spiro-OMeTAD oxidation with a suppressed reversible reaction. Direct electron transfer from spiro-OMeTAD to Sc₃N@C₈₀ gives rise to oxygen-free oxidation of spiro-OMeTAD HTL that delivers significantly improved electrical conductivity and a lower-lying Fermi-level that reduces the Schottky barrier for hole extraction. Both these effects are found to synergistically favor the energy flow in the solar cell and consequently elevate the PCE to 20.77% for MAPbI₃-based perovskite solar cells. The hydrophobic nature of Sc₃N@C₈₀ doped HTL eliminated the hygroscopic issues and rendered a survival PCE of over 17% after 800 hours continuous one-sun illumination exposure in ambient with relative humidity (RH) ranging from 25% to 60%.

The TNT EMFs have been shown to display the potential to complex with organic donors and provide electron transfer from the organic donor to the EMF.^{91,92} In this study, the electron transfer between $Sc_3N@C_{80}$ and spiro-OMeTAD was investigated *via* a photophysical measurement. The oxidation of spiro-OMeTAD was studied by the UV/Vis-NIR absorption titration measurement. As shown in **Figure 2.9a**, by gradually increasing the concentration of $Sc_3N@C_{80}$ (from 0 to 1.0 mg/mL) in the spiro-OMeTADchlorobenzene solution, characteristic absorptions *ca*. 500 nm assigned to the oxidized spiro-OMeTAD^{•+} increased in concentration.^{85,93} The oxidized spiro-OMeTAD^{•+} states were further verified by comparisons between the *in-situ* measured spectrum of $Sc_3N@C_{80}$ and spiro-OMeTAD mixture and the calculated spectrum with spectral superposition of independent $Sc_3N@C_{80}$ and spiro-OMeTAD samples (**Figure S2.8**). The electron-accepting process by $Sc_3N@C_{80}$ was monitored by time-resolved photophysical studies. **Figure 2.9b** exhibits the differential absorption Vis/NIR spectra of $Sc_3N@C_{80}$ doped spiro-OMeTAD, where the photoproducts absorption maxima of 1060 nm confirm the existence of singlet excited state of $Sc_3N@C_{80}^{\bullet}$, ^{94,95} and such electron-reduced radical anions support the electron transfer between $Sc_3N@C_{80}$ and spiro-OMeTAD. The proposed redox reaction is illustrated in **Figure 2.9c**.



Figure 2.9 Redox electronic transaction between $Sc_3N@C_{80}$ and spiro-OMeTAD. (a) UV/Vis-NIR absorption titration of spiro-OMeTAD-chlorobenzene solution with increasing concentration (from 0 to 1.0 mg/mL) of $Sc_3N@C_{80}$. Arrow indicates the excited states of spiro-OMeTAD^{•+}. (b) Differential absorption spectra achieved on femtosecond flash photolysis (387 nm) of a $Sc_3N@C_{80}$ doped spiro-OMeTAD sample under time delays between 0 and 100 ps. Arrow indicates the excited states of $Sc_3N@C_{80}$. (c) Proposed electron transaction mechanism and (d) DFT calculations on

the electron density evolution of the $Sc_3N@C_{80}$: spiro-OMeTAD complex from isolated neutral components (total, negative and positive charge distribution were illustrated). The surface in blue shows the positive difference (electron donor part) and the surface in red shows the negative difference (electron acceptor part). (Iso-value = 0.003). (e) Water contact angle and (f) water adsorption at increasing relative humidity of perovskite coated by spiro-OMeTAD HTLs with LiTFSI and $Sc_3N@C_{80}$ dopants.

Such an electron accepting ability of TNT EMFs was found in polymer solar cells by Ross and coworkers,⁹⁶ where electron transport from poly(3-hexylthiophene) (P3HT) to lutetium functionalized TNT EMF (Lu₃N@C₈₀-PCBH) was evidenced in the polymer: fullerene bulkheterojunction. We further investigated the electron transfer between the $Sc_3N@C_{80}$ and spiro-OMeTAD by performing the Density Functional Theory (DFT) computations on the HTL system. As predicted by the DFT simulations (Figure 2.9d), the total electron density of the spiro-OMeTAD molecule decreases with a corresponding gain of the electron density at the complexation region of the $Sc_3N@C_{80}$. Clearly, electron transfer is evident between the $Sc_3N@C_{80}$ and spiro-OMeTAD systems. This is consistent with EMFs potential to form ground state charge transfer complexes with organic electron donors.⁹⁷ The Sc₃N@C₈₀ instantly interacted electronically with spiro-OMeTAD, rendering intermediate radical states that facilitate the charge transport.98 In this manner, no additional oxygen was needed, which is in distinct contrast to the case of LiTFSI-doped spiro-OMeTAD, where oxygen penetration and ambient exposure can drastically deteriorate the electrical homogeneity and result in the reverse doping issues of HTL.^{99,100} On the other hand, the hydrophobic nature of the Sc₃N@C₈₀ is also expected to benefit the long-term device stability when compared to the hygroscopic LiTFSI dopant. As compared in Figure 2.9e, the $Sc_3N@C_{80}$ -doped spiro-OMeTAD HTL exhibited a water contact angle of 105.6° compared to 71.2° for LiTFSI-doped HTL. The enhancement in moisture non-wettability and corresponding hydrophobic character suggests an improved barrier for water penetration of the HTL and the perovskite layers. This also parallels improved device stability *vide infra*. For example, we also conducted a water adsorption study of perovskite coated with different HTLs through the quartz crystal microbalance with dissipation (QCM-D) measurements (Figure S2.9). Figure **2.9f** shows the water take-up of perovskite coated by different HTLs at increasing relative humidity (RH) levels. Both samples exhibited slow water adsorption at a low RH level of 26%, while the $Sc_3N@C_{80}$ -doped sample exhibits a slower adsorption rate at higher RH level than that of the LiTFSI-doped sample. It is worth noting that at high RH levels of 79%, the Sc₃N@C₈₀-doped sample presented a mass increase by 0.17%, which is ca. 2.5fold less than that of LiTFSI-doped sample. As a result, the hydrophobic $Sc_3N@C_{80}$ doped spiro-OMeTAD HTL is clearly more effective in shielding the perovskite from moisture attack.

The electrical conductance properties of HTLs are crucial for charge transport in the solar cell devices. We employed conducting-atomic force microscopy (c-AFM) to investigate both the surface morphological and electrical landscapes of different HTLs. The pristine spiro-OMeTAD HTL exhibited a morphological evolution after doping with LiTFSI, which was consistent with prior reports.¹⁰¹ Interestingly, the Sc₃N@C₈₀-doped spiro-OMeTAD HTL shows larger domains in comparison to LiTFSI-doped HTL. The corresponding current maps of different HTLs were also compared in **Figure 2.10d-f**, where an obvious current increase was observed upon doped by 1.0 mg/mL Sc₃N@C₈₀.

The c-AFM height and current images of spiro-OMeTAD HTLs with different $Sc_3N@C_{80}$ -dopant concentrations from 0 to 2.0 mg/mL have also been measured by c-AFM (Figure S2.10) and the results are summarized in Figure 2.10g. We found that the detected surface current increases with the increase of dopant concentration and at a $Sc_3N@C_{80}$ concentration of 1.0 mg/mL, high surface current of 20.35 nA have been observed, which is 12-fold higher compared to pristine case and twice greater compared to LiTFSI-doped spiro-OMeTAD HTLs. Figure 2.10h shows a gradual increase in electrical conductivity with the increase in $Sc_3N@C_{80}$ concentration. The $Sc_3N@C_{80}$ doped spiro-OMeTAD HTL with dopant concentration of 1.0 mg/mL exhibited a significantly improved electrical conductivity of 2.3×10^{-4} S cm⁻¹, which is approximately two orders of magnitude larger than that of 4.4×10^{-6} S cm⁻¹ in pristine spiro-OMeTAD HTL (comparable to previously reported value^{102,103}) and three times larger than *ca*. 8×10⁻⁵ S cm⁻¹ of reported LiTFSI-doped spiro-OMeTAD HTLs.¹⁰⁴ Therefore, the observed enhancement in electrical conduction properties of Sc₃N@C₈₀-doped spiro-OMeTAD supports the effectiveness of the EMFs dopant for facilitating the charge transport within the HTL.

For efficient solar cell devices, alignment of the energy levels with a lower Schottky barrier between the perovskite photoactive layer and HTL is crucial for efficient hole extraction and subsequent high PCE. The electron Fermi level of different HTLs has been measured utilizing photoelectron spectroscopy in air (PESA).^{105,106} As shown in the photoelectron emission spectra in **Figure 2.10a**, the pristine sprio-OMeTAD produces a Fermi level of -5.10 eV, while the LiTFSI-doped spiro-OMeTAD provides an even

greater Fermi level of -5.33 eV. The oxidization of spiro-OMeTAD introduces a hole in the highest occupied molecular orbital (HOMO) and shifts the Fermi level downward to lower energy states, ^{107,108} which agrees well with earlier observations vide supra and suggests more effective oxidation by the Sc₃N@C₈₀ EMF. The lowest Fermi level of $Sc_3N@C_{80}$ -doped spiro-OMeTAD HTL is expected to deliver a smaller Schottky barrier after contacting with MAPbI₃ as its conduction band maximum (CBM) is even lower corresponding to -5.46 eV.¹⁰⁹ Better band alignment and thereby reduced Schottky barrier is believed to deliver a lower-lying quasi-Fermi level of hole and a correspondingly higher solar cell open-circuit voltage (V_{OC}) through a more efficient hole extraction process.¹⁰⁵ To illustrate the effectiveness of the excited state extraction from the perovskite to the HTLs, we have employed the confocal photoluminescence (PL) mapping measurement on perovskite coated with different HTLs. The wavelength of the incident monochronic laser is 633 nm, which lies in the absorption range of perovskite to ensure photoexcitation. Figure 2.11c-e compares the microscopic PL landscapes probed at characteristic PL peak of perovskite. The pristine spiro-OMeTAD HTL coated perovskite presents the strongest PL intensity and largest signal range among the samples, suggesting a relatively lower charge extraction efficiency and higher substrate inhomogeneity. In comparison, LiTFSI-doped sample exhibits a marginally reduced PL intensity and significantly smaller signal range, which were additionally reduced in the $Sc_3N@C_{80}$ -doped sample. To quantify the hole extraction ability of different HTLs on perovskite, we extracted the average steady-state PL spectra (Figure 2.11f). The perovskite coated with Sc₃N@C₈₀-doped spiro-OMeTAD HTL exhibited a drastically minimized PL among all the HTLs, indicating that the photon-excited states could be sufficiently extracted from the HTL resulting in minimized radiant recombination. **Figure 2.11g** shows the transient PL decay spectra of the perovskite coated by different HTLs. PL decay lifetimes (τ_1 and τ_2) have been extracted from the biexponential fitting curves and summarized in **Table S2.1**. The fast decay (τ_1) correlates with the charge transport from perovskite to HTLs while the slower decay (τ_2) stems from the radiative recombination within the perovskite.^{110,111} All the samples displayed similar τ_2 values while the τ_1 values have been shortened to 34.5 and 18.1 ns in LiTFSI and Sc₃N@C₈₀doped spiro-OMeTAD samples, respectively, from that of 79.6 ns in the pristine spiro-OMeTAD sample. These results suggest an enhanced charge extraction process by employing the Sc₃N@C₈₀-doped spiro-OMeTAD HTLs, which can be ascribed to their optimized lower Fermi-level and higher electrical conductivity.

Perovskite solar cells based on different HTLs have been fabricated in a planar heterojunction architecture of FTO-glass/SnO₂/MAPbI₃/HTL/gold (**Figure 2.12a**), as shown in the cross-sectional scanning electron microscopy (SEM) image in **Figure 2.12b**. The SnO₂ was utilized as the electron extraction layer here as it displayed a deeper conduction band, giving a barrier-free band alignment with perovskite and thus less voltage loss.¹¹² The HTLs were chosen from the pristine spiro-OMeTAD, LiTFSI-doped spiro-OMeTAD, and Sc₃N@C₈₀-doped spiro-OMeTAD. The Sc₃N@C₈₀-dopant concentration effect on the solar cell performance was initially investigated through the photocurrent density-voltage (J-V) characteristics illustrated in **Figure 2.12c**. As the concentration of Sc₃N@C₈₀ increases from 0 to 1.0 mg/mL, the solar cell exhibited a gradual increase in short-circuit current density (J_{SC}) and open-circuit voltage (V_{OC}). The detailed photovoltaic performance parameters have been summarized in **Table 2.1**.

reference device utilizing pristine spiro-OMeTAD HTL displaying a modest PCE of 14.19% with J_{SC} of 19.81 mA cm⁻², V_{OC} of 1.06 V and FF of 0.68, consistent with recently reported values.¹¹³ As the Sc₃N@C₈₀-dopant concentration increases from 0 to 1.0 mg/mL, we found the device performance displayed a monotonous enhancement with simultaneously improved J_{SC} , V_{OC} , and FF. This can be understood in terms of the $Sc_3N@C_{80}$ -doping effect on Fermi-level descending (Figure 2.11a) and electrical conductivity ascending (Figure 2.10h). The V_{OC} in solar cells is determined by the separation of quasi-Fermi levels of electrons and holes upon illumination.¹⁰⁵ The energy flow at the cathode side was secured by the barrier-free contact between SnO₂ and perovskite that fosters a higher quasi-Fermi level of electrons.¹¹² The lower-lying Fermilevel (closer to the valence band maximum of MAPbI₃) of Sc₃N@C₈₀-doped spiro-OMeTAD HTL gave a minimized Schottky barrier after contact with MAPbI₃, suggesting less energy loss during charge extraction and thus a deeper quasi-Fermi level of holes.¹⁰⁵ Consequently, a larger electron and hole quasi-Fermi level separation rendered a maximum V_{OC} of 1.16 V in perovskite solar cells employing Sc₃N@C₈₀-doped spiro-OMeTAD HTLs. The J_{SC} and FF correspond to the charge carrier transport properties in the solar cell devices. The higher electrical conductivity of Sc₃N@C₈₀-doped spiro-OMeTAD HTL and less interfacial loss endow superior charge transport throughout the device, which is also supported by electrical impedance spectroscopy (EIS) measurements (Figure S2.11). The charge transfer resistance (R_{CT}) extracted from the EIS demonstrated a reduction from 195.8 Ω to 111.6 Ω in pristine and Sc₃N@C₈₀-doped devices, respectively, which confirmed the effectiveness of $Sc_3N@C_{80}$ -dopant on the hole extraction/transport process as well as the subsequently boosted J_{SC} and FF of solar cells.

The PCE dependence on $Sc_3N@C_{80}$ -dopant concentration has been plotted in **Figure 2.12d**. We found that PCE grows as the dopant concentration increases from 0 to 1.0 mg/mL and drops at the highest concentration of 1.4 mg/mL, which mainly originates from the J_{SC} and V_{OC} dependence on dopant concentration (**Figs. S12, 13**). Interestingly, the electrical conductivity of the $Sc_3N@C_{80}$ -doped spiro-OMeTAD HTL displayed a monotonous increase even at a high dopant concentration of 1.4 mg/mL (**Figure 2.10h**). This happens because higher concentrations of $Sc_3N@C_{80}$ tend to aggregation that roughens the HTL surface and render larger electrical inhomogeneity at the interface. This would result in complex interfacial phenomena such as severe conduction electron scattering that can significantly hamper the charge transport across the interface.¹¹⁴ Thus, spiro-OMeTAD HTL with a $Sc_3N@C_{80}$ -dopant concentration of 1.0 mg/mL exhibited a sufficient electrical conductivity and homogeneous film morphology with negligible aggregations which resulted in the optimal PCE of 20.77%.



