Competitive Binding of Organic Dyes between Cucurbiturils and Octa Acid

Shipra Gupta, Yaopeng Zhao, Ramkumar Varadharajan, and V. Ramamurthy

Department of Chemistry, University of Miami, Coral Gables, Florida 33146, United States

ABSTRACT: Employing six cationic water-soluble organic dye molecules as probes, we have attempted to qualitatively understand the factors that govern the attraction between such molecules and the anionic water-soluble host, octa acid (OA). Examination of the competitive host–guest complexation between cucurbit[8]uril (CB[8]) and OA using absorption and emission spectroscopy revealed that the dye molecules included within CB[8] could be “pulled out” by OA. However, an order of magnitude higher concentration of OA was required to shift the equilibrium toward OA, suggesting that attraction between the anionic host OA and the cationic dye molecules such as cresyl violet perchlorate and methylene blue is weaker than the hydrophobic and cation–dipolar interaction between these dye molecules and CB[8]. The importance of Coulomb interaction attraction between OA and dye molecules is also revealed by monomer-to-dimer conversion upon addition of OA to an aqueous solution of monomeric dye molecules. Under conditions where the dye-to-OA ratio is high, freely dissolved monomeric dye molecules are attracted to the exterior of OA and aggregate as dimers on the exterior wall of OA. On the other hand, at high ratios of OA to dye molecules, the dye molecules absorb as monomers on the exterior of OA. Thus, the monomer-to-dimer ratio in aqueous solution can be controlled by adjusting the ratio of dye to OA molecules. The results presented are of value in qualitatively understanding the relative binding properties of ionic guests with ionic hosts. Studies are qualitative in nature, and further detailed quantitative studies planned for the future are likely to provide deeper understanding of the interaction between water-soluble dye molecules, OA, and CB.

INTRODUCTION

The use of dyes as sensitizers in photographic processes and printing technologies,1,2 as laser dyes,3,4 as a component in solar energy conversion systems5–9 and in chemotherapy10,11 point to their varied role in current times. Understanding and controlling the dye aggregation are necessary for their utilization in coloration of materials such as fibers, in photochemical processes such as photography and in medical applications such as photodynamic therapy. H-aggregation, a common intermolecular association, has been extensively investigated both in solution and in confined environments using various electronic spectroscopic methods for many years.14–21 The dye molecules in these systems stack in parallel, face-to-face fashion to produce dimers and higher order aggregates in a sandwichlike arrangement. Such a molecular aggregation depends on several factors including dye concentration and structure, solvent, temperature, and pH. The excitonic coupling between the transition dipoles on neighboring chromophores splits the electronic transitions into higher and lower energy components.14–17 The allowed exclusive transition to a higher excited state for the H-aggregated dimer leads to its blue-shifted absorption, relative to the isolated monomers. The H-aggregated dimer is usually a poor emitter because of its enhanced intersystem crossing in the excited state.22,23 In recent years, modulation of dye aggregation through encapsulation in the cages of supramolecular assemblies has attracted much attention.18–20,24 Formation of host–guest complexes between organic dye molecules and host cucurbit[n]uril (CB[n]) are classic examples.25–30 Depending on the guest size and preferred orientation, CBs can accommodate one or two dye molecules to form 1:1 or 1:2 (host-to-guest) complexes through ion–dipole interaction.31–34 Hydrophobic interaction is also likely to play a role for hydrophobic organic guest molecules. In this work, aiming at assessing the strength of Coulombic attraction between the host octa acid (OA) and six cationic dyes (Scheme 1) in relation to ion–dipole interaction between cucurbit[8]uril (CB[8]) and dyes, we have monitored the change in their absorption and emission spectra in the presence of the above hosts. Differences in absorption maxima of the dyes under different conditions have enabled this study.

