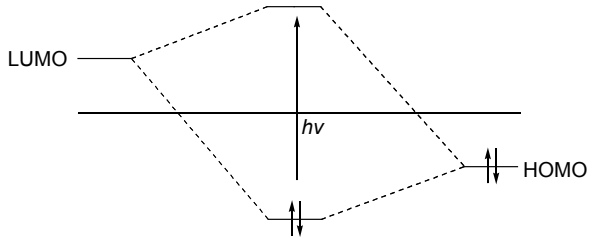
Appendix

Charge Transfer Interactions

Charge transfer interactions, very weak intermolecular forces, result from the mixing of the ground and excited charge-separated states, that is, AB and $A^+ B^-$ states.[1] They are also called electron delocalization interactions caused by charge transfer from occupied molecular orbitals, such as HOMO, of A to vacant molecular orbitals, such as LUMO, of B or charge transfer from occupied molecular orbitals of B to vacant molecular orbitals of A.[2] Charge-transfer complexes AB may be obtained when good electron donors A and acceptors B lie in close proximity. This process is accompanied by transference of an electron due to the creation of intermolecular orbitals, whose separation fortuitously corresponds to a transition in the visible region.[3]



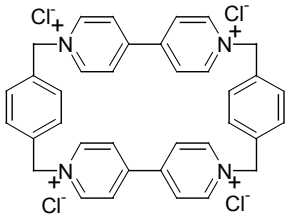
Association constants, K_a (= [AB]/[A][B]), and molar extinction coefficients, ε, may be estimated graphically from the Benesi-Hildebrand equation[3,4,5]

$$[A]l/\text{Abs} = 1/N_D K_a \varepsilon + 1/\varepsilon$$

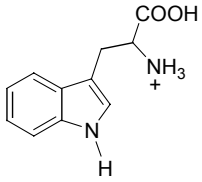
where Abs is the absorbance of the solution, l is the path length (cm) and N_D is the mole fraction of B. A plot of $[A]l$/Abs against $1/N_D$ will be a straight line. From the intercept and slope of this line K_a and ε can be determined.

For example, the mixing of cyclobis(paraquat-*p*-phenylene) **1** and tryptophan **2** in an aqueous solution (50 mM phosphate buffer, pH = 7.0) resulted in the immediate

development of a visible charge transfer band (λ_{max} = 404 nm).[6] The association constant between them was determined by using this band to be 1106 M^{-1}.



1



2

Electrostatic Interactions

Electrostatic interactions are attractions between charges of opposite sign.[3] They are underlying forces in both covalent and ionic bonding and may also be a major component of intermolecular forces. Coulomb's Law gives us the electrostatic force, F, between two point charges, q and q', separated by distance r:

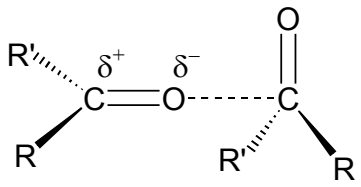
$$F = qq' / 4\pi \varepsilon_m r^2$$

where ε_m is the permittivity of the medium, a measure of its ability to transmit an electric field.

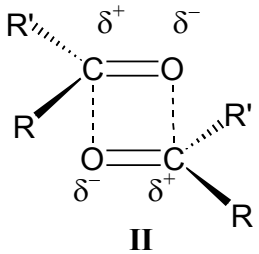
Electrostatic interactions have been widely used in the construction of self-assembled systems. For example, Stupp's group described a new approach to peptide-amphiphile (PA) nanofiber preparation that allows PAs with different bioactive amino acid sequences to be combined into a single fiber driven by electrostatic attraction.[7]

Dipole-Dipole Interactions

Dipole-dipole interactions are interactions between permanently polar molecules or groups. For example, in molecules with carbonyl groups, alignment of one dipole with another can result in significant attractive interactions from matching of either a single pair of poles on adjacent molecules (type **I**) or opposing alignment of one dipole with the other (type **II**).[8] Calculations have shown that type **II** interactions have an energy of about 20 kJ/mole in the solid state but they are relatively weak in solution.