Figure 2.11 Charge extraction study. (a) Photoelectron spectroscopy in air (PESA) spectra of different HTLs. (b) Energy band schematic for MAPbI₃ and different HTLs. Confocal photoluminescence (PL) mapping of perovskite coated by (c) pristine spiro-OMeTAD, (d) LiFTSI-doped spiro-OMeTAD, and (e) Sc₃N@C₈₀-doped spiro-OMeTAD HTLs, probed at 769 \pm 5 nm. Average (f) steady-state PL spectra and (g) transient PL decay of different HTLs.

To manifest the advantage of the $Sc_3N@C_{80}$ -dopant over the conventional LiTFSIdopant, we next characterized the solar cell performance through J-V characteristics, statistics, hysteresis, and stability measurement. **Figure 2.12e** compares the J-V characteristics of perovskite solar cells employing LiTFSI or $Sc_3N@C_{80}$ -doped (1.0 mg/mL) spiro-OMeTAD HTLs, under one-sun illumination (AM1.5G). Solar cells with LiTFSI-dopant exhibited a J_{SC} of 21.71 mA cm⁻², V_{OC} of 1.13 V, FF of 0.74 and PCE of

18.15%, which is comparable to the recently reported values of similar device architectures.^{112,115} By utilizing Sc₃N@C₈₀-dopant instead, simultaneously improved J_{SC} of 23.06 mA cm⁻², V_{OC} of 1.15 V, FF of 0.78 and PCE of 20.77% have been observed. An incident photon conversion efficiency (IPCE) with integrated photocurrent density has also been measured to verify the photocurrent density (Figs. S2.14, 2.15). The J_{SC} from IPCE spectra were calculated to be 22.97 mA cm⁻² and 21.52 mA cm⁻² for solar cells with $Sc_3N@C_{80}$ and LiTFSI-dopants, respectively. The observations on improved J_{SC} and FF agreed well with the higher electrical conductivity; the enhancement in V_{OC} is also consistent with the observation on deeper-lying Fermi level of the Sc₃N@C₈₀-doped spiro-OMeTAD HTLs. The PCE statistics were also compared in Figure S2.16. It is worth noting that the perovskite solar cells using $Sc_3N@C_{80}$ -dopant displayed an average PCE of 20.5%, representing an overall 13% improvement over the 18.1% average PCE of the devices using LiTFSI-dopant. The champion PCE came from the Sc₃N@C₈₀-dopant based device and presented a decent value of 21.09%, with a V_{OC} of 1.16 V, J_{SC} of 23.02 mA cm⁻², FF of 0.82 on the reverse scan. In addition, the scan condition effect on device performance has also been investigated by measuring the light J-V characteristics depending on scan direction and speed. The hysteresis in perovskite solar cells is a multifactorial phenomenon which can be influenced by a wide scope of variables ranging from the composition, stoichiometry, defect density, crystal feature of the absorber, internal and external interfaces, as well as scanning conditions including scan speed, direction, pre-biasing, voltage delays, atmospheric conditions like temperature, humidity, oxygen and light soaking, etc., and preparation methods such as device aging, electrode materials.^{116–118} In this study, we found relatively low hysteresis with a hysteresis factor <0.06 under a scan rate ranging from 10 to 500 mV/s. Such a low scan-rate influence on PCE is consistent with previously reported work on SnO₂ based perovskite solar cells,¹¹² which show distinct contrast to the heavy hysteresis in the TiO₂ based solar cells.¹¹² Overall, the robust PCE with minimal scan rate influence and batch-to-batch deviation suggested the effectiveness of the Sc₃N@C₈₀-dopant.



Figure 2.12 Solar cell device performance study. (a) Schematic of solar cell device, (b) cross-sectional scanning electron microscope image denoting each layer, (c) photocurrent density-voltage (J-V) characteristics of solar cells employing HTL doped by $Sc_3N@C_{80}$ -doped of different concentrations from 0.1 to 1.4 mg/mL, (d) summarized PCE versus $Sc_3N@C_{80}$ -dopant concentration, (e) J-V characteristics and (f) PCE decay trace under constant illumination (AM1.5G) in ambient (from 25% to 60% relative humidity) of

perovskite solar cells employing either LiTFSI or $Sc_3N@C_{80}$ -doped (1.0 mg/mL) spiro-OMeTAD HTLs.

2.4 Electron transfer and single electron bond in M₂@C₇₉N

Note: In this following chapter, I thank Dr. Tianming Zuo for the isolation of La2@C79N sample. I also thank Kyle Kirkpatrick for measuring the experimental EPR data and thank Dr. James Duchamp for $Sc_2@C_{79}N$ synthesis and helpful discussion on the data processing and analysis.

Metallofullerenes with metal clusters encapsulated inside the cage provide a readily available family for the applications and studies of molecular magnets.^{119–122} Trimetallic nitride template (TNT) endohedral metallofullerenes (EMFs) with paramagnetic ion(s), such as Gd³⁺ and Tb³⁺, have been long investigated as MRI agents and quantum computation materials due to the molecular magnetic properties.^{123–125} Shortly after the discovery of TNT-EMFs, a class of stable radical endohedral heterofullerenes, $M_2(\partial_{C_{79}}N)$ (M = Y, Tb, and Gd) have been synthesized and isolated.^{126,127} EPR studies have rapidly confirmed that the unpaired electron spin density is localized in the center of the two metal cations and protected by the $(C_{79}N)^{5-}$ cage.¹²⁷ Recent investigations suggest an extremely giant exchange coupling $j_{Gd}^{eff} = 170 \ cm^{-1}$, which is the largest one among all known lanthanide compounds, between the unpaired electron localized on the Gd-Gd bond and 4-f spins of Gd observed in the Gd₂@C₇₉N molecule.¹²⁸ In a seminal study, $M_2(a)C_{79}N$ (M=Y or Gd) molecules have been proposed as quantum information storage materials and the protected spin states can be manipulated to implement Grover's searching algorithm.¹²⁹

Single electron bonds have long been studied since 1931 in the essential paper by Pauling.¹³⁰ The nature of single electron bonds still remains unclear. Recently, it has been reported that one-electron bonds have no conceptual difference with normal two-electron bonds if interpreted by interference and quasi-classical contributions.¹³¹ Previously, several available molecules were used to observe the single electron bond, such as Li_2^+ and H_2^+ .^{132,133} Currently, we suggest that the stable radical heterofullerene series $M_2@C_{79}N$ (M = Sc, Y, La, Gd, Tb and Lu) provide an ideal example for investigating metal-metal one-electron bonds. It has been well established that the electron spin is stabilized by and two metal cations and protected by the cage from any chemical attacks.¹²⁶ Couplings between the unpaired electron and the metal cation as well as the unpaired electron and the f-spins of certain rare earth elements have been observed.^{134,135} The outstanding magnetic properties of $M_2@C_{79}N$ make it possible to understand the nature of single-electron bonds via magnetic measurements, such as EPR.

In previous studies, it has been proposed that fullerenes form electron donor-acceptor systems with various organic donors, such as N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) under photoexcitation.¹³⁶ Specific metallofullerenes, such as La@C₈₂ and La₂@C₈₀ have been observed to complex with TMPD and show unusual ground state charge transfer completely without any kinds of excitation.^{137,138} It is phenomenal to observe the conversion from single-electron bond inside M_2 @C₇₉N to a normal two-electron bond by accepting one extra electron from organic donor at the ground state.

In previous studies, $M_2@C_{79}N$ with Y, Tb and Gd were reported.^{126,127} Other IIIB and lanthanide metals are possible to extend the $M_2@C_{79}N$ family, due to their similarities and extensive presence in endohedral metallofullerenes.¹³⁹ In this study, great effort has been devoted to synthesize and isolate $M_2@C_{79}N$ (M = Sc, La and Dy) to expand the stable radical metallofullerene family. A surprising result is that although La₂@C₇₉N and Pm₂@C₇₉N are present and are characterized by chromatography, Sc₂@C₇₉N is absent, which indicates the instability of Sc₂@C₇₉N. We carefully examined M₂@C₇₉N (M = Sc, Y, La, Dy, Gd and Tb) molecules and found the lengths of the single-electron bond between two metals vary from 3.5 to 4.1 Angstrom. The variation of bond lengths suggests a change of bond strength, which, we believe, is significant to the stabilities of the M₂@C₇₉N molecule. In addition, we observed the electron transfer and spin site exchange behaviors between M₂@C₇₉N and TMPD in the standard titration using EPR and UV/vis spectra. The extra electron bond to a normal two-electron bond. The experimental results are augmented by theoretical computations to obtain further understandings of the observations.

Recently, a family of stable single molecular radical heterofullerenes (RHFs), $M_2@C_{79}N$ (M = Y, Gd, and Tb) attract vast attention. It has been recognized that the unpaired electron density is localized between the two metal cations. In a seminal study,¹⁴⁰ it suggests that the coupling between unpaired electron and 4-f spins of Gd is extremely significant. The magnetic properties of the RHFs enable them as the promising material for the next generation electronic devices, such as quantum computing.^{141,142} Before this study, Y, Ga and Tb based RHFs have been isolated and reported.^{126,127} It has been well established that the metal inside has a significant impact on the physical properties of RHFs. For example, Gd-based RHF shows much higher yields than other RHFs. In addition, another series of metallofullerenes, $M_3N@C_{2n}$ (2n = 68 – 96) have been

synthesized with Sc, Y, and each lanthanide (excluding Pm, Eu, Sm, and Yb).^{143,144} These observations encourage us to extend the M₂@C₇₉N family with other IIIB and lanthanide metals. Sc-based TNT-EMFs were the first discovered and have the highest yields among all metallofullerenes so far. La is present in a large family of metallofullerenes that show application potentials, such as La₂@C₈₀.^{145,146} La₂@C₇₉N has been observed as La₂@C₇₉N⁺ since 1999 in the gas-phase formation of endohedrally La-doped azafullerene ions.¹⁴⁷ The presence of La₂@C₇₉N has been observed in an early study of M₂@C₇₉N molecules.¹²⁷ Dy is one of the rare earth metals and has a cation radius close to Gd and Tb, which have been successfully synthesized as M₂@C₇₉N (M = Gd and Tb). Therefore, in this study, we devoted significant efforts to synthesize and isolate three RHFs, Sc₂@C₇₉N, La₂@C₇₉N as well as the surprising instability of Sc₂@C₇₉N.



Figure 2.13 Overview of current discovered $M_2@C_{79}N$ molecules. Yellow indicates the $M_2@C_{79}N$ molecules previously reported. Orange color indicates the molecules reported in the current study. Green indicates the unstable molecule $Sc_2@C_{79}N$. Gray color indicates unknown molecules, which need future work.

Preparation of M₂(*a*)C₇₉N. A Krätschmer-Huffman (K-H) generator was employed to synthesize $M_2(a)C_{79}N$ (M = Sc, La, and Dy) by vaporizing graphite rods with a mixture of graphite powder and M_2O_3 (M = Sc, La, and Dy) powders. Copper was utilized as a catalyst. The toluene-soluble extract from the K-H generator was then processed by cyclopentadiene-functionalized Merrifield peptide resin (CPDE-MPR) using chemical separation. The eluent was further separated by two-stage HPLC, using 5PBB and 5PYE columns. As reported previously,¹⁴⁸ M₂@C₇₉N RHFs co-elute with C₈₄ on a 5PBB column, and therefore we collected in a wide range around the peak of C₈₄ to avoid any possible loss of the $M_2@C_{79}N$ sample. The sample collected during the first stage with the 5PBB column was further separated on a 5PYE column. The high-resolution LD-TOF mass spectrometry confirmed the $M_2(a)C_{79}N$ (M = Sc, La, and Dy). For example, the isolation of La₂(a)C₇₉N is illustrated in Figure 2.14. (Sc₂(a)C₇₉N and Dy₂(a)C₇₉N see Appendices) On a 5PYE column, the La portion, which includes La₂@C₇₉N has a retention time of 44.99 minutes. The La portion, as suggested by the mass spectrum, contains both $La(a)C_{81}N$ and $La_2(a)C_{79}N$. A high resolution spectrum confirms that the La portion contains a series of La@C_{2n} (2n \leq 82) and a series of La₂@C_{2n} (2n \leq 78). A theoretical $La_2(a)C_{79}N$ mass spectrum in Figure 2.14 (b) further confirms the existence of $La_2(a)C_{79}N$. An intriguing and critical observation is that the tiny amount of $Sc_2(a)C_{79}N$ disappears during the separation process exposed to O_2 . However, other $M_2 @C_{79}N$ (M = Y, La, Gd, Tb, and Dy) molecules are quite stable. For example, $Y_2@C_{79}N$ remains unchanged for six months exposed to O_2 and $Gd_2(a)C_{79}N$ shows no reaction with several active chemicals, such as 5,5-dimethyl-1-pyrroline-N-oxide)-OH (DMPO).



Figure 2.14 Experimental Evidence of La₂@C₇₉N. (a) HPLC chromatogram of the La₂ portion on a 5PYE column (10 mm × 250 mm). The inserted mass spectrum confirms that it contains both La₂@C₇₉N and La@C₈₁N. (b) Comparison of the experimental mass spectrum of La₂@C₇₉N and its theoretical isotope distribution (top) (c) High-resolution LD-TOF mass spectrum of La₂ portion. It demonstrates that in addition to the existence of both La₂@C₇₉N and La@C₈₁N, there are a series of La@C_{2n} ($2n \le 78$) presenting in the La₂ portion. Flow rate: 2.0 ml toluene/minute; Detection: 390 nm.



Figure 2.15 The mass experimental and computational spectra of $Sc_2@C_{79}N$.

The absence of Sc₂@C₇₉N samples inspires us to explore the formation of the M₂@C₇₉N family. As previously reported, there are five electrons formally transferred from the inner cluster $(M_2)^{5+}$ to the outer cage $(C_{79}N)^{5-}$. The stability of $(C_{79}N)^{5-}$ has been confirmed to be comparable to that of its isoelectronic I_h - $(C_{80})^{6-}$ cage, since their HOMO-LUMO gaps are 2.67 eV and 3.16 eV, respectively, which are similar to other stable M₃N@ I_h -C₈₀ molecules.^{149–152} M₂@C₇₉N molecules, although they are radicals, are suggested stable because the spin density is localized inside the cage and stabilized by the two metal cations. The spin density between the two metal cations can be interpreted as a single electron bond in the (M₂) cluster. The stability of a M₂@C₇₉N is determined by both the cage $(C_{79}N)^{5-}$ and the inner cluster $(M_2)^{5+}$. We examine the cages of M₂@C₇₉N series (M = Sc, Y, La, Gd, Tb, and Dy) and they have no change. (see Appendices) Therefore, we propose that the stability of a M₂@C₇₉N molecule mainly depends on the stability of the $(M_2)^{5+}$ inner cluster, which is decided by the strength of the single electron bond.



