

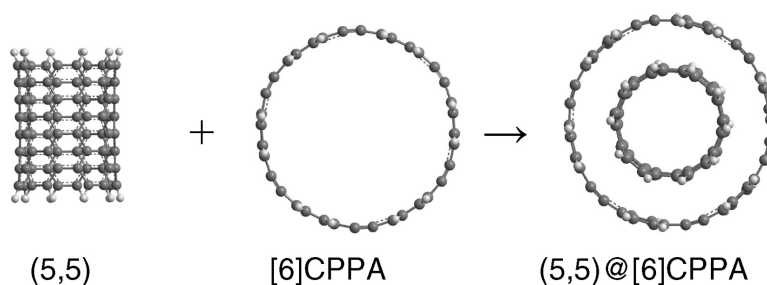
Communication

Size-Selective Supramolecular Chemistry in a Hydrocarbon Nanoring

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Size-Selective Supramolecular Chemistry in a Hydrocarbon Nanoring

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Supramolecular chemistry has been a very active area since the seminal work of Lehn.^{1–4} Macrocycles are versatile building blocks for supramolecular design. Conjugated macrocycles with a belt-like shape in which the conjugated orbitals are hybridized orbitals directed radially^{5–7} (as compared to pure p-orbitals normal to a plane in polyacenes and polyaphenes) provide especially intriguing opportunities for such design; carbon nanotubes⁸ and hydrocarbon nanorings^{6,9–15} are exemplary cases.

Multiwalled carbon nanotubes contain noncovalent concave–convex π – π interactions¹⁶ that are hard to characterize because of the structural heterogeneity of most nanotube preparations; it is important to understand these not only for progress in layered nanotube design but also to guide the design of supramolecular complexes of nanotubes as a fabrication element of nanodevices. Kawase et al. have synthesized a class of hydrocarbon nanorings, in particular, $[n]$ paraphenyleneacetylene or $[n]$ CPPA, that serve as well-defined model compounds for studying concave– π supramolecular interactions and also as potential supramolecular elements in their own right.^{6,9–15} It is difficult to carry out experimental studies of these supramolecules in the gas phase.

Kawase and Kurata attribute the driving force in forming $[n]$ -CPPA supramolecular complexes to concave–convex π – π interactions.⁶ Very recently, we have developed density functionals that provide an accurate description of such noncovalent π interactions,^{17–21} and so it is now possible to use theoretical modeling to study gas-phase complexes in which $[6]$ CPPA acts as the host (Figure 1). Our calculations employed the recently developed M06-L¹⁹ and M06-2X²¹ density functionals,²² both of which include a dependence of the energy on spin kinetic energy density as well as local spin density and their gradients; M06-2X also includes some Hartree–Fock exchange. Both functionals have been designed to include medium-range correlation energy. The geometries were optimized at the M06-L/MIDI! level, where MIDI!²³ is a well-balanced and economical double- ζ basis set that gives reasonably good molecular geometries and partial atomic charges. The binding energies (D_e) were calculated at the M06-2X/6-31+G(d,p) level of theory, and basis set superposition errors have been corrected by the counterpoise²⁴ method. The combination of M06-L/MIDI! geometries and M06-2X/6-31+G(d,p) energetics has been validated for noncovalent interactions (see Supporting Information).

Table 1 gives the geometric parameters of the host molecule, $[6]$ CPPA, and the binding energies in six supramolecular complexes. The guest molecules we studied are: hexamethylbenzene (HMB), fullerenes (C60 and C70), and three armchair-type nanotubes: (3,3), (4,4), and (5,5). The $[6]$ CPPA host molecule is almost circular with a long axis between opposite ethynylene carbons and a short axis between the center of opposite phenylenes. The calculated lengths of the long axis in the isolated $[6]$ CPPA and supramolecules are between 13.25 and 13.34 Å, and those for the short axis are between 12.89 and 12.98 Å, in good agreement with experimental¹¹ and ab initio²⁵ results.