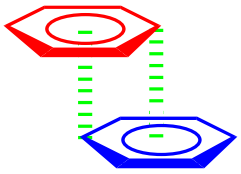
I



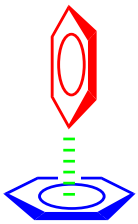
II

π-Stacking Interactions

π-stacking interactions are weak electrostatic interactions between aromatic rings, often in situations where one is relatively electron rich and the other is electron poor.[8] There are two types of π-stacking interactions: face-to-face and edge-to-face as shown below.



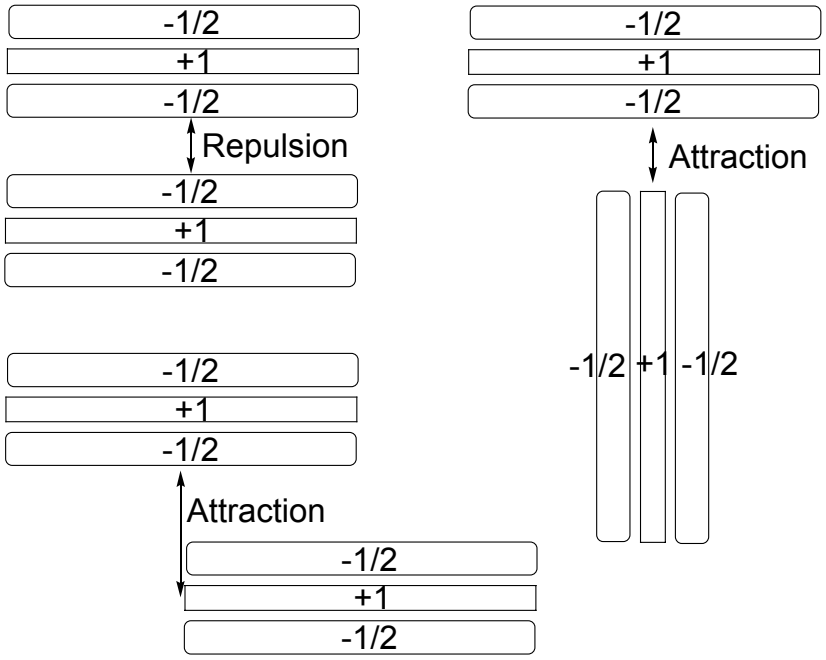
Face-to-face



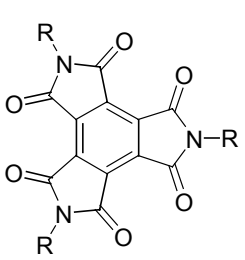
Edge-to-face

π-stacking interactions can be well modeled with high-level *ab initio* methods, which implicitly include quadrupolar, inductive and short-range interactions between adjacent π-systems, but it has been difficult in the past to analyze such interactions successfully using simpler methods.[1] However, in 1990, Hunter and Sanders[9] proposed a simple model of the charge distribution in a π-system in order to explain the strong geometrical requirements for interactions between aromatic molecules. The key feature of the model is that it considers the positively charged σ-framework and the negatively charged π-electrons separately and demonstrates that net favorable π-π interactions are actually the result of π-σ attractions that overcome π-π repulsions as shown below. The relative orientation of the two interacting molecules is determined by the electrostatic repulsions between two negatively charged π-electron parts. These rules successfully predicted the geometry of intermolecular interactions in the crystal structures of aromatic

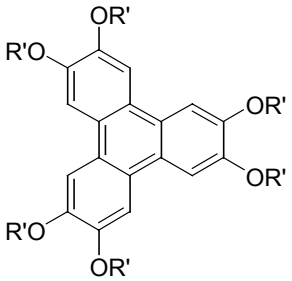
molecules and rationalize a range of host-guest phenomena. Recently Sinnokrot and Sherrill[11] found all substituted benzene dimers bind more strongly than benzene dimer based on their theoretical calculations by electronic structure methods. Both electrostatic and dispersion interactions contribute to the increased binding of the monosubstituted dimers.