Figure 2.16 The Electronic structures of $M_2@C_{79}N$ (M = Sc, Y, La, and Gd). The HOMO-LUMO gaps are shown in red color.

Investigations on single electron bond. Single-electron bonds are mostly observed for atoms from groups 1, 13 and 14 of the periodic table, such as H_2^+ and alkali-metal dimers. ^{153,154} IIIB and lanthanide metals are rarely reported forming single electron metal-metal bonds. In this study, we report our observation of the single-electron bond within a metal cluster $(M_2)^{5+}$ (M = Sc, Y, La, Gd, Tb, and Dy) that is capsulated by a $(C_{79}N)^{5-}$ cage. The strength of the single electron bond is largely affected by the metals. Although the cages of $M_2@C_{79}N$ (M = Sc, Y, La, Gd, Tb, and Dy) almost keep the same, the distances between the two metals vary a lot. The DFT optimized structures suggest that the bond length of M_2 (M = Sc, Y, La, Gd, Tb, and Dy) are 4.13 Å, 3.89 Å, 3.75 Å, 3.48 Å, 3.50 Å, and 3.51 Å, respectively. Generally, for the same kind of chemical bond, the bond length is closely related to the bond length and a shorter bond length typically indicates a stronger bond. As illustrated in **Figure 2.16**, the HOMO-LUMO gaps of $M_2@C_{79}N$ (M = Sc, Y, La, and Gd) are calculated as 1.84 eV, 2.39 eV, 2.46 eV, and 2.74

eV, respectively. The trend of band gaps agrees with that suggested by the bond lengths. The calculation data are also confirmed by the experimental observations. As previously reported, $Gd_2@C_{79}N$ is synthesized with a much higher yield than $Y_2@C_{79}N$ and $Gd_2@C_{79}N$ shows chemical inertness to several active chemicals.



Figure 2.17 Experimental and computational EPR spectra. (a) experimental EPR spectra of $Y_2@C_{79}N$ with 1 equivalent TMPD. (b) experimental EPR spectra of $Y_2@C_{79}N$ with 5 equivalent TMPD. (c) the computational EPR spectrum of $Y_2@C_{79}N$. (d) the computational EPR spectrum of TMPD.

Currently, we observed the switch of the metal-metal bond inside a $M_2@C_{79}N$ molecule between a single-electron bond and a normal two-electron bond in the presence of TMPD at the ground state. It has long been recognized that fullerenes and metallofullerenes are electron acceptors and can accept electrons from organic donors. Most electron transfers occur under photo excitations. A few examples, such as $La@C_{82}$ and $La_2@C_{80}$, have been shown to transfer electrons at the ground state. Although the ground state charge transfer

is not common, $M_2(a)C_{79}N$ is recently observed the ground state charge transfer with TMPD. In a seminal study, it has been reported that the TMPD radical has two characteristic peaks, 572 nm and 621 nm, in nitrobenzene. In this study, although the $Y_2(a)C_{79}N$ has absorption in the range from 450 nm to 650 nm, shows the two peaks at 572 nm and 621 nm after adding around 1 equivalent TMPD. The charge transfer is further confirmed by EPR spectra. The spectrum of $Y_2(a)C_{79}N$ has been reported as three symmetric resonances in a 1:2:1 intensity ratio. As illustrated in Figure 2.17 a, 1 equivalent TMPD is added into the pure $Y_2(a)C_{79}N$ solution and a set of multiple peaks is present around 3316 G, which is located between the two peaks of the $Y_2(a)C_{79}N$. The simulated EPR spectrum of TMPD and $Y_2(a)C_{79}N$ further confirmed the experimental spectrum. The calculated EPR g-factors of $Y_2@C_{79}N$ and TMPD are 1.9820 and 2.0036, (Figure 2.17 c and d) which are consistent with the experimental factors, 1.9817 and 2.0066. The mixture of $Y_2(a)C_{79}N$ and TMPD is recognized as an equilibrium system. As shown in Figure 2.17 b, adding 5 equivalent TMPD into the pure $Y_2@C_{79}N$ solution leads to the intensity increase of the TMPD peak in the EPR spectrum. It has recognized that two parallel π systems have interactions and the complexation often leads to electron transfer under photoexcitation or even at the ground state.



Figure 2.18 The EPR spectra of (a) $Y_2@C_{79}N$ and (b) $Gd_2@C_{79}N$ with 1 equivalent TMPD.

The electron transfer behavior between $M_2(a)C_{79}N$ and TMPD provides an ideal method to study the metal-metal single electron bond. In the EPR spectrum of the mixture, two signals are present, which are for the [TMPD]⁺ radical and the neutral $Y_2(a)C_{79}N$ radical. With the adding of TMPD and the increase of $[TMPD]^{++}$ radical signal, the Y₂@C₇₉N signal decreases and no other signal appears. The result suggests that the $Y_2(a)C_{79}N$ is converted to a molecule with all electrons paired. The potential to obtain one electron to transform the current single electron bond to a normal double electron bond can measure the single electron bond strength. $Gd_2(a)C_{79}N$ also shows the ability to accept electrons from TMPD in nitrobenzene at the ground state. We observed the Gd based EHFs are less able than Y based EHFs to accept electrons or to be reduced by TMPD. As previously reported, Gd based metallofullerenes often have lower reduction potentials than Y based metallofullerenes. For example, the reduction potential of $Gd_3N@I_h-C_{80}$ is 1.44 V and that of $Y_3N@I_h-C_{80}$ is 1.37 V.^{155,156} To estimate the electron accepting ability difference between $Y_2(a)C_{79}N$ and $Gd_2(a)C_{79}N$, a quantitive EPR study is performed on $Y_2(a)C_{79}N$ and $Gd_2(a)C_{79}N$ both with 1 equivalent TMPD. The mixture of $Y_2(a)C_{79}N$ with TMPD spectrum in Figure 2.18(a) shows much more significant signals of [TMPD]⁺ than that of $Gd_2(a)C_{79}N$ mixture in Figure 2.18(b). The integrations indicate the ratios of $Y_2(a_1C_{79}N / [TMPD]^{+}$ and $Gd_2(a_1C_{79}N / [TMPD]^{+}$ are 1:4 and 1:12, respectively. We acknowledge the overlays between $[TMPD]^{+}$ and $M_2(a)C_{79}N$ signals may lead to a large error in the estimation, and the ratio of $Y_2(a)C_{79}N / [TMPD]^{+}$ is underestimated and the ratio of $Gd_2(a_{P_{79}N} / [TMPD]^{+})$ is overestimated in a reasonable range. As suggested by DFT-based computations, the distance of two Y cations inside the fullerene cage decrease from 3.89 Å to 3.67 Å, when $Y_2(a)C_{79}N$ accepts one extra electron. It also confirms that the extra electron is located in the center of two Y cations and pairs with the single electron. However, the distance of two Gd cations just increases a tiny distance, from 3.48 to 3.49 Å, when $Gd_2(a)C_{79}N$ accepts one electron from TMPD. The bond length change from a single-electron bond to a double-electron bond implies that the Gd-Gd single electron bond is far more stable than the Y-Y single electron bond. We acknowledge that more experimental data may be required to comprehensively understand the metal-metal single electron bond, the current observations show that the strength of single electron bond largely depends on the metal. Based on the experimental data and computational data, we propose that the metal-metal electron bond strength increases from Sc to Gd and then decreases to Lu.

2.5 Conclusion

Great efforts have been devoted to investigate the application of fullerenes and metallofullerenes as materials for electronic devices. In this chapter, our contributions to applications and corresponding fundamental studies are demonstrated. The delocalized electron system of fullerenes makes them easy to be organized on graphene surfaces.

However, we discovered that the graphene surfaces are not always flat, but have rippled areas. Therefore, we studied the effects of rippled areas and find the rippled areas may change the packing style of molecules on the surface due to the difference of binding energies at different locations. The delocalized electron system also enables fullerenes and metallofullerenes electron transfer abilities. It has been shown that specific metallofullerenes show electron transfer with TMPD at the ground state. In this chapter, we explore different organic donors and find TNT-EMFs show the ground state electron transfer with spiro-OMeTAD. This observation inspires us to apply TNT-EMFs as solar cell electron transfer layer material and then enhance the stabilities of perovskite solar cells due to the hydrophobic nature of fullerene cages. $M_2(a)C_{79}N$ family has been reported having single electron bonds within the cage. We observed that the single electron bonds convert to regular double electron bonds in the presence of organic donor, such as TMPD. The metal-metal single electron bonds have different abilities to accept one electron and become regular double electron bonds due to the metal atoms. As shown in this chapter, a Y-Y single electron bond is less stable than a Gd-Gd single electron bond since they are more likely to accept one electron from an organic donor molecule. I acknowledge further work is necessary for the fundamental understanding of the electron transfers and the applications. This chapter, I believe, will be helpful for other studies regarding the application of fullerenes and metallofullerenes as electronic device materials.

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Chapter 3 Studies of Fullerene/Metallofullerene Chromatography Retention Behavior

Abstract

High performance liquid chromatography (HPLC) is widely applied for purification. Nowadays, fullerenes and metallofullerenes are synthesized via the arc-discharge technique and the product is a mixture containing a large collection of various fullerene molecules. The purification is essential to do further investigations. For the past three decades, the HPLC techniques for fullerene/metallofullerene isolation have been advanced to a high level. Isomers with a tiny difference are even possible to be resolved using multi-step HPLC separations. The retention mechanism, on the other hand, still remains unclear. Recently, a new family of C_{80} metallofullerene isomers, $A_3N@C_{80}-D_{5h}$, is reported and the retention behavior data for both A₃N@C₈₀-D_{5h} and A₃N@C₈₀-I_h are readily available. Chromatographic HPLC retention behavior is monitored for two different HPLC stationary phases, pentabromobenzyl and pyrenylethyl and augmented by DFT computational results. In this chapter, I would like to introduce our proposed mechanism for the separation of the two similar metallofullerene isomers and based on the experimental factors, we built a new model to estimate retention times of fullerenes and metallofullerenes starting with only computational data. After that, we validate the model using two series of metallofullerenes and discuss the dipole effects on the retention behaviors.

Note: In this following chapter, I thank Tianming Zuo for measuring experimental chromatographic retention data.

3.1 Polarizability Effects Dominate the Chromatographic Retention Behavior of Spheroidal and Ellipsoidal Metallofullerene Nanospheres

In early chromatographic studies of fullerenes, it was readily recognized that a linear relationship exists between the chromatographic retention parameter, (capacity factor, K), and the empty-cage fullerene carbon cage number (N) for a number of different chromatographic phases.¹⁻⁴ In a seminal study by Kappes and coworkers,² it was shown that certain low polarity chromatographic stationary phases; such as, pyrenylethyl (PYE) exhibit weak induced dipole-dipole interactions and London dispersion forces with fullerenes and endohedral metallofullerenes (EMF's). It is well established that the stationary phase-fullerene cage π - π polarizability⁵ dominates the chromatographic retention processes yielding a linear relationship between the chromatographic retention capacity factor (K), and the empty-cage fullerene carbon cage number (N) in the range of C_{60} - C_{100} .¹⁻⁴ This linear dependence with the stationary phase is remarkable in view of the significantly different cage shapes and symmetries of the fullerene and EMF cages.^{6–9} For the case of metallofullerenes, the polarizability and corresponding fullerene cage number have been used to predict the number of π -electrons transferred from the endohedral cluster to the fullerene cage. For the trimetallic nitride template endohedral metallofullerenes (TNT-EMFs),⁷⁻¹⁰ A₃N@C₈₀(A= Sc, Y, Lu, Tm, Ho, Er, Tb, and Gd)¹¹⁻ ¹⁸ with icosahedral I_h symmetry, this formally represents 6 π -electrons transferred from the $(A_3N)^{6+}$ cluster. After the initial discovery of the TNT EMFs, a second minor D_{5h} isomer¹⁹ was first reported by ¹³C NMR and later further characterized by an X-ray single crystal crystallographic structure study.²⁰



Figure 3.1 The TNT-EMFs cage isomers. (a) spherical $Sc_3N@C_{80}-I_h$. (b) ellipsodial $Sc_3N@C_{80}-D_{5h}$.

In the current study, we explore the subtle factors that influence the chromatographic retention mechanism(s) of the TNT-EMFs cage isomers $A_3N@C_{80}$ -I_h and $A_3N@C_{80}$ -D_{5h} for Group IIIB and lanthanide trimetallic nitride clusters, $(A_3N)^{6+}$ illustrated in **Figure 3.1** by prototype, $Sc_3N@C_{80}$ -I_h and $Sc_3N@C_{80}$ -D_{5h}.²¹ The experimental results²² are interpreted in conjunction with DFT computational data for the fullerene and metallofullerene cage polarizability, charge transfer from the internal cluster $(A_3N)^{6+}$, and influence of fullerene cage symmetry. Although the encapsulation of a metal cluster may alter the polarizabilities of the fullerene cage due to the phenomenon of depression of polarizability,^{23,24} it has been shown that the mean polarizabilities of EMFs in comparison with the same fullerene cage are almost equal as a result of screening effects.^{25–27}



Figure 3.2 Chromatographic retention parameter log K versus empty-cage fullerene and A₃N@C₈₀-I_h carbon cage number. Toluene mobile phase, flow rate1 ml/min. a) PBB column, A = Gd (86.2), Tb (86.1), Ho and Er (85.7), Tm, Lu, and Y (85.4), Sc (83.3); b) PYE column, A = Gd (86.5), Tb (85.8), Ho and Er (85.7), Tm and Lu (85.2), Y (84.6), Sc (85.4). The PBB empty-cage fullerene regression line (y = 0.0348x-1.9649, R² = 0.999) and PYE fullerene (y = 0.0284x-1.7694, R² = 0.993).

The retention times of the TNT-EMFs A₃N@C₈₀-I_h and A₃N@C₈₀-D_{5h} (A= Sc, Y, Lu, Tm, Ho, Er, Tb, and Gd) are summarized in **Table 3.1** and the fullerene empty-cage data is given in **S1a** and **S1b**.²² The HPLC columns employed in this study are the 3-[(pentabromobenzyl)oxyl]propylsilyl column (PBB), the 2-(1-pyrenyl)ethylsilyl column (PYE) with toluene as the mobile phase. The PYE column provides overall stronger retention of the TNT EMFs as illustrated in **Table 3.1** and **Figure 3.2** because of stronger extended π - π stacking interactions. Furthermore, the A₃N@C₈₀-D_{5h} isomers are only resolvable from the A₃N@C₈₀-I_h isomers on the PYE column with the corresponding retention time data provided in **Table 3.1**. Recently, computational DFT results have been reported describing the polarizabilities for the empty-cage fullerenes (C₆₀, C₇₀, C₇₈, and C₈₄) and the TNT EMFs, Sc₃N@C₆₈-D₃, Sc₃N@C₇₈-D_{3h} Sc₃N@C₈₀-D_{1h} and Sc₃N@C₈₀-D_{5h} shown in **Figure 3.3** were obtained from earlier studies.^{27,28} These polarizabilities are plotted versus experimentally measured chromatographic retention data obtained in the current study (S1a and S1b). The computational polarizability and Mulliken charge densities results for $(C_{80}-I_h)^{6-}$ and $(C_{80}-D_{5h})^{6-}$ as well as the polarizability anisotropy ($\Delta \alpha$) for the fullerene, C_{70} -D_{5h} and C_{60} -I_h cages were performed using the B3LYP functional as provided in a Gaussian 09 program package. All of the molecules were geometry optimized at the B3LYP level with a 6-31G* basis set.(S3) Where is S3?