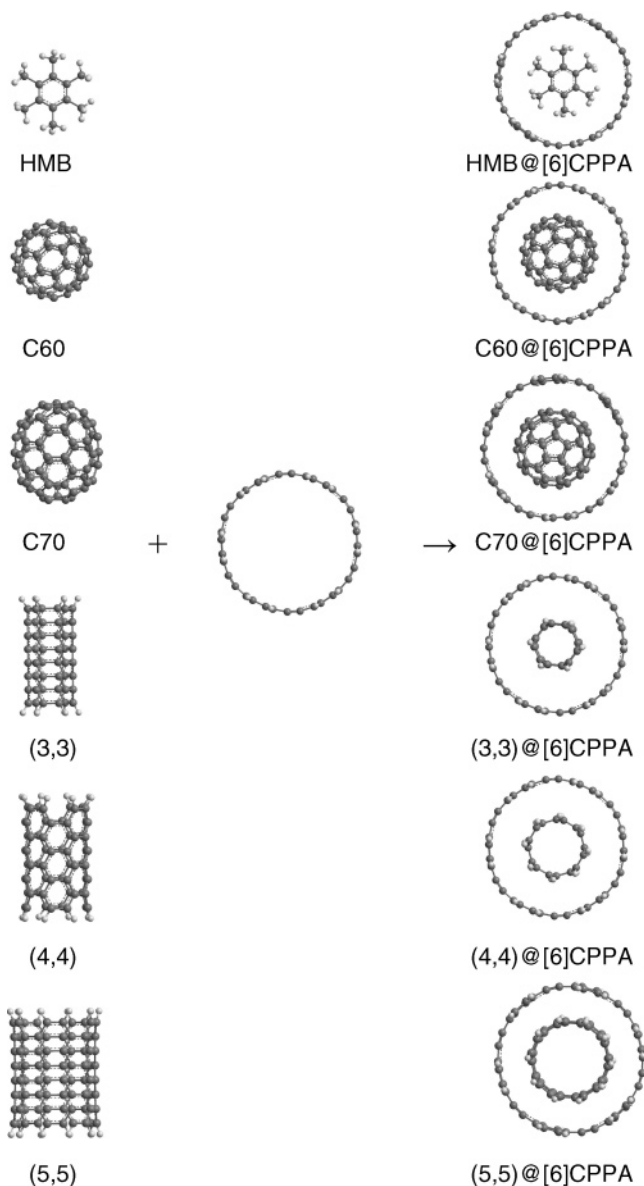


Figure 1. Supramolecular chemistry in $[6]$ CPPA.

For the binding energy of the HMB@[6]CPPA supramolecule, our DFT calculation gives 14.7 kcal/mol, which is in good agreement with the best estimate (14–19 kcal/mol) of Garcia Cuesta et al.²⁵ Note that Garcia Cuesta et al. have also shown that popular density functionals, such as B3LYP, VSXC, B97-1, PBE, PW91, and HCTH, fail badly for the calculation of the supramolecular interactions in HMB@[6]CPPA. The guest molecule is bonded to

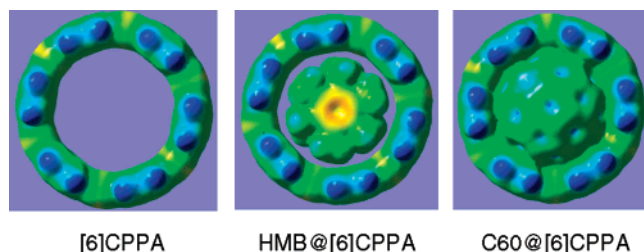
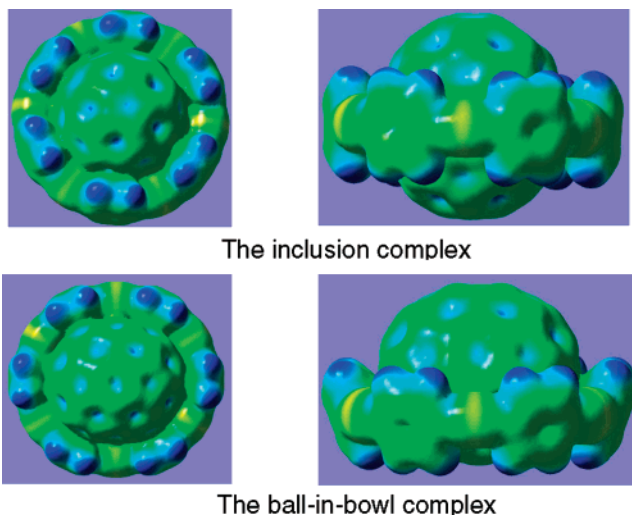
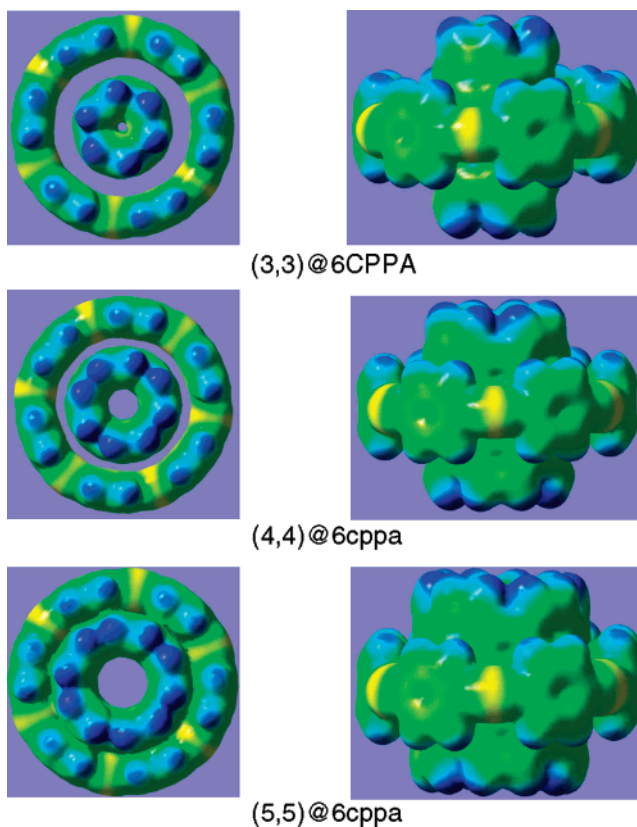
Table 1. Geometric Parameters of the Host Molecule ([6]CPPA) and Binding Energies of the Supramolecules