Recent examples of self-assembled systems based on π-stacking interactions are complementary C_3-symmetric complexes based on electron-poor mellitic triimide **3** and electron-rich hexaalkoxytriphenylene **4** prepared by Park et al.[11]



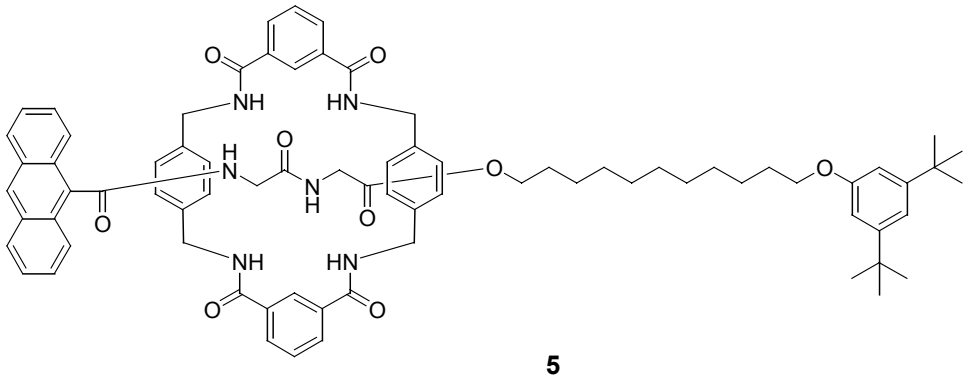
3



4

Hydrogen Bonding Interactions

Hydrogen bonding is one of important stabilization forces for supramolecular complexes. It happens between a hydrogen atom covalently connected to a strongly electronegative atom (hydrogen bond donor) such as oxygen, fluorine, or nitrogen, or even a carbon atom in some systems such as chloroform and paraquat derivatives, and an electronegative atom (hydrogen bond acceptor), such as oxygen, chlorine, and fluorine, which have at least one lone electron pair. A hydrogen bond can be represented as D-H···A, where D and A represent hydrogen bonding donor and acceptor, respectively. The strength of the hydrogen bond depends on the angle of D-H···A and the distance between H and A. In order for hydrogen bonding to arise, traditionally it is thought that the distance between H and A should be less than the sum of van der Waals radii of the hydrogen atom and the acceptor atom. Leigh et al.[12] successfully prepared rotaxane **5** by hydrogen bonding between the amide NH on the beadlike part and carbonyl oxygen groups on the rodlike part.



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REFERENCES

1. Lindoy, L. F.; Atkinson, I. M. *Self-Assembly in Supramolecular Systems*; Stoddart, J. F. Ed.; Royal Society of Chemistry: Cambridge, 2000, Chapter 2.
2. Morokuma, K. *Acc. Chem. Res.* **1977**, *10*, 294-300.
3. Isaacs, N. *Physical Organic Chemistry, 2nd Ed.*; John Wiley & Sons, Inc.: New York, 1995, Chapter I.
4. Trotter, P.; Hanna, M. W. *J. Am. Chem. Soc.* **1966**, *88*, 3724-3729.
5. Knutz, I. D.; Gasparro, F. P.; Johnston, M. D.; Taylor, R. P. *J. Am. Chem. Soc.* **1968**, *90*, 4778-4781.
6. Goodnow, T. T.; Reddington, M. V.; Stoddart, J. F.; Kaifer, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 4335-4337.
7. Niece, K. L.; Hartgerink, J. D.; Donners, J. J. J. M.; Stupp, S. I. *J. Am. Chem. Soc.* **2003**, *125*, 7146-7147.
8. Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; John Wiley & Sons, Inc.: New York, 2000; Chapter 1.
9. Park, L. Y.; Hamilton, D. G.; McGehee, E. A.; McMenimen, K. A. *J. Am. Chem. Soc.* **2003**, *125*, 10586-10590.
10. Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525-5534.
11. Sinnokrot, M. O.; Sherrill, C. D. *J. Phys. Chem. A* **2003**, *107*, 8377-8379.
12. Wurpel, G. W. H.; Brouwer, A. M.; Stokkum, I. H. M.; Farran A.; Leigh, D. A. *J. Am. Chem. Soc.* **2001**, *123*, 11327-11328