In previous studies,² it has been demonstrated that TNT-EMFs that contain significant dipole moments have significantly longer retention times and sharply deviate from the linear regression line for both empty-cage fullerenes and isolated pentagon rule (IPR) metallofullerenes. Examples of metallofullerenes with significant dipole moments include certain monometallic EMFs ($A(a)C_{82}$) and pentalenes containing non-IPR TNT EMFs (e.g., Y₃N@C₂-C₇₈, Y₃N@C₈-C₈₂, and Y₃N@C₈-C₈₄).²⁹ However, the spheroidal A₃N@C₈₀-I_h and ellipsodial A₃N@C₈₀-D_{5h} metallofullerenes in the current study do not have significant permanent dipole moments. As illustrated in Figure 3.2, numerous studies have clearly demonstrated a linear relationship between the chromatographic capacity factor K (K = $(t_r - t_0)/t_0$, where t_r is the retention time and t_0 is the dead time) and the number of π electrons on empty fullerene cages and EMFs (carbon number). This linearity holds for a wide range of different molecular cage symmetries for both empty cages and EMFs. This relationship is illustrated for the TNT-EMFs $A_3N@C_{80}$ -I_h (A= Sc, Y, Lu, Tm, Ho, Er, Tb, and Gd) for both the PBB and PYE stationary phases.

TNT-EMFs	5	t _R (minute)	Δt_{R} (minute)	К	ΔΚ
Gd ₃ N@C ₈₀	I _h	43.12 ± 0.16	1.72 ± 0.22	4.91± 0.02	
	D_{5h}	44.84 ± 0.15		5.15 ± 0.02	0.24 ± 0.03
Tb ₃ N@C ₈₀	I _h	41.50 ± 0.04	1.79 ± 0.06	4.58 ± 0.00	
	D_{5h}	43.29 ± 0.04		4.82 ± 0.00	0.24 ± 0.00
Ho ₃ N@C ₈₀	I _h	41.25 ± 0.05	2.15 ± 0.07	4.68 ± 0.02	
	D _{5h}	43.40 ± 0.05		4.98 ± 0.02	0.30 ± 0.03
Er ₃ N@C ₈₀	I _h	41.09 ± 0.06	1.91 ± 0.08	4.66 ± 0.02	
	D _{5h}	43.00 ± 0.05		4.92 ± 0.02	0.26 ± 0.03
Tm ₃ N@C ₈₀	I _h	40.18 ± 0.11	1.53 ± 0.16	4.50 ± 0.03	
	D_{5h}	41.71 ± 0.11		4.71 ± 0.03	0.21 ± 0.04
Lu ₃ N@C ₈₀	I _h	40.06 ± 0.04	1.75 ± 0.10	4.49 ± 0.04	
	D _{5h}	41.81 ± 0.07		4.73 ± 0.04	0.24 ± 0.06
Y ₃ N@C ₈₀	I _h	38.92 ± 0.12	1.57 ± 0.18	4.28 ± 0.02	
	D_{5h}	40.49 ± 0.13		4.49 ± 0.02	0.21 ± 0.03
Sc ₃ N@C ₈₀	I _h	44.00 ± 0.02	1.38 ± 0.03	4.87 ± 0.03	

D_{5h}	45.38 ± 0.02	5.05 ± 0.03	0.18 ± 0.04
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Table 3.1. Chromatographic Retention Behavior of $A_3N@C_{80}$ (I_h and D_{5h}) EMFs (PYE column, toluene mobile phase, 2ml/min)

The A₃N@C₈₀-I_h series have predicted cage sizes of a formal ~86 π electrons and are consistent with the electronic model of the TNT-EMFs,⁴ where the neutral open shell (C₈₀-I_h)⁰ cage is highly stabilized by transfer of 6 electrons, (C₈₀-I_h)⁶. For the PYE column, the chromatographically predicted electron transfer is 4.6-6.5 π electrons. Whereas for the PBB column the range is 5.4-6.2 π electrons for the lanthanides, but Sc₃N@C₈₀-I_h exhibits reduced transfer (3.3 π electrons) with this column, with overall weaker chromatographic retention. The reduced electron transfer for the Sc metallofullerene could be due to *p*-*d* orbital back donation as predicted in computational studies.³⁰⁻³² The log K parameter for the lanthanide TNT-EMFs also exhibits a reasonably linear relationship with lanthanide ionic radii values as illustrated in **S2** for both the PBB and PYE columns with progressive stronger retention from the smallest lanthanide ion, Lu³⁺ to the largest Gd³⁺ consistent with arguments based on lanthanide ion contraction across the lanthanide series.



Figure 3.3 Chromatographic retention parameter ln t_r/t_o versus DFT polarizability for fullerenes and EMFs, Sc3N@C2n (n = 34, 39 and 40). Toluene mobile phase, flow rate1 ml/min. a) PBB column, regression line (y = 0.0503x-3.85, R2 = 0.997); b) PYE column, EMFs, (y = 0.0411x-3.58, R2 = 0.997); c) PYE column, fullerenes, (y = 0.0410x-3.13, R2 = 0.997).

However, a surprising feature of the data shown in **Table 3.1** is the small, but the constant difference ($\Delta K = 0.24 \pm 0.04$) between the chromatographic retention parameter K of the A₃N@C₈₀-I_h and A₃N@C₈₀-D_{5h} isomers. This implies that to a first order approximation the retention parameter difference (ΔK) between these isomers is independent of differences in the metal atom of the internal cluster, (A₃N)⁶⁺. As previously noted,² Kappes has argued that the major retention mechanism for fullerenes on PYE phase chromatographic columns is based mainly on van der Waals interactions and can be modeled mainly by dispersion forces resulting primarily from interactions between π -electrons on the PYE stationary phase and the π system of the fullerene and/or

EMF analytes. Eq. 1 and Eq. 2 represent the corresponding models for empty-cage fullerene and EMF chromatographic retention parameters (t_R and t_R^*) and the stationary phase interaction. The polarizabilities, dipole moments, and ionization potentials for the

empty-cage fullerenes and EMFs are given by $(\alpha_2, \mu_2, \text{ and } I_2)$ and $(\alpha_2^*, \mu_2^*, \text{ and } I_2^*)$, respectively. In this model, **Eq. 2** assumes that the empty-cage fullerenes and EMFs have the same center-center van der Waals distance, r and the same ionization potential *vide infra*. The dipole moments for the A₃N@C₈₀-I_h and A₃N@C₈₀-D_{5h} isomers computational

results show negligible dipole moments *vide infra*, $\mu_2^* \approx 0$ and **Eq. 3.1** reduces to **Eq. 3.2** under these conditions.³³

$$\ln\left(\frac{t_R}{t_0}\right) = c + \left(\frac{da\alpha_1}{T}\right)\alpha_2 \tag{3.1}$$

$$\ln\left(\frac{t_R^*}{t_0}\right) = c + \left(\frac{da\alpha_1}{T}\right)\alpha_2^* + \frac{b}{a}\left(\frac{da\alpha_1}{T}\right)(\mu_2^*)^2$$
(3.2)

where $a = \frac{3}{2} \frac{I_1 I_2}{(I_1 + I_2)}$, $b = \frac{1}{4\pi\epsilon_0}$, c = constant,

and $d = \frac{1}{Rr^6}$



Figure 3.4 The small site-specific polarizability differences between $(C_{80}-I_h)^{6-}$ and $(C_{80}-D_{5h})^{6-}$. (a) Mulliken charge distribution of $(C_{80}-I_h)^{6-}$. (b) Mulliken charge distribution of $(C_{80}-D_{5h})^{6-}$.

Recently, computational DFT results have been reported^{28,29} describing the polarizabilities for a series of empty-cage fullerenes (C_{60} , C_{70} , C_{78} , and C_{84}) as well as the TNT EMFs, Sc₃N@C₆₈-D₃, Sc₃N@C₇₈-D_{3h} Sc₃N@C₈₀-D_{Ih} and Sc₃N@C₈₀-D_{5h} and these results are shown (**Figure 3.3**) versus our experimentally measured chromatographic

parameter, $\ln\left(\frac{t_R}{t_0}\right)$. In agreement with **Eq. 3.2**, there is a linear dependence for both stationary phases versus the DFT calculated polarizability of the empty-cage fullerenes, but as expected with different slopes (see **Figure 3.1**). In addition, for the PYE column there is a characteristic offset between the lines for the empty-cages and the EMFs which is due to the expected charge transfer from the internal $(Sc_3N)^{6+}$ cluster of ~6 π -electrons as previously noted. Although this is a limited data set, a surprising result is the same

slope is observed for the empty-cage and the EMF correlations in **Figure 3.3.** This is consistent with the assumption for **Eq. 3.2** regarding the empty-cage fullerenes and EMFs having the same center-center van der Waals distance, r and the same ionization potential between the PYE stationary phase. In addition, there is a small difference in the DFT calculated polarizability²⁷ reported for the Sc₃N@C₈₀-I_h (119.3 Å³) and Sc₃N@C₈₀ -D_{5h} (120.0 Å³) isomers which is consistent with the experimental difference as shown in **Table 3.1**. Assuming the slope (m = 0.041) for the plot of ln(t_r/t_o) versus the calculated

polarizability (**Figure 3.3**) is equal to $\left(\frac{da\alpha_1}{r}\right)$ as suggested by Kappes and coworkers leads to a predicted value of $\Delta K = 0.20$ which is fortuitously close to the experimental difference of $\Delta K = 0.18$ for the Sc₃N@C₈₀-I_h and Sc₃N@C₈₀-D_{5h} isomers. Moreover, a further test of this conjecture, our similar DFT calculations just for the charged empty cages, $(C_{80}-I_h)^{6-}$ and $(C_{80}-D_{5h})^{6-}$ leads to polarizabilities of 105.1 Å³ and 104.0 Å³ for the $(C_{80}-D_{5h})^{6-}$ and the $(C_{80}-I_h)^{6-}$ cages. These values lead to a predicted value of $\Delta K = 0.15$ which is approximately 60% of the experimental average value. Although the charge distributions of the $(C_{80}-I_h)^{6-}$ and $(C_{80}-D_{5h})^{6-}$ isomers are very similar, there are subtle site-specific differences which are at the pentagon C₅ axis carbons and hexagon belt carbons along the horizontal symmetry plane in the $(C_{80}-D_{5h})^{6-}$ isomer which presumably lead to the small site-specific polarizability differences (**Figure 3.4**). It has been suggested that the anisotropic polarizability factor is a better parameter to predict the chemical structure differences of fullerenes and metallofullerenes.²⁸ For example, the

calculated (DFT B3LYP) difference of anisotropy ($\Delta \alpha$) for the fullerene, C₇₀ -D_{5h} and C₆₀-I_h cages have values of 12.18 Å³ (70 a.u.) and 0.00 Å³, respectively in agreement

with previously reported values.²⁸ In similar fashion, the difference of anisotropy ($\Delta \alpha$) for the similar symmetry (C_{80} - D_{5h})⁶⁻ and the (C_{80} - I_h)⁶⁻ cages have values of 4.47 Å³ and 0.00 Å,³ respectively (see **S3.4**). In future studies, the polarizability anisotropic parameter could evolve as a key predictor of subtle chemical structural differences in chromatographic retention and other intermolecular interactions.

To summarize, the results of the current study suggest that in the absence of significant dipole moments and after correction for the number of π -electrons transferred to the fullerene cage, the chromatographic retention times of the TNT EMFs are dominated by the polarizability of the fullerene cage. More importantly, site-specific and anisotropic polarizability differences appear to explain subtle chromatographic retention differences in this series of spheroidal A₃N@C₈₀-I_h and elipsodial A₃N@C₈₀-D_{5h} isomers. We acknowledge that other factors including non-vanishing permanent dipole moments and molecular diffusion differences at the stationary phase site could also be important in controlling chromatographic retention of these isomers, but these subtle differences in retention times are consistent with experimental and computational polarizability differences.

3.2 DFT Prediction of Chromatographic Retention Behavior for a Trimetallic Nitride Metallofullerene Series

The high pressure liquid chromatography (HPLC) retention behavior of fullerenes and metallofullerenes provides a convenient system for studying the intermolecular interactions between conjugated spheroidal π systems and stationary chromatographic phases. Previous studies have established in the absence of significant dipole moments, a linear relationship exists between chromatographic HPLC retention times and the

polarizability of fullerenes and endohedral metallofullerenes (EMFs). Previous studies have shown that density functional theory (DFT) can accurately predict the polarizability and dipole moments of fullerenes and EMFs. In the current study, we extend this approach to predict the chromatographic retention behavior of the yttrium and terbium trimetallic nitride metallofullerene series $Y_3N@C_{2n}$ (n = 39 - 44) and Tb₃N@C_{2n} (n = 40 -44). The results of this study demonstrate that the chromatographic retention behavior of the EMF series can be predicted even for systems that violate the isolated pentagon rule (IPR) with significant dipole moments and significant differences in the symmetry of the fullerene cage. The results of this study can be readily extended to predict the dominant factors for the interactions between other fullerene and metallofullerene homologous series.

The discovery of trimetallic nitride template endohedral metallofullerenes (TNT-EMFs) provides a new class for studying the retention behaviors of fullerenes and EMFs.^{19,20,34–37} During the last two decades, various TNT-EMFs have been synthesized and isolated,^{19,20,34,35,37} and some of them contain pentalene motifs that violate the isolated pentagon rule (IPR).^{38–40} In the current study, a series of TNT-EMFs, A₃N@C_{2n} (A = Y and Tb, n = 39 – 44) are readily available,^{22,41,42} and these homologous series contains fullerene cages with significantly different symmetries and non-IPR fullerenes. Thus, these two EMF series are ideal for modeling and predicting the chromatographic retention behavior with different cage sizes and charge transfers from the internal cluster, members with significant dipole moments, and fullerene cage symmetries.

In our previous study,⁴³ we observed the chromatographic retention behavior of spherical $A_3N@C_{80}$ -I_h and elipsodial $A_3N@C_{80}$ -D_{5h} (A = Sc, Y, Lu, Tm, Ho, Er, Tb) for two

different HPLC stationary phases, PBB and PYE. We proposed that site polarizability differences dominated the chromatographic retention behavior for the C_{80} -I_h and C_{80} -D_{5h} cages in the absence of significant dipole moments. In the current study, we extend the range of EMFs to include a series of TNT-EMFs, from A₃N@C₇₈ to A₃N@C₈₈, to explore the factors that dominate the chromatographic retention behavior. In previous DFT computational studies it was found that the encapsulations of metallic clusters change the polarizabilities of outer fullerene cage surface because of the phenomenon polarizabilities of EMFs and those of corresponding empty-cage fullerenes are extremely small due to screening effects.^{25,26} In this study, we interpret the experimental data in conjunction with DFT computational polarizabilities and propose that a linear relationship exists between the fullerene cage polarizabilities and the retention behavior after correction for charge transfer even for cages with significant dipole moments.