RESULTS AND DISCUSSION

We have examined the absorption and emission characteristics of six water-soluble organic dyes18,35–48 (Scheme 1) in aqueous solution, in borate buffer, and in the presence of hosts OA and/or CB[8] in borate buffer. Because all six dyes exhibit a similar behavior, results of two, namely, cresyl violet perchlorate...
(CVP) and methylene blue (MB) are presented and discussed below. Results from the other four [thionin acetate (TA), acridine orange (AO), toluidine blue (TBO), and azure B (AB)] are included as Supporting Information. Because all studies are conducted in borate buffer solution (pH \(\approx 9\)), we recorded the absorption and emission spectra in borate buffer and compared them with those in aqueous solution. Except for the decreased absorption intensity of the dyes in the buffered solution relative to that in neutral solution, no other changes were noticeable.

**Interaction of CVP and MB with OA.** Figures 1 and 2 show the effect of OA on the absorption and fluorescence spectra of CVP (1.0 \(\times\) \(10^{-5}\) M) and MB (8.2 \(\times\) \(10^{-6}\) M) in borate buffer solution at room temperature. The main absorption maxima of CVP and MB in the absence of OA were at 588 and 664 nm. These were attributed to the monomers of the dyes present in buffer solution. Addition of OA to the solution containing the dyes resulted in a decrease in the monomer absorption and a rise in the dimer absorption. The sharp decrease in the monomer absorption of both dyes with the addition of OA implies the equilibrium shift of the system toward the dimer with a corresponding quenching of their fluorescence as both the dye dimers are nonemissive. The decrease of the intensity of absorption and the shift of maxima to a shorter wavelength occurred continuously until the OA concentration reached 1.8 \(\times\) \(10^{-6}\) M OA (for CVP) and 1.0 \(\times\) \(10^{-5}\) M (for MB). Further addition resulted in the decrease of dimer absorption (543 nm for CVP and 600 nm for MB) with a concomitant increase in monomer absorption (602 nm for CVP and 670 nm for MB); the fluorescence intensity showed a similar pattern that reached a peak at OA concentrations of 1.7 \(\times\) \(10^{-4}\) M for CVP and 1.2 \(\times\) \(10^{-3}\) M for MB.

The above changes in absorption and emission spectra are a reflection of the changes in the monomer–dimer equilibrium caused by OA. We believe that the model outlined below accounts for the above spectral changes. Under our experimental conditions, in the absence of OA, the absorption and emission characteristics of the dye molecules are reflective of them remaining mostly as monomers. At early stages of OA addition, as the dye molecules outnumber OA, aggregation (dimers) due to Coulombic interaction between oppositely charged host and guest molecules occurs around a limited number of OA molecules. Thus, upon addition of small amounts of OA, the equilibrium shifted from monomers to dimers, the latter being present on the exterior walls of the host OA. Upon further addition, the aggregates dissociate to monomers, resulting in a one-to-one interaction between the dye and OA molecules. The spectral changes corresponding to dimer-to-monomer conversion upon further addition of OA are consistent with the aggregated dye molecule redistributing themselves amongst the large number of OA molecules. All six dyes studied showed such a behavior (Figures S1–S4). The observed small red shifts in the \(\lambda_{\text{max}}\) of the absorption/fluorescence for all six dyes upon addition of OA are presented in Table 1. Interestingly, the absorption maxima of monomers...
are different for the ones adsorbed on the OA surface and the ones that are free. Scheme 2 is a cartoon depiction of this phenomenon. It is clear that with judicial choice of the concentration of the host OA, one can control the monomer–dimer equilibrium in aqueous solution. Luckily, the difference in absorption maxima allowed us to infer this phenomenon.

Although the above experiments confirmed that the cationic dye molecules are attracted to the anionic OA, they do not provide any indication whether the dye molecules are located at the exterior surface or within the cavitand. To probe whether the dye molecule–OA interaction occurs on the exterior of the OA (Coulombic interaction) or within the cavitand (hydrophobic and Coulombic interaction), we examined the dye interaction with OA capsules (made up of two molecules of OA) enclosing a guest molecule. Such a OA capsular assembly where the guest is already included capsules can offer only its exterior containing 16 carboxylate anions for interaction with the dye. Dehydro-epi-androsterone (DHAS) strongly binds to OA to form a very stable capsular complex, we depict as DHAS@OA<sub>2</sub>. In this case, only the exterior walls are available for interaction with dye molecules.

