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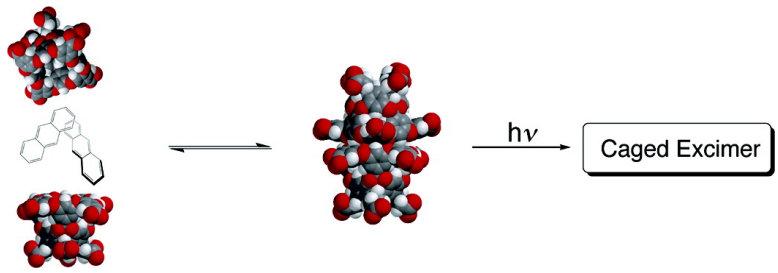

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A Hydrophobic Nanocapsule Controls the Photophysics of Aromatic Molecules by Suppressing Their Favored Solution Pathways

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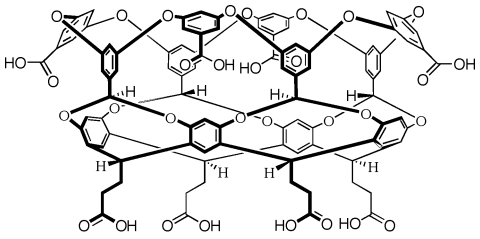
Enzymes exert selectivity in chemical reactions by either positive or negative catalysis.[1] Likewise, other forms of confined media may bring about selectivity in a chemical[2] or photochemical reaction[3] not only by rate acceleration, but also by rate deceleration of unwanted processes. We provide in this report examples where a well-defined, supramolecular capsule[4] alters the excited-state chemistry of aromatic guests by suppressing their most favored solution pathways.[5] The capsule, formed by the assembly of two molecules of cavitand **1**, encapsulates guest molecules in aqueous solution in a manner depending on the complementarity between host and guest. Hence, the precise nature of the alternative chemical pathway promoted by the capsule is a function of the volume and shape of the guest. We examine three guests—naphthalene, anthracene, and tetracene—to illustrate this point.[5] Two molecules of the smaller guests naphthalene and anthracene are held within the capsule. As a result, their excimer emissions are greatly enhanced through increased effective concentration. In the case of anthracene, however, the capsule also holds the contents in a prereaction excimer state that cannot attain the correct geometry for photodimerization.[6] Hence, the capsule allows an unprecedented examination of the anthracene excimer. In contrast, only one molecule of the larger tetracene is stored in the capsule, and in this case the normal excimer emission and photodimerization properties of the guest are shut down.[5]



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A 10^{-4} M solution of naphthalene in free aqueous borate buffer showed only monomer emission.[7] However, in a similarly buffered solution containing an equivalent of host **1**, both a red-shifted monomer emission (τ: 62 ns) and an excimer emission (τ: 74 ns) were observed.[7] This emission spectrum was unchanged in the presence of excess host, added to ensure no free guest. NMR analysis confirmed guest encapsulation and the formation of a 2:2 complex.[7] Models of this species suggest that, even with two guests, there is a considerable amount of free space inside the capsule. Thus, although each naphthalene molecule experiences an effective concentration of ~3 M, their relatively small size means that they are not forced into permanent close proximity and both monomer and excimer emissions are observed.

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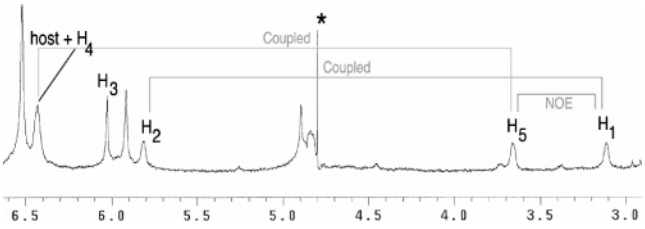

Figure 1. Guest signals of the ^{1}H NMR spectrum of the 2:2 complex between anthracene and host **1** (1 mM in borate buffer solution). See Figure 2 for proton designations. The * donates the suppressed water signal.

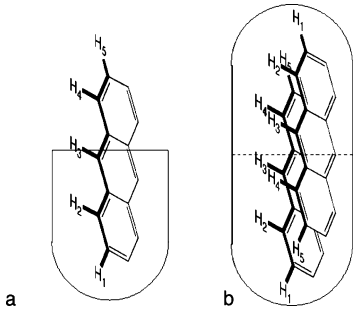

Figure 2. Representations of the 1:1 and 2:2 complexes between anthracene and host **1**.