Figure 3.5. DFT-computed dipole moments of the $(C_{2n})^{6-}$ (n = 39 – 44). The pentagons are highlighted in red.

The retention times of the TNT-EMFs, $A_3N@C_{2n}$ (A = Y and Tb, n = 39 – 44) with the PYE column are summarized in **Table 3.2**. In **Figure 3.6**, log K versus the empty fullerene cage size regression line is provided in the Appendices. Based on the regression line for the empty cages, we have predicted transferred electrons from internal clusters for the TNT-EMFs series (Y₃N@C_{2n}, n = 39 – 44 and Tb₃N@C_{2n}, n = 40 – 44). With the experimental retention data in hand, we have augmented the chromatographic retention behavior data with DFT computational polarizability data and the internal metal cluster charge transfer to the fullerene cage surface (**Figure 3.6**). Furthermore, the polarizabilities of the EMFs series and corresponding empty-cage fullerenes, (C₇₈-C₂)⁶⁻, (C₈₀-T_h)⁶⁻, (C₈₀-D_{5h})⁶⁻, (C₈₂-C₈)⁶⁻, (C₈₄-C₈)⁶⁻, (C₈₆-D₃)⁶⁻, and (C₈₈-D₂)⁶⁻ are plotted versus experimental chromatographic retention data (**S3**). The results are illustrated in **Figure 3.7**. The computational data are obtained with a Gaussian 09 package (**S5**) program. All structures of EMFs and empty-cage fullerenes are fully optimized at the B3LYP level with 6-31G* basis set.



Figure 3.6 Chromatographic retention parameter log K of $A_3N@C_{2n}$ (A = Y or Tb, n = 39 – 44) versus empty-cage fullerene retention times. Toluene mobile phase, flow rate 1 mL/min. a) PYE column, $Y_3N@C_{78}$ -C₂ (87.0), $Y_3N@C_{80}$ -I_h (84.7), $Y_3N@C_{80}$ -I_h (85.4), $Y_3N@C_{82}$ -C_s (87.8), $Y_3N@C_{84}$ -C_s (92.2), $Y_3N@C_{86}$ -D₃ (90.3), $Y_3N@C_{88}$ -D₂ (93.1). b) PYE column, Tb₃N@C₈₀-I_h (85.6), Tb₃N@C₈₀-I_h (86.4), Tb₃N@C₈₂-C_s (88.9), Tb₃N@C₈₄-C_s (92.3), Tb₃N@C₈₆-D₃ (90.4), Tb₃N@C₈₈-D₂ (93.3).

In previous studies, it was well recognized that a linear relationship existed between the total number of π electrons of fullerenes and/or EMFs and the chromatographic capacity factor K, K = $(t_r - t_o)/t_o$, where t_r is the retention time and t_o is the dead time. This linear

relationship has been confirmed for a wide range of fullerenes and EMFs of different symmetries and metal clusters. It has been shown that this linear relationship can be employed to predict the degree of electron transfer for EMFs. As illustrated in **Figure 3.6**, the chromatographically predicted electron transfer for the $A_3N@C_{2n}$ (n = 39 – 44) series is 4.3 – 9.0 electrons. As previously reported, excess π electrons are transferred to the cage C_{78} (9.0 for $Y_3N@C_{78}$ - C_2) and the cage C_{84} (8.2 for $Y_3N@C_{84}$ and 8.3 for Tb₃N@C₈₄), respectively, because of significant dipole moments for these non-IPR cages⁴⁴ and stronger chromatographic retention behavior is readily observed, (**Table 3.2**). Whereas, for the cages of C_{86} , reduced electron transfer (4.3 electrons for $Y_3N@C_{86}$ and 4.4 for Tb₃N@C₈₆) is shown and results in weaker chromatographic retention.
TNT-EMFs	t _R (minute)	t _o (minute)	К	log K
$Y_3N@C_{78}-C_2$	43.60	7.32	4.96	0.70
$Y_3N@C_{80}\text{-}I_h$	38.92	7.32	4.32	0.64
$Y_3N@C_{80}-D_{5h}$	40.49	7.32	4.53	0.66
$Y_3N@C_{82}-C_s$	46.10	7.32	5.30	0.72
$Y_3N@C_{84}-C_s$	59.80	7.33	7.16	0.85
Y ₃ N@C ₈₆ -D ₃	53.10	7.32	6.25	0.80
Y ₃ N@C ₈₈ -D ₂	62.40	7.32	7.52	0.88
$Tb_3N@C_{80}\text{-}I_h$	42.86	7.68	4.58	0.66
$Tb_{3}N@C_{80}-D_{5h}$	44.94	7.72	4.82	0.68
$Tb_3N@C_{82}\text{-}C_s$	47.68	7.13	5.69	0.76
$Tb_3N@C_{84}\text{-}C_s$	50.34	6.20	7.12	0.85
$Tb_3N@C_{86}-D_3$	51.63	7.09	6.28	0.80
$Tb_3N@C_{88}\text{-}D_2$	62.85	7.33	7.58	0.88

Table 3.2 Chromatographic Retention Behaviors of $Tb_3N@C_{2n}$ and $Y_3N@C_{2n}$ (n = 39 - 44) EMFs (PYE column, toluene mobile phase, 2mL/min)

As demonstrated in earlier studies,² the retention mechanism for fullerenes and EMFs on non-polarity chromatographic columns is mainly due to van der Waals interactions. In a seminal study, Kappes and his coworkers reported that the retention behavior of fullerenes and EMFs can be modeled mainly based on the interactions between the π system of the PYE stationary column and the π -electrons of the fullerene and/or EMFs, and the model can be described in terms of polarizabilities, dipole moments and ionization potentials. In this model, polarizabilities, dipole moments and ionizations are given by $(\alpha_1, \mu_1, \text{ and } I_1)$ for PYE stationary phase, $(\alpha_2, \mu_2, \text{ and } I_2)$ for empty-cage fullerenes and $(\alpha_2^*, \mu_2^*, \text{ and } I_2^*)$ for the EMFs, respectively. When EMFs do not show significant dipole moments, equation 3.2 can be reduced to the form of equation 3.1 if the molecular dipole moment $\mu_2^* \cong 0$.

In our previous study, we proposed that a small but constant difference of site-specific polarizabilities between the spheroidal $A_3N@C_{80}-I_h$ and elipsodial $A_3N@C_{80}-D_{5h}$ (A = Sc, Y, Lu, Tm, Ho, Er, Tb) was the dominant factor for chromatographic retention times in the absence of significant dipole moment. Currently, we explore the HPLC retention behavior for a series of EMFs, $A_3N@C_{2n}$ (A = Y and Tb, n = 39 - 44), and augment the experimental data with DFT-computational polarizabilities and dipole moments. It has been well established that pentalene motifs on fullerene and/or EMFs readily lead to enhanced dipole moments and then sharply increase the chromatographic retention times.²⁹ As noted previously, fullerene retention behavior is mainly determined by polarizabilities and dipole moments of fullerenes and EMFs. Thus, equation 3.2 provides a convenient method to make corrections for the presence of significant dipole moments, and the corrected retention time data should show the same relationship between polarizability and chromatographic retention behaviors as argued above. As suggested by Kappes and co-workers, the value of $\frac{da\alpha_1}{T}$ can be calculated based on the slope in Figure 3.6, and the calculated value (m = 0.041) is consistent with our previous study. In equation 3.2, the ionization potentials for both empty-cage fullerenes and EMFs are assumed to be the same, and this assumption has been tested by a series of empty-cage fullerenes (C₆₀, C₇₀, C₇₈ and C₈₄) and the TNT-EMFs (Sc₃N@C₆₈-D₃, Sc₃N@C₇₈-D_{3h} $Sc_3N@C_{80}$ - D_{Ih} and $Sc_3N@C_{80}$ - D_{5h}) on PYE column, due to the same slope for ln (t_r / t_o) versus polarizabilities.⁴³ The ionization potentials of pyrene (7.50 \pm 0.05 eV) and fullerenes are readily available and reported by the Mautner group and the Boltalina group, respectively. The corrections are summarized in S3.2. There is a linear relation (R^2) = 0.9889) between the polarizabilities of empty-cage fullerenes with -6 charges $(C_{2n})^{6-1}$ and corresponding chromatographic retention times (S3.5). The linear relationship establishes that the chromatographic retention times of TNT-EMFs are dominated by the polarizabilities of the fullerene cages after corrections for significant dipole moments and the number of π -electrons transferred to the fullerene cages. Based on this approach, we can estimate the retention times based on DFT-computational polarizabilities, dipole moments, and predicted charge transfer. As illustrated in Figure 3.7 (b) and Figure 3.7 (d), the slopes for predicted retention times versus experimental retention times are 0.98 and 0.97 for $Y_3N@C_{2n}$ (n = 39 - 44) and $Tb_3N@C_{2n}$ (n = 40 - 44), respectively, both of which are fortuitously close to the same slope. We acknowledge that the deviations from the linear regression line in Figure 3.7 (b) and 3.7 (d) are possibly due to significant errors in the dipole moment corrections as well as other subtle factors effecting the retention behavior. It is important to note, that our computational approach only accounts for the charge transfer to the outer cages, and assumes no role for the specific metals of the encapsulated trimetallic nitride cluster, $(A_3N)^{6+}$ with regard to chromatographic retention behavior.



Figure 3.7. Predicted retention time versus experimental retention time for EMFs, Y₃N@C_{2n} (n = 39 – 44) and Tb₃N@C_{2n} (n = 40 – 44). **a)** Y₃N@C_{2n} (n = 39 – 44), predicted retention time without corrections for charge transfer and dipole moment. (y = 0.8210x-0.9620, R² = 0.7932) **b)** Y₃N@C_{2n} (n = 39 – 44), predicted retention time with corrections for charge transfers and dipole moments. (y = 0.9807x, R² = 0.9813) **c)** Tb₃N@C_{2n} (n = 40 – 44), predicted retention time without corrections of charge transfer and dipole moment. (y = 0.8339x-0.9960, R² = 0.8207) **d)** Tb₃N@C_{2n} (n = 40 – 44), predicted retention time with corrections for charge transfers and dipole moments. (y = 0.9677x, R² = 0.9906)

We have explored the chromatographic retention behaviors for a series of diverse fullerenes (C_{78} , C_{80} -I_h, C_{80} -D_{5h}, C_{82} , C_{84} , C_{86} , C_{88}) and EMFs ($A_3N@C_{2n}$, A = Y and Tb, n = 39 - 44). To summarize, the results demonstrate that after the correction for dipole moment and the number of π -electrons transferred to the fullerene cages, a linear relationship exists between the chromatographic retention times and polarizabilities for a wide range of fullerenes and EMFs with different molecular cage symmetries and shapes and we can estimate the retention times with only small errors. It is remarkable that this approach ignores the influence due to different metal atoms in the endohedral cluster and recognize they do have a finite, but minor effect on chromatographic retention behavior. We also acknowledge that other subtle factors may have minor effects on the retention behaviors of fullerenes and/or EMFs. As demonstrated vide infra, we believe these subtle factors should be consistent with polarizabilities, and just have tiny effects on retention times. In addition, the effects of anisotropic polarizabilities, which still remain unknown, may also impact the retention behaviors and should be included for a more accurate model in future studies. In conclusion, the current study shows the linear relationship between fullerene and EMF retention behaviors and polarizabilities for a series of diverse fullerenes and EMFs, and also provides a method to predict retention behaviors of any other aromatic π -systems.

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Chapter 4 Oxygen Chemisorption Sites on Activated Carbons Characterized by Flow Dynamic Nuclear Polarization

Note: In this following chapter, I thank Dr. Juan Gu for performing the EPR and DNP experiments.

Activated carbons (or carbonaceous chars) are widely used in many industrial and medical adsorbent applications because of their distinct ability to adsorb numerous gaseous and/or liquid analytes. The structure of these activated carbons exhibits a 3dimensional network of micro- and mesopores with a highly developed internal graphitic surface area and porosity. Although various spectroscopic and analytical methods for the characterization of activated carbon materials have been reported, the heterogeneity of the surface of activated carbons has been difficult to characterize. Even more challenging is characterizing the interaction between important analytes and the endogenous surface radicals known to be present in almost all activated carbons. In this study, we utilized flowing benzene to characterize the industrially important O2 chemisorption on the surface of cellulose activated carbons via solid/liquid intermolecular transfer (SLIT) ¹H dynamic nuclear polarization (DNP). Although a scalar ¹H DNP Overhauser enhancement is rarely observed since the ¹H nuclide exhibits only a minor nuclearelectron hyperfine interaction, we find that the introduction of oxygen (air) to the flowing benzene/activated carbon interface completely suppresses a scalar (positive) ¹H DNP Overhauser effect in high temperature activated carbons (550-600 °C). Moreover, this scalar (positive) ¹H DNP Overhauser effect is completely suppressed upon introduction of oxygen (air) to the flowing benzene/activated carbon interface. This result is consistent with triplet radical carbene-like zig-zag sites at the planar edges of disordered graphene that react with oxygen to form quenched radical sites. Whereas, a solid-state DNP effect is observed at lower temperatures representing a different radical center (e.g., aromatic heteroatom radical sites) with no discernable evidence of O₂ chemisorption or radical site quenching. In summary, the endogenous free-radical structure of activated carbons is strongly dependent on the temperature range for the heat-treated temperature (HTT) preparation of the activated carbons. These results illustrate that the flow solid/liquid intermolecular transfer (SLIT) ¹H DNP technique is a novel approach for studying the dynamics, structure, and chemistry of the intermolecular interactions of gaseous (O₂) and liquid (benzene) analytes at the surface radical sites of activated carbons.

4.1 Background of Activated Carbon and DNP Technique

Activated carbon (AC), chars, and biochars are important industrial materials which are prepared from a large number of different carbonaceous materials, including cellulose, coconut shells, wood, organic polymers, coal, and petroleum pitch.^{1,2} Activated carbons (ACs) are used in a wide variety of industrial and technological applications, such as catalyst supports, air purification, and water treatment.^{3–7} The nature of the carbonaceous precursor and the method of activation have a strong influence on the pore structure and adsorption capacity of the resulting AC. Various methods of activation have been used to obtain ACs with a high surface area and porosity.^{8–11} One approach utilizes chemical activation at lower temperatures (350 - 600°C) with chemical additives including ZnCl₂, KOH, NaOH, and H₃PO4.^{12–15} Whereas, physical activation refers to gasification of the carbonaceous material by heat temperature treatment (HTT) in the range of 400-1000 °C.^{16–19} The resulting ACs have porous surface structures that can be divided according

to pore diameter into micropores, mesopores, and macropores with diameters < 2 nm, 2-50 nm, and > 50 nm, respectively.²⁰ The distribution of these pores, in combination with the corresponding specific surface area parameter, is dependent on the starting carbonaceous materials and the activation process employed. Various spectroscopic approaches including, XPS, NMR, FTIR, MS and DNP have been utilized to characterize the surface chemistry of these AC materials.^{21–25} In addition, the pore structures of AC are usually characterized by nitrogen gas adsorption at 77 K and related approaches.²⁶

It is well known that radicals are a chemically reactive moiety on the surface of ACs. Electron paramagnetic resonance (EPR) is an excellent spectroscopic tool for directly examining stable radicals because of the inherent high sensitivity of this technique. The EPR spectrum for AC radicals usually consists of a broad line with only subtle changes in the g factor and minor changes due to hyperfine interactions with other NMR active nuclides.^{27–29} Although EPR does not provide detailed chemical structural information of the radical centers on activated carbons, it does provide information on the time dependence, spin exchange, and delocalization of these radical centers. Dynamic nuclear polarization (DNP) is a rapidly evolving technique for characterizing electron/nuclear interactions of the solid/liquid interface of surfaces, such as, carbonaceous materials.^{30–33} An inherent advantage of DNP is the large enhancements in the NMR signal which is ultimately proportional to the magnetogyric ratios of the electron and nuclear spin, (e.g., 660 for the ¹H nuclide).^{34,35} In addition, because of numerous technical developments there has been a resurgence of interest in utilizing DNP for characterizing surfaces. For example, DNP has been utilized to characterize several different surface materials^{36,37} as well as the more recently three-dimensional structure of an organo-metallic complex on an amorphous silica surface.³⁸ Moreover, the liquid state DNP Overhauser effect has been applied for signal enhancement of flow imaging^{39,40} in biological systems.⁴¹



Figure 4.1 The DNP instrument.