Figure 3 shows the change in UV and fluorescence spectra of CVP when titrated with DHAS@OA<sub>2</sub>. The spectral behavior on titration of CVP with DHAS@OA<sub>2</sub> closely resembled that with OA alone, as shown in Figure 1. Similar to that upon addition of OA, the monomers present in solution were converted to dimers that, upon further addition of DHAS@OA<sub>2</sub>, became monomers. Comparison of the spectral changes with OA and DHAS@OA<sub>2</sub> points to the purely electrostatic interaction between the dye and the OA, with the hydrophobic interior of the OA cavity playing no role.

Table 1. Change in $\lambda_{\text{max}}$ of Absorption and Fluorescence before and after Addition of OA and CB[8] to Dyes in Buffer Solution (in Sodium Borate Buffer; pH = 9.0)<sup>a,b</sup>

| dyes | absorption ($\lambda_{\text{max}}$/nm) | fluorescence ($\lambda_{\text{max}}$/nm) |
|------|-----------------------------------|----------------------------------|
|      | in the absence of OA | dye + OA | dye + CB[8] | dye + CB[8] → OA | in the absence of OA | dye + OA | dye + CB[8] | dye + CB[8] → OA |
| CVP  | 588 | 602 | 546 | 604 | 630 | 639 | 639 |
| MB   | 664 | 670 | 622 | 668 | 692 | 702 | 699 |
| TA   | 600 | 605 | 560 | 605 | 625 | 636 | 637 |
| AO   | 492 | 498 | 470 | 498 | 531 | 531 | 580 |
| TBO  | 629 | 638 | 582 | 639 | 675 | 680 | 679 |
| AB   | 650 | 663 | 603 | 660 | 687 | 694 | 692 |

The concentration of OA is indicated in figures. <sup>a</sup>Data taken from Figures 1, 2, 4–9, and S1–S8.

Scheme 2. Cartoon Representation of the OA Concentration-Dependent Monomer–Dimer Equilibrium<sup>a</sup>