guest molecule	formula	long axis (Å)	short axis (Å)	D_e (kcal/mol)
none		13.28	12.98	0
HMB	C ₁₂ H ₁₈	13.27	12.89	14.7
HMB (exp.) ¹⁰	C ₁₂ H ₁₈	13.3	13.0	
C60	C ₆₀	13.34	12.96	28.0
C70	C ₇₀	13.29	12.99	31.1
(3,3)	C ₄₈ H ₁₂	13.31	12.98	5.4
(4,4)	C ₆₄ H ₁₆	13.25	12.94	24.0
(5,5)	C ₈₀ H ₂₀	13.28	12.94	43.3

the host through multiple CH- π hydrogen bonds and medium-range dispersion-like interactions. We have shown²⁰ that most of the previous functionals are problematic for describing this kind of noncovalent interactions. The ability of the new-generation M06-2X functional and its prototype, the M05-2X functional, to treat medium-range correlation energy and its effect on nonbonded interactions quantitatively^{18,20,21,26-30} open a new practical avenue for obtaining detailed information about and understanding of supramolecular chemistry.

Table 1 shows that the binding energy for the C60@[6]CPPA complex is much greater than that of HMB@[6]CPPA. This is also in agreement with the experiments of Kawase et al.^{10,11} To understand the nature of the difference, we plotted in Figure 2 the supramolecular electrostatic potential calculated at the M06-2X/6-31+G(d,p) level. Figure 2 shows that there is an overlap of electron density between C60 and [6]CPPA, but no significant overlap occurs for HMB@[6]CPPA.

For the C70@[6]CPPA system, we located two supramolecular complexes. The global minimum is an inclusion supramolecular complex, in which C70 is standing in the middle of [6]CPPA. A closer comparison shows that the center of C60 is aligned with the center of [6]CPPA in the C60@[6]CPPA complex, whereas the center of C70 is about 1.1 Å above the center of [6]CPPA in C70@[6]CPPA (see upper part of Figure 3). These results agree very well with the ¹H NMR spectra of Kawase et al., who have shown that the ¹H NMR spectrum of C60@[6]CPPA has only one sharp singlet (at 7.37 ppm) for the aromatic protons,¹¹ whereas the spectrum of C70@[6]CPPA has two singlets (6.929 and 7.484 ppm) of equal density for the upper and lower aromatic protons, respectively. The binding energy of the C70@[6]CPPA inclusion complex is 31.1 kcal/mol. This shows that C70 is more strongly bound than C60 in the gas phase, which agrees reasonably with the experimental¹² association constants in nonpolar C₆H₆, but disagrees with the extraction experiments in polar CD₂Cl₂;¹² this discrepancy can be explained by an electrostatic solvation effect, as discussed in Supporting Information. The smallest distance between a fullerene carbon and a nanoring carbon is 3.1 Å for both the C60