In the current study, a flow solid/liquid intermolecular transfer (flow SLIT) DNP approach was employed to characterize the cellulose AC/flow analyte (benzene) interaction. The AC samples were prepared from cellulose pyrolyzed in a nitrogen atmosphere at different temperatures ($350 - 600 \,^{\circ}$ C). Benzene was chosen as a model adsorbent *messenger* for monitoring the analyte/AC surface interaction in the presence and absence of O₂.³¹ The flow SLIT DNP experiment allows monitoring the adsorbent/surface activated carbon under pristine conditions with an endogenous radical system.

4.2 Experimental Methods

A set of AC samples was prepared by heating powdered cellulose (Thomas Scientific Co.) in a stream of dry nitrogen. Two grams of cellulose were placed in a quartz heating tube and flushed with nitrogen gas. The gas was delivered to within 1-2 cm of the bottom of the heating tube via a concentric quartz tube so that the gas would flow over the top of the sample. In the second set of experiments, cellulose powders were treated with concentrated H₃PO₄ by soaking in aqueous solutions. After soaking, samples were rolled thoroughly to remove excess water and washed with deionized water twice. The H₃PO₄ treated cellulose sample was then dried and charred at 500°C as described *supra vide*. The samples were brought up to a maximum temperature over a period of 1 hr and heated at that temperature for six hours under nitrogen gas flow. The samples were then cooled under nitrogen. The heating tube was then slightly evacuated, sealed, and transferred to the DNP ceramic sample tube in a glove box. In this manner, the activated carbon samples were never exposed to oxygen.

The EPR spectra were recorded using a Varian E-3 EPR spectrometer with 4 mm sample tubes and 100 KHz modulation. The X-band microwave frequency was 9.3 GHz and the magnetic field was swept in the region of ~0.34 T. All spectra were recorded at room temperature. The linewidths were measured as the peak to peak distance of the first derivative of the EPR signal. The spin concentration of the free radicals was measured by comparison with a standard sample of α , α -diphenyl- β -picryl-hydrazyl (DPPH). The flow DNP apparatus used in the flow DNP experiment is shown in **Figure 4.2**. The samples of 20-30 mg of activated carbon were removed from the glove box and then placed in the microwave cavity of the EPR spectrometer and connected to the benzene

reservoir and the high magnetic field detector. The benzene was degassed by bubbling with dry nitrogen gas prior to and during the experiment. While benzene flowed (2 ml/min) over the activated carbon sample, the microwave power was turned on and the polarization was built up at low field (~ 0.3 T). Subsequently, the benzene was rapidly (3-5 s) transferred to the high magnetic field (4.7 T) where the ¹H or ¹³C NMR signal of benzene was detected.



Figure 4.2 The proposed structures of activated carbon. a) cellulose char prepared at 450 °C and b) cellulose char prepared at 600 °C.

4.3 Results and Discussion

In previous studies, it has been well established that a number of NMR nuclides (e.g., ¹H, ¹³C, ³¹P etc.) exhibit polarization transfer with unpaired electron systems^{42–45} and a variety of enhanced NMR signals have been observed in materials such as activated carbons, chars and tars.⁴⁶ The mechanisms of continuous wave DNP are various and among them, the Overhauser effect (OE)⁴⁷ and solid effects (SE)^{48,49} are widely used in studies of liquids as well as solids. In liquids, the OE is currently the only mechanism for the direct polarization of liquids.⁵⁰ The molecular rotational and translational motion and chemical exchange lead to time-dependent dipolar and scalar interactions between the electrons and the nuclei and then relaxation processes.⁵¹ In solids, the OE effects are dominated by mobile electrons, such as those within the conduction band.⁵² A theoretical explanation of the OE is that the changes in the nuclear spin population caused by the zero- and double- quantum transition lead to the DNP effect.⁵³ The observed enhancement is shown as $\varepsilon = \langle I_Z \rangle / \langle I_{eq} \rangle$. Together with solving the rate equations for this system, the enhancement is described as the following equation:

$$\varepsilon = 1 - \rho f S \frac{\gamma_s}{r_l} \tag{4.1}$$

with

$$\rho = \frac{W_2 \cdot W_0}{W_0 + 2W_I + W_2}$$
$$f = \frac{W_0 + 2W_I + W_2}{W_0 + 2W_I + W_2 + W^0}$$
$$S = \frac{\langle S_0 \rangle \cdot \langle S_Z \rangle}{\langle S_0 \rangle}$$

where W_0 and W_2 are the zero- and double-quantum transitions, respectively. W_I is the rate of the NMR transitions. W^0 is the nuclear relaxation rate in the absence of unpaired electron spins. S_i and I_i are the electron and nuclear spin operators. ρ is the coupling parameter, which is controlled by scalar and dipolar couplings. The coupling can also be described in terms of the electron Larmor frequency ω_{0S} and the correlation time τ , which shows the degree of molecular motion. It has been well established that the OE depends on the condition $\omega_{0S}\tau < 1$, and if ω_{0S} becomes large, the condition will not be satisfied. This relationship also illustrates the inefficiency of the OE at high magnetic fields.⁵⁴

The solid effect is a mixing state effect caused by the psedosecular term B in the Hamiltonian which contains terms of $S_Z I^+$ and $S_Z I^-$.⁵⁵ The mixed states are $|1'\rangle = |1\rangle + q|2\rangle$, $|2'\rangle = |2\rangle + q|1\rangle$, $|3'\rangle = |3\rangle + q|4\rangle$ and $|4'\rangle = |4\rangle + q|3\rangle$. Considering the first order perturbation theory, the coefficient q is calculated as:⁵⁶

$$q = -\frac{3}{4} \frac{\gamma_{S} \gamma_{I}}{\omega_{OI}} \frac{1}{r^{3}} \sin\theta \cos\theta e^{-i\varphi}$$
(4.2)

where r, θ and φ are the polar coordinates for the unpaired electron-nuclear vector. The zero-quantum or double-quantum transitions are caused by the irradiation at $\omega_{os} + \omega_{ol}$ or $\omega_{os} - \omega_{ol}$, and the enhancement scale is ω_{ol}^{-2} , which leads to the restriction of the application of SE at high magnetic fields. In the experiments, the SE requires the presence of a polarizing agent with a narrow EPR spectral line.⁵⁰ The homogeneous width and the inhomogeneous breadth of the agent's EPR spectrum should be much smaller than ω_{ls} to ensure that no more than one of the forbidden transitions is excited at the same time.

The DNP technique has undergone a renaissance in the last 2 decades because of fundamental and technical developments,^{57,58} but there are a few DNP studies of activated carbons before this period. Maciel, Wind, and coworkers previously reported ¹H DNP and EPR studies of cellulose chars prepared at different heat treatment temperatures (HTTs), 250-700 °C.⁵⁹ This ¹H DNP study was conducted with a modified solid-state NMR instrument and the ¹H nuclei monitored was assumed to be residual aromatic hydrogens present in the chars. Also, in a series of low-field DNP studies Odinstov, Clarkson⁶⁰ and coworkers reported both scalar (positive) and dipolar (negative) ¹H DNP Overhauser enhancements for aqueous suspensions of hardwood and softwood chars at 360 K, respectively. Moreover, with increasing temperature (300 to 360 K) the DNP enhancement shift from a negative to positive Overhauser enhancement for the hardwood char.



Figure 4.3 The EPR spin concentration (red) and Linewidth (blue) of cellulose chars prepared at different heat treatment temperatures.

To facilitate the discussion of the flow ¹H DNP and EPR results, we have proposed a model for the reactive radical centers in ACs based on low and high HTTs that is illustrated in **Figure 4.2**. As reported in previous EPR studies, we have also found that the unpaired electron spin increases with an increase in the activation temperature of the ACs in the HTT range of 350 - 600 °C, but decreases after 600 °C (**Figure 4.3**). In addition, it has been reported that the line-shape of the EPR spectra is between Gaussian and Lorentzian at low temperatures, and at a higher temperature range of 500 - 750 °C, the EPR signals become narrow and completely Lorentzian because of electron-electron spin exchange processes.⁶⁰ In the current study, we also measured the unpaired spin concentration of the cellulose char samples prepared at several HTTs ranging from 350 -

700 °C, (**Figure 4.3**). At a HTT of 350 °C, we observe an EPR line-width of 11.3 g and a spin count of 0.13 x10²⁰ electrons. The maximum spin concentration (25 x10²⁰) as well as the minimum EPR line-width (0.9 g) was reached at a HTT = 600 °C. When the HTT increases to 700 °C, the linewidth broadens (4.7 g) and the spin count decreases (2.9 x10²⁰). These results are consistent with earlier studies of HTT of ACs that report increasing electron spin exchange with increasing HTT.⁶³ For example, Maciel, Wind, and coworkers⁶⁴ reported that electron spin exchange times (τ_{ε}) dramatically increase from 8 x10⁻⁸ s (450 °C) to 6 x10⁻¹¹ s (600 °C) for a similar set of HTTs cellulose activated carbons. These results are consistent with greater unpaired electron delocalization with greater development of the basal graphitic planes at higher temperatures.



Figure 4.4 ¹H SLIT DNP enhancement curve as a function of microwave frequency at various temperatures. (color available online)

As previously indicated, benzene represents a *messenger* for the radical surface sites/activated carbon 1 H DNP interaction at a low magnetic field (0.33T), but monitored

at a high magnetic field (4.7 T). The high magnetic field NMR provides greater NMR chemical shift dispersion and higher sensitivity. The flowing benzene ¹H enhancement curves for HTT cellulose ACs are illustrated in Figure 4.4. It is readily apparent that there are dramatic changes in the benzene flow ¹H DNP enhancement as a function of HTT. The ¹H DNP enhancement curves, for the samples heated at 450°C and 500°C, are anti-symmetrical about the ω_s microwave offset and become a maximum at the microwave frequency $\frac{(\omega - \omega_S)}{2\pi} \approx \pm 14$ MHz. Since $\omega_I / 2\pi$ is equal to ~14 MHz for the ¹H NMR nuclide, we conclude that a solid-state effect (SE) is present in these activated carbons in this temperature range. Therefore, the results suggest that in these lower temperature chars a more localized interaction between the unpaired electron and flowing benzene hydrogens occur in these samples and that the unpaired electron spin centers in these chars move slowly on a scale comparable to ω_s^{-1} . For the AC sample prepared at HTT 525°C the ¹H DNP enhancement curve is not completely symmetrical and is antisymmetrical about the electron frequency ω_s . In this temperature range, there appear to be at least two distinctly different unpaired electron center/benzene interaction centers on the AC surface. A new time-dependent interaction, Overhauser effect, resulting from electrons undergoing spin-exchange interactions yields a symmetric curve at ω_s while the solid-state effect, resulting from the fixed electron on the chars yields an anti-symmetric curve. The observation of the time-dependent Overhauser scalar electron-nuclear interaction indicates the presence of delocalized electrons undergoing a more rapid spinexchange interaction in the 525°C AC that dominates in the 600°C AC. Unlike the ACs pyrolyzed at lower temperatures, the cellulose samples pyrolyzed at 550°C and 600°C exhibit only a scalar Overhauser effect since the ¹H DNP enhancement curves are

completely symmetric about the electron frequency ω_s . This result is also consistent with earlier reported EPR data exhibiting a significant narrowing of the line-width and corresponding decrease in the electron spin exchange times (τ_{ε}). Maciel and coworkers reported a value of $\tau_{\varepsilon} = 6 \times 10^{-11}$ s for activated carbons prepared at 600°C.⁶⁴ However, it should be noted that the Overhauser enhancements observed in the current study are significantly less (~60 times) than the scalar ¹H DNP Overhauser limit, $\varepsilon = +660$. This result suggests that the total number of unpaired electron sites that are accessible to the interaction with the flowing benzene is limited and/or an inappropriate time scale for a strong scalar Overhauser interaction.



Figure 4.5 DNP characterization of adsorption of oxygen on the cellulose char. 1) 1 H DNP enhancement curve as a function of microwave frequency for the 600°C cellulose char. (blue) 2) After purging with air for 30 min. (orange) 3) After purging with nitrogen for 30 min. (grey)

An alternative method for the preparation of activated carbons is a chemical approach where inorganic additives (e.g., $ZnCl_2$) or acids (H₃PO₄) are added before HTT.

Compared to physical activation, the main advantages of the chemical activation method are lower temperature activation temperatures and better control of porosity.^{65–67} A disadvantage is that chemical activation usually requires a clean-up step; for example, water washing step to remove the acid or inorganic additive.^{68,69} The ¹H DNP enhancements for chemically activated H₃PO₄ 500°C HTT AC sample and the corresponding untreated 500°C AC sample are shown in **Figure 4.5**. The H₃PO₄ treated 500°C cellulose char exhibits a positive Overhauser enhancement; whereas, the untreated 500°C activated carbon exhibits the usual solid-state effect and only a minor Overhauser enhancement. Therefore, the dominant Overhauser effect observed in the H₃PO₄ treated 500°C activated carbon illustrates a more delocalized unpaired electron center reminiscent of HTT activated carbons at much higher temperatures. The increased delocalized aromatic electron centers of the activated carbon due to the H₃PO₄ additives at lower temperatures is confirmed by the flow ¹H DNP technique.



Figure 4.6 DNP Characterization of Adsorption of Oxygen on the Cellulose Char. 1) Initial ¹H DNP enhancement curve as a function of microwave frequency for the 525°C cellulose char. (green) 2) After purging with air for 30 min. (orange) 3) After purging nitrogen for 30 min. (grey) 4) After 3 days (measured under N₂). (yellow)

Although a scalar positive ¹H DNP enhancement for benzene was observed for both the 600°C HTT and the 500°C H₃PO₄ chemically treated samples, a similarly small, but negative ¹³C DNP enhancement was observed for the 600°C activated carbon. The ¹³C DNP enhancement for the 600°C AC together with the corresponding ¹H DNP enhancement curve is illustrated in **Figure 4.6**. There are two possibilities for this small negative ¹³C DNP enhancement observed for benzene. One possibility is a small dipole-dipole ¹³C Overhauser effect and the other is a three-spin effect with transfer of the activated carbon radical polarization to the ¹H and then subsequently to the ¹³C benzene nuclide (see **Figure 4.6**). If the latter possibility is the case, the three-spin effect should be suppressed by using deuterated benzene (C₆D₆).⁷⁰ In the flow DNP experiments

utilizing C_6D_6 we do not observe any measurable ¹³C DNP enhancement (see **SI**). The three-spin ¹³C DNP results suggest that only a small scalar enhancement is observed for benzene for the 600 °C HTT sample.