"Doubling" the size of the guest demonstrates the flipside of encapsulation. Thus, the largest guest examined, tetracene, normally undergoes photochemical-induced dimerization,[5] and in free solution both monomer and excimer emissions are observed. In the presence of host **1**, however, only monomer emission is observed. NMR reveals that only one tetracene is trapped with the host because the length of the guest is sufficient to fill the entire length of the capsule. Hence, in this case, rather than increasing the effective molarity of two guests, the capsule isolates one guest molecule from the solution and shuts down its normal photochemistry dimerization.

Anthracene represents a fascinating "intermediate" case of encapsulation. The ^{1}H NMR spectrum of the 1:1 complex between **1** and anthracene showed five signals for the encapsulated guest (Figure 1).[7] Either a 1:1 or a 2:2 complex can account for this observed dissymmetry along the long axis of the guest (Figure 2). In the latter complex, encapsulation necessitates reduced guest symmetry because the tapering nature of each cavitand allows only one guest to bind deeply at any given moment. As a result, the two guests lie out-of-register. As is generally the case with molecules binding to these cavitands, guest signals are shifted upfield, with the deeper protons experiencing the larger shifts. The two most shifted guest signals in the NMR of the complex occur at δ 3.10 and 3.65 ppm (Figure 1). In a 1:1 complex these signals would correspond to protons H_1 and H_2 and would be coupled. A COSY NMR demonstrates that they are not.[7] Rather, this pair of signals are, respectively, coupled with those at δ 5.72 and 6.40

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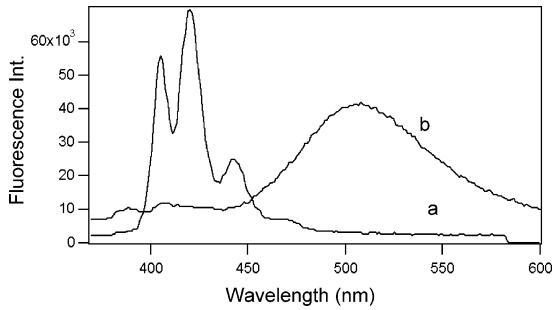

Figure 3. Fluorescence emission spectrum of anthracene in: (a) 10 mM aqueous borate buffer solution and (b) the same buffer solution but in the presence of 1 equiv of host **1**.

ppm. The 2:2 complex accounts for this observation; it is H_2 and H_4, respectively, that absorb at δ 5.72 and 6.40 ppm. This deduction is confirmed by a NOESY spectrum, which shows that although the signals at δ 3.10 and 3.65 ppm are not coupled, they are spatially proximal. Hence, these signals correspond to H-1 and H-5 on different guest molecules.

The out-of-register positioning of the encapsulated guests radically alters their photochemistry. Solution excitation of anthracene results in the rapid and quantitative formation of anthracene dimer;[6] the emission spectrum reveals monomer emission and only the weakest excimer emission ($\lambda_{max} \approx 530$ nm; $\tau < 2$ ns).[8] Consequently, studies of the anthracene excimer have focused on low-temperature (<77 K) photodissociation of anthracene dimer in either rigid glass or the crystalline state.[9−11] These studies have identified two kinds of excimer. The first, termed "stable dimer", has in-register anthracenes that, rather than being π-stacked, are at an angle of 55° to each other (with respect to their short axis) and has a short, <10 ns, lifetime. The second one, known as the "sandwich excimer", is a symmetrical π-stacked excimer with a longer lifetime (>200 ns) especially at lower temperatures.[10]

Remarkably, after addition of 1 equiv of host **1**, the exclusive monomer fluorescence of a 10^{-5} M anthracene solution in borate buffer is almost entirely replaced by a broad emission with a maximum at 510 nm (Figure 3). This emission has a long lifetime (263 ns). These data, the similarity of the absorption and excitation spectra of the complex,[7] and their similarity to the absorption spectrum of the "sandwich excimer" at 10 K[9] suggest that the excimer observed in this study is a π-stacked one. Furthermore, even after 10 hours of irradiation there was no evidence of conversion to anthracene dimer. Thus, the cohesiveness of the capsule holds the two anthracene molecules in an excimer-like state, but it also prevents the reaction progressing over the TS to the anthracene dimer product. In solution at room temperature anthracene dimerizes rapidly with a unit quantum yield, while within the capsule the reaction cannot (quite) take place.[12]

The message conveyed by the probes, naphthalene anthracene, and tetracene is clear. Confinement within the cavity of dimer $\mathbf{1}_2$ can suppress photochemical pathways that are normally favored in solution. How that pathway is modulated is, however, a function of shape complementarity between the potential guest and the cavity of the host. We are currently exploring other photochemical processes with the capsule formed by **1** and will report on these soon.