**Figure 2.** Electrostatic potential surfaces of [6]CPPA, HMB@[6]CPPA, and C60@[6]CPPA; the positive regions are in blue, whereas the negative regions are in red.**Figure 3.** Electrostatic potential surfaces (left: top-view; right: side-view) of the two C70@[6]CPPA supramolecular complexes; the positive regions are in blue, whereas the negative regions are in red.**Figure 4.** Electrostatic potential surfaces (left: top-view; right: side-view) of the three supramolecular complexes involving nanotubes; the positive regions are in blue, whereas the negative regions are in red.

and C70 inclusion complexes; these distances are shorter than the 3.6 Å value for HMB, thereby accounting for the larger interaction energies. We also found a local minimum of a ball-in-bowl shape (C70 is lying in the middle of [6]CPPA) with an energy 7.2 kcal/mol higher than the inclusion complex. Note that the geometry of the host molecule is deformed much more significantly in the ball-in-bowl C70@[6]CPPA complex with the long axis being 13.7 Å and short axis being 12.7 Å. The nearest-neighbor intermolecular carbon-carbon distance in the ball-in-bowl complex is 3.0 Å.

C70 has been compared to the (5,5) armchair nanotube,³¹ but due to their different curvature, the smallest intermolecular C–C distance in their complexes are 3.1 and 3.4 Å, respectively. The latter is closer to the intersheet spacing of 3.4 Å in graphite. However, the interaction between flat conjugated carbon rings or planar grapheme sheets represents a balance of medium-range dispersion-like correlation energy (π – π stacking) and exchange repulsion, whereas concave–convex π – π interactions can, in principle, also have a polar electrostatic component;^{6,7} in particular, it was argued that the interaction consists of a dispersion-like (correlation energy) part and a polar electrostatic part, with the latter arising from the interaction of the electron-rich concave surface with the relatively electron-poor convex surface.⁶ Although experiment⁶ and theory²⁵ indicate that charge transfer is insignificant, so the supramolecular binding may be attributed to correlation energy, in particular to the same medium-range correlation energy that is responsible for nonpolar attractive van der Waals forces, it is important that a theoretical model is able to treat both dispersion-like and charge transfer interactions in a balanced way since some older functionals overestimate charge transfer interactions.³² The M06-2X functional has been well-validated for charge transfer interactions.²¹ Furthermore, with the new density functionals, the medium-range correlation effects responsible for attractive interactions between π systems³³ are included in the functional itself and do not have to be less reliably added on as a damped-dispersion molecular-mechanics-like term.

Although our improved density functionals do not include the correct long-range dipole–dipole limit of dispersion forces in the nonoverlapping region, they are capable of predicting the distance dependence at medium range.^{20,26} The ability of the new density functionals to predict and explain the supramolecular chemistry of carbon nanorings at van der Waals distances is very encouraging because density functional theory can be applied economically to predict and analyze large structures and can therefore be used conveniently for supramolecular design. To illustrate this further, we predict the size selectivity of nanotube/nanoring assemblies. We truncated the nanotubes with four replicas of the unit cell, and we capped the nanotubes with hydrogens. The results in Table 1 show that the interaction in (5,5)@[6]CPPA is much stronger than that in (3,3)@[6]CPPA and (4,4)@[6]CPPA. We also found that (6,6) cannot form a stable inclusion supramolecular complex with [6]-CPPA because the (6,6) molecule is too large to fit inside the nanoring. (The (6,6) complex has the empirical formula C₁₄₄H₄₈, illustrating the large size of the systems for which useful calculations are now possible.) As shown in Figure 4, (5,5)@[6]CPPA has closer van der Waals contacts than (3,3)@[6]CPPA and (4,4)@[6]CPPA, and the (5,5)@[6]CPPA complex has significant electron density overlap between the guest and host molecules. The nearest-neighbor distances between a nanoring carbon and a nanotube carbon are 4.5, 3.8, and 3.4 Å in the (3,3), (4,4), and (5,5) complexes, respectively. The strong binding in the (5,5)@[6]CPPA complex involves both medium-range dispersion-like attraction and orbital overlap. Note that even though the overlap is small in the (4,4)@[6]CPPA complex, the interaction energy in (4,4)@[6]CPPA is almost comparable to that in C60@[6]CPPA.