In early AC work over fifty years ago, Walker and others found that ACs undergo chemisorption of oxygen instead of physisorption, but the nature of the chemical reactive site has not been established.^{71,72} In later studies, Bradbury and Shafizadeh reported that maximum chemisorption of oxygen occurs at a HTT of 550°C.⁷³ A seminal paper in understanding this phenomenon was reported by Radovic and Bockrath who propose that the surface chemistry of chars, ACs, and graphene carbons depends on the chemical nature and presence of graphene edge sites.⁷⁴ Furthermore, these graphene–like edge sites are either aryne-like for armchair edges and carbene-like for zigzag edge sites. Of these graphene edge types, the zigzag edge appears to be more chemically reactive. For example, it has been reported that the removal of chemisorbed molecular oxygen on activated carbon fiber materials leads to a change in the type of majority carriers, from holes to electrons, through charge transfer from the functional groups to the interior of nanographene sheets. Periasamy and coworkers have proposed a triplet carbene radical site for the zigzag edge of activated carbons that with adsorption of oxygen yields an intermediate with electron deficiency in the graphene skeleton and a negative charge at the terminal oxygen (see Figure 4.1 and 4.5).⁷⁵ In this paper, Periasamy and coworkers also describe various oxygen oxidation reactions consistent with this intermediate including conversion of triphenyl phosphine (PPh₃) to triphenyl phosphine oxide $(Ph_3P=O).$



Figure 4.7 DNP Characterization of Influence of the Organic Additive on the Cellulose Char. 1) ¹H DNP enhancement curve as a function of microwave frequency for the 500°C cellulose char. (blue) 2) ¹H DNP enhancement curve as a function of microwave frequency for the 500°C cellulose char treated by phosphoric acid. (red)

We have examined the effect of oxygen on the flow ¹H DNP enhancement for the HTT 600°C activated carbon as shown in **Figure 4.7**. The scalar ¹H DNP enhancement was completely quenched when dry air (O_2) was bubbled through the benzene solution (instead of N_2). Moreover, the scalar ¹H DNP enhancement was completely restored after purging with dry nitrogen for 30 min. The ¹H DNP enhancement regains its initial line-shape and magnitude before exposure to O_2 , indicating that the chemisorption of oxygen on the HTT 600 °C activated carbon is reversible. It is surprising that the scalar enhancement is completely quenched in the presence of O_2 especially in view of the solid-state ¹H DNP unquenched result obtained for the other activated carbon radical center formed at a lower temperature, 525°C *vide infra*. In support of quenching the

radical site, Maciel and coworkers reported a four-fold reduction (~16 x 10^{19} to ~4 x 10^{19} spins) in EPR signal intensity for an activated carbon HTT at 550°C.²⁹ Collectively, these results suggest a chemisorption of O₂ process consistent with conversion of the paramagnetic activated carbon radical center to a diamagnetic center. As illustrated in **Figure 4.7**, the HTT 600 °C results are in accord with a triplet carbone radical reaction site for ACs that chemisorbs O₂ forming a peroxy intermediate. As proposed by Periasamy and coworkers, this peroxy intermediate exhibits a negative charge on the terminal oxygen and delocalized positive charge at the weak C-O bond.



Figure 4.8 The DNP enhancement for the 600°C cellulose char. a) The ¹³C DNP enhancement as a function of microwave frequency for the 600°C cellulose char. b) The ¹H DNP enhancement as a function of microwave frequency for the 600°C cellulose char.

In contrast with the effect of oxygen on the HTT 600°C sample, the HTT 525 °C AC sample exhibits a solid-state ¹H DNP enhancement that is not quenched in the presence of O₂ as illustrated in Figure 4.8. There are a small distortion and overall reduction in the intensity centered at ω_s consistent with a small scalar Overhauser solid-state ¹H DNP enhancement upon exposure to O_2 . However, the original line-shape and intensity is completely recovered when the source of O₂ is removed. In contrast with the HTT 600°C sample, this result suggests a dominant O₂ adsorption process (solid-state) and only minor evidence for chemisorption (scalar Overhauser). The observation of a solid-state ¹H DNP during the presence of O₂ substantiates the presence of an intact paramagnetic radical center and the decrease in the ¹H DNP intensity can be rationalized by Heisenberg electron-electron exchange processes and/or competition for the radical sites by O₂. The activated carbons prepared at the lower HTTs could have residual heteroatom (O or N) functionality with phenoxy, semiquinone, or even nitrogen radical sites. For example, the ¹H DNP enhancement curve for the HTT 525 °C sample resembles results for an immobilized silica 2,6-di-t-butoxyphenoxy radical system/flowing benzene system.⁷⁶⁻⁷⁸In any case, the lower HTT solid-state DNP result suggests an unpaired electron site(s) that is substantially different than the dominant site described for the HTT 600 °C AC sample.



Figure 4.9 ¹H SLIT DNP Characterization of Adsorption of Oxygen on WESTVACO CHR 146 Char. 1. ¹H DNP enhancement as a function of microwave frequency. 2. After bubbling air for 30 min. 3. After purging with N_2 for 30 min. 4. After 1 day (measure under N_2).



Figure 4.10 Comparison of ¹³C DNP (blue) and ¹H DNP enhancement for the 600°C Cellulose Char. (a) The ¹³C DNP (blue) and ¹H DNP (red) Enhancement as a Function of Microwave Frequency for the 600°C Cellulose Char. (b) Zeeman energy level for the nuclear-electron system. (c) Three-spin effect.

In summary, we propose that there are different radical center sites in ACs and carbonaceous chars for adsorption and/or chemisorption of O₂. It is well established that the properties of these AC radical center sites are influenced by various factors including, nature of the carbonaceous source (AC, char, biochar), heat treatment temperature (HTT), and inorganic additives (KOH, NaOH, and H_3PO_4). Based on the flow ¹H DNP and EPR results, we have proposed a model for the radical centers for both low temperature and high-temperature heat treatment ACs (Figure 4.1). As previously indicated, the proposed HTT 600 °C model AC radical center consists of a carbene radical site for the zigzag edge of ACs that with adsorption of oxygen yields a diamagnetic intermediate with electron deficiency in the graphene skeleton and a negative charge at the terminal oxygen. It should be noted that the positive charge can be extensively delocalized across a given basal plane. Also, the ¹H DNP results suggest that chemisorption of O_2 is consistent with the conversion of the paramagnetic activated carbon radical center to a diamagnetic center. In addition, the EPR data also suggests that even at the optimum temperature for chemisorption (550-600 °C) there are some radical sites not accessible to O₂ adsorption either because of their remote location in the basal plane and/or limited pore accessibility. Whereas, the radical sites for the ACs samples prepared at the lower HTT could be phenoxy, semiguinone, or even uniquely different carbon sites, but do not appear to be clear examples of O₂ chemisorption. Clearly, the flow DNP approach with other analytes (H₂O, ¹³CO₂, ¹⁵NO_x, toluene, phenol, etc) could be important in further elucidating these radical centers in activated carbons, chars, and biochars.

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Appendices:

Appendix A

S1.1 Computational Method

Density Functional theory (DFT) based computations were performed using a Gaussian 09 package.¹ All molecules were fully optimized at B3lyp/6-31G(d) level.^{2–5} The simulated UV/vis spectra were calculated using TD-DFT method starting with the optimized structures.⁶ The ¹³C NMR chemical shifts were estimated employing the energy-minimized structure and the SMD solvent model. The experimental and computational NMR chemical shifts of C₆₀ were used as the references. The electron densities were calculated at the same level and plotted by GaussView. The polarizability was calculated using Gaussian 09 package at B3lyp/6-31G(d) level and the bond polarizabilities are computed based on the C atom coordinates and the α_{xx} , α_{yy} and α_{zz} .



Figure S1.1 The Schlegel projections of (a) $D_{5h}(1)$ - C_{90} and (b) $D_{5d}(1)$ - C_{100} .⁷ The spiral stripes show the differences of the two structures. The Blue line indicates the identical part and the red lines shows the difference. The number sequences are from the Spiral Program. Numbers represent the orders of pentagons in the spirals.



Figure S1.2 LDI-TOF mass spectrum for unreacted materials after 48 hours of reaction with aminopropanol. Reaction conditions are 15 mL of added aminopropanol to a stirring solution of 500 mg of soot extract in 500 mL toluene solvent. This mass spectrum represents the organic layer, unreacted species.



Figure S1.3 Bond Polarizability Distribution of $C_1(30)$ - C_{90} . 39 unreactive bonds (blue) and 36 reactive bonds (red).



Figure S1.4 Structure of $C_1(30)$ - C_{90}

Table S1.1 $C_1(30)$ - C_{90} connection information

	carbon_1	carbon_2
bond_label	label	label
1	2	1
2	3	2
3	5	4
4	8	6

5	8	7
6	9	8
7	10	2
8	10	9
9	11	10
10	19	16
11	21	20
12	22	21
13	25	24
14	26	9
15	26	25
16	27	21
17	27	26
18	28	27
19	29	25
20	37	36

21	38	37
22	43	42
23	46	45
24	50	48
25	50	49
26	52	51
27	53	52
28	56	50
29	56	54
30	56	55
31	74	52
32	74	55
33	74	73
34	75	73
35	77	55
36	77	76

37	78	77
38	81	73
39	82	81
40	14	12
41	15	13
42	18	17
43	19	18
44	22	19
45	23	22
46	31	30
47	32	30
48	33	31
49	35	34
50	37	31
51	41	18
52	41	39

53	41	40
54	43	30
55	44	43
56	47	44
57	57	44
58	58	57
59	60	59
60	61	57
61	63	62
62	64	63
63	65	63
64	66	65
65	67	65
66	70	69
67	72	68
68	72	71

69	81	80
70	83	79
71	86	85
72	87	84
73	89	72
74	89	88
75	90	89



Figure S1.5 Bond Polarizability Distribution of $C_1(32)$ - C_{90} . 39 unreactive bonds (blue) and 36 reactive bonds (red).



Figure S1.6 Structure of $C_1(32)$ - $C_{90.}$

Table S1.2 $C_1(32)$ - C_{90} connection information

bond_label	carbon_1 label	carbon_2 label
1	2	1
2	3	2

3	4	3
4	7	4
5	8	7
6	11	2
7	12	7
8	12	11
9	13	10
10	14	11
11	26	25
12	27	12
13	27	26
14	28	27
15	29	28
16	30	28
17	32	31
18	34	32

19	37	35
20	37	36
21	38	37
22	39	32
23	39	38
24	40	39
25	46	45
26	55	54
27	61	59
28	61	60
29	63	62
30	64	38
31	64	63
32	65	61
33	65	64
34	66	65

35	67	63
36	83	82
37	85	26
38	85	84
39	86	85
40	5	4
41	9	6
42	16	15
43	17	16
44	20	18
45	21	19
46	23	22
47	24	23
48	33	31
49	41	23
50	42	41

51	43	41
52	46	31
53	47	46
54	48	44
55	50	49
56	51	50
57	53	52
58	57	50
59	57	56
60	58	57
61	68	3
62	71	70
63	72	71
64	73	69
65	75	74
66	76	75

67	79	78
68	81	75
69	81	77
70	81	80
71	87	71
72	88	16
73	88	87
74	89	88
75	90	87



Figure S1.7 Bond Polarizability Distribution of $D_{5d}(1)$ – C_{120} . 100 unreactive bonds (blue) and 20 reactive bonds (red).



Figure S1.8 Structure of $D_{5d}(1)$ - C_{120} .

Table S1.3 $D_{5d}(1)$ - C_{120} connection information.

bond_label	carbon_1 label	carbon_2 label
1	4	1
2	5	2
3	8	3
4	8	4

5	9	4
6	10	5
7	10	9
8	11	5
9	11	6
10	14	7
11	15	8
12	16	9
13	17	10
14	18	11
15	19	12
16	22	13
17	22	14
18	23	14
19	23	15
20	24	15

21	24	16
22	25	16
23	26	17
24	26	25
25	27	17
26	27	18
27	28	18
28	28	19
29	29	19
30	29	20
31	31	21
32	32	22
33	33	23
34	34	24
35	35	25
36	36	26

37	37	27
38	38	28
39	39	29
40	40	30
41	40	31
42	41	31
43	41	32
44	42	32
45	42	33
46	43	33
47	43	34
48	44	34
49	44	35
50	45	35
51	46	36
52	46	45

53	47	36
54	47	37
55	48	37
56	48	38
57	49	38
58	49	39
59	50	39
60	50	40
61	51	41
62	52	42
63	53	43
64	54	44
65	55	45
66	56	46
67	57	47
68	58	48

69	59	49
70	60	50
71	60	51
72	61	51
73	61	52
74	62	52
75	62	53
76	63	53
77	63	54
78	64	54
79	65	57
80	66	57
81	66	58
82	67	58
83	67	59
84	68	59

85	68	60
86	69	61
87	70	62
88	71	63
89	72	66
90	73	67
91	74	68
92	74	69
93	75	69
94	75	70
95	76	70
96	77	73
97	78	73
98	78	74
99	79	75
100	80	78

101	83	82
102	86	85
103	89	88
104	90	84
105	92	91
106	93	81
107	95	94
108	97	96
109	98	87
110	100	99
111	103	102
112	106	105
113	109	108
114	110	104
115	112	111
116	113	101

117	115	114
118	117	116
119	118	107
120	120	119



Figure S1.9 Bond Polarizability Distribution of $D_{5d}(10666)$ – C_{120} . 60 unreactive bonds (blue) and 60 reactive bonds (red).



Figure S1.10 Structure of D_{5d}(10666)-C_{120.}

Table S1.4 $D_{5d}(10666)$ - C_{120} connection information.

bond_label	carbon_1	carbon_2
	label	label
1	4	3
2	5	4
3	6	5

4	9	8
5	10	9
6	11	10
7	17	16
8	18	17
9	19	18
10	20	19
11	21	20
12	22	21
13	28	27
14	29	21
15	29	28
16	30	29
17	31	19
18	33	17
19	33	32
20	34	33
----	----	----
21	35	34
22	41	9
23	41	40
24	42	41
25	43	7
26	43	42
27	44	43
28	45	5
29	45	44
30	46	45
31	52	28
32	52	51
33	53	52
34	54	53
35	56	55

36	57	34
37	57	56
38	58	57
39	64	42
40	66	44
41	73	53
42	73	72
43	74	56
44	74	73
45	75	74
46	88	4
47	88	87
48	89	88
49	90	89
50	92	91
51	93	10

52	93	92
53	94	93
54	100	18
55	102	20
56	109	89
57	109	108
58	110	92
59	110	109
60	111	110
61	3	2
62	12	11
63	15	14
64	16	15
65	23	22
66	24	23
67	25	1

68	27	23
69	27	26
70	35	15
71	36	35
72	37	13
73	39	11
74	39	38
75	40	39
76	47	3
77	47	46
78	48	47
79	51	50
80	59	58
81	61	60
82	62	40
83	64	63

84	65	64
85	66	65
86	67	66
87	68	46
88	69	49
89	71	51
90	71	70
91	72	71
92	76	58
93	76	75
94	77	76
95	79	78
96	80	65
97	82	81
98	83	72
99	84	75

100	87	86
101	95	94
102	97	96
103	98	16
104	100	99
105	101	100
106	102	101
107	103	102
108	104	22
109	105	85
110	107	87
111	107	106
112	108	107
113	112	94
114	112	111
115	113	112

116	115	114
117	116	101
118	118	117
119	119	108
120	120	111



Figure S1.11 Bond Polarizability Distribution of $D_{5d}(10765)-C_{120}$. 90 unreactive bonds (blue) and 30 reactive bonds (red).