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Supporting Information Available: Experimental details, excitation and absorption spectra, NOESY and COSY spectrum of anthracene included in the capsule formed by **1**, and emission and NMR spectra of naphthalene and tetracene included in the capsule formed by **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Garcia-Garibay, M. A. *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 399−406. (b) Retey, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 355−361. (c) Breslow, R.; Huang, D.-L. *J. Am. Chem. Soc.* **1990**, *112*, 9621−9623.

(2) (a) Kang, J.; Santamaría, J.; Hilmersson, G.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1998**, *120*, 7389−7390. (b) Kang, J.; Rebek, J., Jr. *Nature* **1997**, *385*, 50−52. (c) Chen, J.; Körner, S.; Craig, S. L.; Rudkevich, D. M.; Rebek, J., Jr. *Nature* **2002**, *415*, 385−386. (d) Warmuth, R.; Kerdelhué, J. L.; Carrera, S. S.; Langenwalter, K. J.; Brown, N. *Angew. Chem., Int. Ed.* **2002**, *41*, 96−99.

(3) (a) *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH: New York, 1991. (b) Ramamurthy, V.; Eaton, D. F. *Acc. Chem. Res.* **1988**, *21*, 300. (c) Weiss, R. G.; Ramamurthy, V.; Hammond, G. S. *Acc. Chem. Res.* **1993**, *26*, 530−536. (d) Turro, N. J. *Acc. Chem. Res.* **2000**, *33*, 637−646. (e) Tung, C. H.; Wu, L. Z.; Zhang, P. P.; Chen, B. *Acc. Chem. Res.* **2003**, *36*, 39−47.

(4) (a) Gibb, C. L. D.; Gibb, B. C. *J. Am. Chem. Soc.* **2004**, *126*, 11408−11409. (b) Kaanumalle, L. S.; Gibb, C. L. D.; Gibb, B. C.; Ramamurthy, V. *J. Am. Chem. Soc.* **2004**, *126*, 14366−14367.

(5) (a) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley & Sons: London, 1970. (b) Lapouyade, R.; Nourmamode, A.; Bouas-Laurent, H. *Tetrahedron* **1980**, *36*, 2311−2316. (c) Reichwagen, J.; Hopf, H.; Del Guerzo, A.; Desvergne, J.-P.; Bouas-Laurent, H. *Org. Lett.* **2004**, *6*, 1899−1902.

(6) Bouas-Laurent, H.; Castellan, A.; Desvergne, J. P.; Lapouyade, R. *Chem. Soc. Rev.* **2000**, *29*, 43−55 and **2001**, *30*, 248−263.

(7) See Supporting Information.

(8) (a) McVey, J. K.; Shold, D. M.; Yang, N. C. *J. Chem. Phys.* **1976**, *65*, 3375−3376. (b) Kobyashi, T.; Ngakura, S.; Szwarc, M. *Chem. Phys.* **1979**, *39*, 105−110. (c) Hashimoto, S.; Fukazawa, N.; Fumumura, H.; Masuhara, H. *Chem. Phys. Lett.* **1994**, *219*, 445−451. (d) Hashimoto, S.; Ikuta, S.; Asahi, T.; Masuhara, H. *Langmuir* **1998**, *14*, 4284−4291.

(9) (a) Chandross, E. A. *J. Chem. Phys.* **1965**, *43*, 4175−4176. (b) Chandross, E. A.; Ferguson, J.; McRae, E. G. *J. Chem. Phys.* **1966**, *45*, 3546−3553. (c) Chandross, E. A.; Ferguson, J. *J. Chem. Phys.* **1966**, *45*, 3564−3567.

(10) (a) Fielding, P. E.; Jarnagin, R. C. *J. Chem. Phys.* **1967**, *47*, 247−252. (b) Mataga, N.; Torihashi, Y.; Ota, Y. *Chem. Phys. Lett.* **1967**, *1*, 385−387.

(11) Ferguson, J.; Mau, A. W.-H. *Mol. Phys.* **1974**, *27*, 377−387.

(12) Host systems have been employed previously to align molecules for photodimerization: (a) Rao, K. S. S. P.; Hubig, S. M.; Moorthy, J. N.; Kochi, J. K. *J. Org. Chem.* **1999**, *64*, 8098−8104. (b) Yoshizawa, M.; Takeyama, Y.; Okano, T.; Fujita, M. *J. Am. Chem. Soc.* **2003**, *125*, 3243−3247. (c) Herrmann, W.; Wehrle, S.; Wenz, G. *Chem. Commun.* **1997**, 1709−1710. (d) Moorthy, J. N.; Venkatesan, K.; Weiss, R. G. *J. Org. Chem.* **1992**, *57*, 3292−3297. (e) Pattabiraman, M.; Natarajan, A.; Kaanumalle, L. S.; Ramamurthy, V. *Org. Lett.* **2005**, *7*, 529−532.

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