In summary, the supramolecular interactions in a hydrocarbon nanoring host, [6]CPPA, have been shown with recently developed density functionals to be very strong and size-selective. The density functional results in the present study are in agreement with experiments and a previous ab initio study for HMB@[6]CPPA, which, along with validation studies in Supporting Information, lends credibility to the predictions for larger complexes for which ab initio calculations are prohibitively resource consuming. We also

calculated the interaction strengths of two supramolecules where the guest molecules are fullerenes and in three supramolecules where guest molecules are truncated nanotubes. The size selectivity in the supramolecular complexes in which truncated nanotubes act as guest molecules results from the combined effect of dispersion-like attractive forces and π -electron overlap between the guest and host. Such overlap would be expected to enhance interfacial electronic charge transport.^{34–36} The ability of new density functionals to analyze and accurately model attractive interactions due to medium-range correlation energy opens new possibilities for computer-aided supramolecular design.

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Supporting Information Available: Detailed discussions, Cartesian coordinates, validation results, software, and binding energies with and without counterpoise corrections. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Lehn, J. M. *Science* **1985**, *227*, 849.
- (2) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89.
- (3) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304.
- (4) Lehn, J. M. *Science* **1993**, *260*, 1762.
- (5) Scott, L. T. *Angew. Chem., Int. Ed.* **2003**, *42*, 4133.
- (6) Kawase, T.; Kurata, H. *Chem. Rev.* **2006**, *106*, 5250.
- (7) Tahara, K.; Tobe, Y. *Chem. Rev.* **2006**, *106*, 5274.
- (8) Tasis, D.; Tagmatarchis, N.; Binaco, A.; Prato, M. *Chem. Rev.* **2006**, *106*, 1105.
- (9) Kawase, T.; Darabi, H. R.; Oda, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2662.
- (10) Kawase, T.; Seirai, Y.; Darabi, H. R.; Oda, M.; Sarakai, Y.; Tahiro, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 1621.
- (11) Kawase, T.; Tanaka, K.; Fujiwara, N.; Darabi, H. R.; Oda, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1624.
- (12) Kawase, T.; Tanaka, K.; Seirai, Y.; Shiono, N.; Oda, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 5597.
- (13) Kawase, T.; Tanaka, K.; Shiono, N.; Seirai, Y.; Oda, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1722.
- (14) Kawase, T.; Oda, M. *Pure Appl. Chem.* **2006**, *77*, 831.
- (15) Kawase, T.; Nishitaka, Y.; Nakamura, T.; Ebi, T.; Matsumoto, K.; Kurata, H.; Oda, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1086.
- (16) Cumings, J.; Zettl, A. *Science* **2000**, *289*, 602.
- (17) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. Phys.* **2005**, *7*, 2701.
- (18) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 1009.
- (19) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101.
- (20) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2007**, *3*, 289.
- (21) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2007**, in press (<http://dx.doi.org/10.1007/s00214-007-0310-x>).
- (22) Kohn, W.; Becke, A. D.; Parr, R. G. *J. Phys. Chem.* **1996**, *100*, 12974.
- (23) Easton, R. E.; Giesen, D. J.; Welch, A.; Cramer, C. J.; Truhlar, D. G. *Theor. Chim. Acta* **1996**, *93*, 281.
- (24) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
- (25) Garcia Cuesta, I.; Pedersen, T. B.; Koch, H.; Sanchez de Meras, A. *ChemPhysChem* **2006**, *7*, 2503.
- (26) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2006**, *110*, 5121.
- (27) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2006**, *110*, 10478.
- (28) Zhao, Y.; Truhlar, D. G. *Org. Lett.* **2006**, *8*, 5753.
- (29) Zhao, Y.; Truhlar, D. G. *J. Org. Chem.* **2006**, *72*, 295.
- (30) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364.
- (31) Kawase, T.; Fujiwara, N.; Tsutsumi, M.; Oda, M.; Maeda, Y.; Wakahara, T.; Akasaka, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 5060.
- (32) Ruiz, E.; Salahub, D. R.; Vela, A. *J. Am. Chem. Soc.* **1995**, *117*, 1141.
- (33) Ortmann, F.; Schmidt, W. G.; Bechstedt, F. *Phys. Rev. Lett.* **2005**, *95*, 186101.
- (34) Ishii, H.; Sagiyama, K.; Ito, E.; Seki, K. *Adv. Mater.* **1999**, *11*, 605.
- (35) Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. *Adv. Funct. Mater.* **2005**, *15*, 1617.
- (36) Kurlancheek, W.; Cave, R. J. *J. Phys. Chem. A* **2006**, *110*, 14018.

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