Figure S1.12 Structure of D_{5d}(10765)-C_{120.}

Table S1.5 $D_{5d}(10765)$ - C_{120} connection information.

bond_label	carbon_1 label	carbon_2 label
1	3	2
2	4	3
3	7	6

4	8	7
5	11	10
6	12	11
7	15	14
8	16	15
9	19	18
10	20	19
11	21	1
12	22	21
13	23	19
14	23	22
15	24	23
16	25	17
17	25	24
18	26	25
19	27	15

20	27	26
21	28	27
22	29	13
23	29	28
24	30	29
25	31	11
26	31	30
27	32	31
28	33	9
29	33	32
30	34	33
31	35	7
32	35	34
33	36	35
34	37	5
35	37	36

36	38	37
37	39	3
38	39	38
39	40	21
40	40	39
41	41	40
42	42	41
43	43	22
44	43	42
45	44	43
46	45	24
47	45	44
48	46	45
49	47	26
50	47	46
51	48	47

52	49	28
53	49	48
54	50	49
55	51	30
56	51	50
57	52	51
58	53	32
59	53	52
60	54	53
61	55	34
62	55	54
63	56	55
64	57	36
65	57	56
66	58	57
67	59	38

68	59	58
69	60	41
70	60	59
71	61	60
72	63	42
73	63	62
74	64	63
75	65	44
76	67	46
77	67	66
78	68	67
79	69	48
80	71	50
81	71	70
82	72	71
83	73	52

84	75	54
85	75	74
86	76	75
87	77	56
88	79	58
89	79	78
90	80	79
91	83	82
92	84	83
93	86	85
94	87	86
95	89	88
96	90	89
97	92	91
98	93	92
99	95	81

100	95	94
101	96	95
102	97	83
103	98	86
104	99	89
105	100	92
106	103	102
107	104	103
108	106	105
109	107	106
110	109	108
111	110	109
112	112	111
113	113	112
114	115	101
115	115	114

116	116	115
117	117	103
118	118	106
119	119	109
120	120	112



Figure S1.13 Bond Polarizability Distribution of $D_{5h}(10766)-C_{120}$. 90 unreactive bonds (blue) and 30 reactive bonds (red).



Figure S1.14 Structure of D_{5h}(10766)-C_{120.}

Table S1.6 $D_{5h}(10766)$ - C_{120} connection information.

bond_label	carbon_1 label	carbon_2 label
1	2	1
2	5	4
3	6	5
4	9	8

5	10	9
6	13	12
7	14	13
8	17	16
9	18	17
10	20	1
11	21	1
12	22	21
13	23	19
14	23	22
15	24	23
16	25	17
17	25	24
18	26	25
19	27	15
20	27	26

21	28	27
22	29	13
23	29	28
24	30	29
25	31	11
26	31	30
27	32	31
28	33	9
29	33	32
30	34	33
31	35	7
32	35	34
33	36	35
34	37	5
35	37	36
36	38	37

37	39	3
38	39	38
39	40	21
40	40	39
41	41	40
42	42	41
43	43	22
44	43	42
45	44	43
46	45	24
47	45	44
48	46	45
49	47	26
50	47	46
51	48	47
52	49	28

53	49	48
54	50	49
55	51	30
56	51	50
57	52	51
58	53	32
59	53	52
60	54	53
61	55	34
62	55	54
63	56	55
64	57	36
65	57	56
66	58	57
67	59	38
68	59	58

69	60	41
70	60	59
71	61	60
72	63	42
73	63	62
74	64	63
75	65	44
76	67	46
77	67	66
78	68	67
79	69	48
80	71	50
81	71	70
82	72	71
83	73	52
84	75	54

85	75	74
86	76	75
87	77	56
88	79	58
89	79	78
90	80	79
91	83	82
92	84	83
93	86	85
94	87	86
95	89	88
96	90	89
97	92	91
98	93	92
99	95	81
100	95	94

101	96	95
102	97	83
103	98	86
104	99	89
105	100	92
106	103	102
107	104	103
108	106	105
109	107	106
110	109	108
111	110	109
112	112	111
113	113	112
114	115	101
115	115	114
116	116	115

117	117	103
118	118	106
119	119	109
120	120	112



Figure S1.15 Cap Structures of (a) $D_{5d}(1)-C_{120}$, (b) $D_{5d}(10666)-C_{120}$, (c) $D_{5d}(10765)-C_{120}$ and (d) $D_{5h}(10766)-C_{120}$.

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Appendix B



Figure S2.1. STM topography images of one single-twin rippled graphene. (a) STM topographic image of continuous graphene forming twin wrinkles on Cu(111) ($V_s = -1.06 \text{ V}$, I = 0.315 nA). The insert STM image shows the graphene Moiré pattern on both sides of this twin wrinkle on the right flat area of (a), shows the Moire pattern of graphene on Cu(111) surface ($V_s = -0.750 \text{ V}$, I = 0.315 nA). (b) Zoomed-in image of (a) ($V_s = -0.600 \text{ V}$, I = 0.850 nA). (c) Line profile of the single-twin wrinkle of graphene, measured along the blue line in b. (d) Further zoomed-in STM topographic image of single-twin wrinkle of graphene ($V_s = -0.560 \text{ V}$, I = 0.8750 nA). (e) Atomic STM image of one of the twin wrinkles in Fig. d showing the honey-comb structure of graphene ($V_s = -0.560 \text{ V}$, I = 0.8750 nA). (f) Schematic model of one side of the twin wrinkle.



Figure S2.2. STM images of a set of PTCDA decay data from self-assembled herringbone pattern to two sub-stable arrangements on flat graphene type A on Cu. (a-i) are the typical decayed images from initial seed state to the final self-assembled herringbone pattern. All these nine images were obtained under the same scanning conditions: $V_s = -2.500$ V, I = 0.030 nA, and with the same size of 23 nm × 23 nm. The purple curved frame in all nine images show the type of sub-stable arrangement.

S2.1: Computation details

All computations are based on density functional theory (DFT) using ORCA 3.0.3 package. The C₆₀ molecule and planar graphene flake were fully optimized at B3LYP/def2-SVP level as provided by ORCA. Curved graphene flake was optimized under constraints to obtain curved structure, also at B3LYP/def2-SVP level. Intermolecular interactions were computed using DFT-D (BLYP D3) method with def2/SVP basis set. A partial search on typical orientations was employed to find the energetically favored orientations. Rotation and translation barriers were also calculated for C₆₀/planar-graphene.



Figure S2.3. Typical fullerene orientations on graphene. The computational results suggest that the (b) is the energetically favored orientations.



Figure S2.4. Side and top views of (a) curved graphene and (b) planar graphene. (c) and (d) showing the scale of curved graphene in the out-of-plane and in-plane directions, respectively, based on the experimental measurements.



Figure S2.5. Energy curves for fullerene on the peak location. Two typical orientations are comprehensively studied.



Figure S2.6. Energy curves for fullerene on the valley location. Two typical orientations are comprehensively studied.



Figure S2.7. Energy curves for PTCDA molecules on the peak and in valley locations. The energies are calculated using hex-center orientations.



Figure S2.8 Absorption spectrum of $Sc_3N@C_{80}$ and spiro-OMeTAD mixture (with electronic interaction, exp.) and calculated spectrum of spectral superposition of independent $Sc_3N@C_{80}$ and spiro-OMeTAD samples at identical concentration (without electronic interaction, cal.)



Figure S2.9 Schematics of QCM-D measurement. (a) quartz crystal chip coated by perovskite and different HTLs. (b) setup configuration showing the measurement details, where different salt solutions were employed to produce nitrogen with well-controlled RH (4 level RH from 26% to 79%).



Figure S2.10 c-AFM height and current images of spiro-OMeTAD HTLs with different $Sc_3N@C_{80}$ -dopant concentrations from 0 to 2.0 mg/mL.
Table S2.1 Photovoltaic performance parameters of perovskite solar cells utilizing spiro-
OMeTAD HTLs with different $Sc_3N@C_{80}$ -dopant concentrations.

Sc ₃ N@C ₈₀ -dopant	J _{SC}	V _{OC}	FF	PCE
concentrations (mg/mL)	$(mA cm^{-2})$	(V)	(100%)	(%)
0	19.81	1.06	0.68	14.19
0.1	20.52	1.07	0.69	15.19
0.2	20.84	1.10	0.72	16.53
0.3	21.79	1.14	0.72	17.83
0.4	22.00	1.14	0.75	18.75
0.6	22.93	1.16	0.77	20.48
1.0	23.06	1.15	0.78	20.77
1.4	21.78	1.12	0.74	18.05



Figure S2.11 Nyquist plot of solar cells using different HTLs, measured at the opencircuit-voltage condition of each device in dark.



Figure S2.12 Photocurrent density dependence on the $Sc_3N@C_{80}$ -dopant concentration in perovskite solar cells (measured under one-sun illumination).



Figure S2.13 Open-circuit voltage dependence on the $Sc_3N@C_{80}$ -dopant concentration in perovskite solar cells (measured under one-sun illumination).



Figure S2.14 Incident photon conversion efficiency (IPCE) spectra and integrated current density (under one-sun illumination) of perovskite solar cells using LiTFSI-doped spiro-OMeTAD HTL.



Figure S2.15 Incident photon conversion efficiency (IPCE) spectra and integrated current density (under one-sun illumination) of perovskite solar cells using $Sc_3N@C_{80}$ -doped spiro-OMeTAD HTL (1.0 mg/mL).



Figure S2.16 Statistical histograms of PCE from perovskite solar cells using LiTFSI and $Sc_3N@C_{80}$ -doped (1.0 mg/mL) spiro-OMeTAD HTLs. (total device number is 15 for each group, Gaussian fit is utilized)

Appendix C



S3.1a: Plot of empty-cage fullerenes versus Log K on PBB column



S3.1b: Plot of empty-cage fullerenes versus Log K on PYE column



S3.2: Plot of log K versus Lanthanide EMFs radii (PYE and PBB columns)

S3.3: Computational Study: Density functional theory (DFT) computations were performed using the B3LYP functional as provided in the Gaussian 09 program package. All of the molecules were geometry optimized at the B3LYP level with a 6-31G* basis set.

S3.4: average and anisotropic polarizability

Fullerene and	α_{xx}	α_{yy}	α_{zz}	Average	Anisotropic
Charged				Polarizability	Polarizability
Fullerene				α (Å ³)	$\Delta \alpha(\text{\AA}^3)$
Cages					
C ₆₀ -I _h	69.47	69.47	69.46	69.47	0.00
C ₇₀ -D _{5h}	92.99	83.63	83.62	86.75	9.37
$(C_{80}-I_h)^{6-}$	104.0	104.0	104.0	104.0	0.00
(C ₈₀ -I _h) ⁶⁻	102.4	106.4	106.4	105.1	4.00

The polarizability anisotropy was calculated from the equation and the values for C_{60} -I_h and C_{70} -D_{5h} agree with previous published values.

$$\Delta \alpha = [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]^{1/2} / \sqrt{2}$$



S3.5: fullerene carbon cage number versus log K

S3.6: Summary of corrections based on dipole moments and provided formula

$$\ln\left(\frac{t_R^*}{t_0}\right) = c + \left(\frac{da\alpha_1}{T}\right)\alpha_2^* + \frac{b}{a}\left(\frac{da\alpha_1}{T}\right)(\mu_2^*)^2$$

	3	$I_1 I_2$. 1		. 1
where $a =$	2	$\frac{12}{(1+1)}$	$b = \frac{1}{4\pi c}$, c = constant,	$d = \frac{1}{D m^6}$
	2	$(I_1 + I_2)$	$4\pi\epsilon_0$		KT ²

Fullerenes	$(C_{78}-C_2)^{6-}$	$(C_{80}-I_h)^{6-}$	(C ₈₀ -D _{5h}) ⁶⁻	$(C_{82}-C_s)^{6-}$
I (pyrene) (eV)	7.5	7.5	7.5	7.5
I (fullerenes) (eV)	7.26	7.30	7.30	7.25
$da\alpha_1/T$	0.032	0.032	0.032	0.032

dipole moment (D)	0.69	0.00	0.00	0.37
Correction	0.30	0.00	0.02	0.12
original ln (tr/to)	1.78	1.67	1.71	1.84
corrected ln (tr/to)	1.61	1.67	1.71	1.79
EMFs	$(C_{84}-C_s)^{6-}$	$(C_{86}-D_3)^{6-}$	(C ₈₈ -D ₂) ⁶⁻	
IP (pyrene)	7.5	7.5	7.5	
IP (fullerenes)	7.17	7.16	7.09	
$da\alpha_1/T$	0.032	0.032	0.032	
dipole moment (D)	0.38	0.00	0.0	
correction	0.23	0.04	0.00	
original ln (tr/to)	2.10	1.99	2.14	
corrected ln (tr/to)	2.05	1.99	2.14	

S3.7: Computational Study: Density functional theory (DFT) computations were performed using the B3LYP functional as provided in the Gaussian 09 program package. All of the molecules were geometry optimized at the B3LYP level with a 6-31G* basis set. Polarizabilities and dipole moments are also calculated at the B3LYP level with a 6-31G* basis set.



S3.8: polarizability versus chromatographic retention behaviors for both $Tb_3N@C_{2n}$ (n = 39 - 44) and $Y_3N@C_{2n}$ (n = 39 - 44)



S3.9: Polarizabilities of empty-cage fullerenes and EMFs, $Y_3N@C_{2n}$ (n = 39 – 44) versus (a) chromatographic retention behavior parameter ln (t_r / t_o) (y = 0.0317x-1.5884, R² = 0.9889). PYE stationary phase and toluene mobile phase, flow rate 2 mL/min.

Appendix D



Figure S4.1 Scheme for DNP experiments instruments.



Figure S4.2 ¹³C SLIT DNP Spectrum (50.1 MHz) for C₆H₆/600°C Cellulose Char: a) static NMR spectrum M_0^H , b) flow NMR spectrum M_z^{HL} at 2ml/min, c) flow DNP spectrum M_z^* at 2 ml/min.



Figure S4.3 ¹³C SLIT DNP Spectrum (50.1 MHz) for C6D6/600°C Cellulose Char: a) static NMR spectrum M_0^H , b) flow NMR spectrum M_z^{HL} at 2ml/min, c) flow DNP spectrum M_z^* at 2 ml/min.