"The dimer predominates at an intermediate concentration of OA"
walls of OA either as dimers or monomers. If they adsorb as monomers, we surmised that dimer-to-monomer conversion could be monitored by their characteristic absorption and emission characteristics. As expected, on gradual addition of CB[8] to an aqueous solution of CVP at room temperature, the absorption of the CVP monomer decreased sharply while that of the CVP dimer increased. Figure 3. (a) UV−visible absorption and emission spectra of CVP in the presence of OA. (a) Absorption spectra: $\lambda_{\text{max}}$ for the monomer before addition of DHAS@OA = 588 nm and after addition of DHAS@OA = 602 nm; the initial [OA] = 0 M, [OA] needed for maximum aggregation = 2.0 $\times$ 10$^{-6}$ M, and [OA] needed for maximum deaggregation = 2.2 $\times$ 10$^{-5}$ M. (b) Fluorescence spectra: $\lambda_{\text{max}}$ for the monomer before addition of DHAS@OA = 630 nm and after addition of DHAS@OA = 638 nm; the initial [OA] = 0 M, [OA] needed for maximum aggregation = 2.0 $\times$ 10$^{-6}$ M, and [OA] needed for maximum deaggregation = 2.2 $\times$ 10$^{-5}$ M; [CVP] = 1.07 $\times$ 10$^{-5}$ M, titrated with DHAS@OA capsule at room temperature. The black lines represent the decrease in absorbance/emission, and the red lines represent the increase in absorbance/emission after the turning point. Figure 4. (a) UV−visible absorption and emission spectra of CVP in the presence of CB[8]. (a) Absorption spectra: $\lambda_{\text{max}}$ for the monomer before addition of CB[8] = 588 nm and for aggregate after addition of CB[8] = 546 nm; the initial [CB[8]] = 0 M, [CB[8]] at maximum aggregation = 1.15 $\times$ 10$^{-5}$ M. (b) Fluorescence spectra: $\lambda_{\text{max}}$ for the monomer before addition of CB[8] = 630 nm, and after addition of CB[8], the fluorescence diminishes. [CVP] = 1.01 $\times$ 10$^{-5}$ M titrated with CB[8] at room temperature showing a decrease in absorbance/emission on addition of CB[8]. The red lines depict the decrease in absorption/emission. Figure 5. UV−visible absorption and emission spectra of MB in the presence of CB[8]. (a) Absorption spectra: $\lambda_{\text{max}}$ for the monomer before addition of CB[8] = 664 nm and after addition of CB[8] = 622 nm; the initial [CB[8]] = 0 M, [CB[8]] at maximum aggregation = 1.5 $\times$ 10$^{-5}$ M. (b) Fluorescence spectra: $\lambda_{\text{max}}$ for the monomer before addition of CB[8] = 692 nm and after addition of CB[8] = 681 nm; the initial [CB[8]] = 0 M, [CB[8]] maximum for aggregation = 6.0 $\times$ 10$^{-6}$ M; [MB] = 8.2 $\times$ 10$^{-6}$ M titrated with CB[8] at room temperature showing a decrease in absorbance/emission on addition of CB[8].
of the dimer increased and blue-shifted from 588 to 546 nm for CVP (Figure 4a). A similar observation was made in the case of MB, where the monomer maximum at 664 nm shifted to dimer maximum at 622 nm (Figure 5a) with a corresponding quenching of the fluorescence of monomers (Figures 4b and 5b). The results from all other four dyes that showed a behavior similar to those of CVP and MB are presented in the Supporting Information (Figures S5–S8). The absorption maxima for all six dyes included within CB[8] tabulated in Table 1 are consistent with our expectation of the dyes forming a 2:1 complex with CB[8].

The inclusion of the dyes as dimers within CB[8] gave us an opportunity to examine the relative binding abilities of CB[8] and OA with the dyes. To probe this possibility, OA was introduced into a solution containing dyes included within CB[8]. As illustrated in Figure 6a, upon addition of OA, the absorption maximum of CVP continuously shifted toward the monomer (604 nm). Consistent with the appearance of monomer, the fluorescence of CVP also recovered (Figure 6b). A similar observation was made also in the case of MB (Figure 7). The absorption spectra shown in Figures 8 and 9 for the remaining dyes clearly show that there is an isosbestic point upon sequential addition of CB[8] and OA. These support the notion that there is a direct conversion from dimer to monomer when OA is introduced into the solution of the dye–CB[8] complex. This is different from the earlier observation during the addition of OA to the solution containing only dyes (Figures 1 and 2). In this case, depending on the concentration of OA, the dye molecules remained as either monomer or dimer. The fact that the dye molecules present within CB[8] are attracted to OA suggests that the Columbic interaction between OA and the dyes is comparable to the interaction between the negatively polarized carbonyl groups present at the portals of CB and the dye. The fact that
almost an order of magnitude higher concentration of dye is required to attract the dye from CB[8] suggests that the former is weaker than the forces that hold dyes within CB[8]. In the case of CB[8], in addition to the interaction between polarized portals and the cationic dyes, hydrophobic interactions may also be involved. The visualized model for the displacement of the dye molecules from the cavity of CB[8] is illustrated in a cartoon fashion in Scheme 3.

The absorption spectra presented above clearly show that dye molecules present as monomers in aqueous solution can be converted to dimers upon addition of a small amount of OA. Further increase of OA converts the dimers into monomers. These processes involve multiple weak forces. Detailed understanding requires careful binding studies and isothermal calorimetric measurements. The data in hand do not allow us to make any statements that require quantitative measurements. The more interesting observation relates to the conversion of monomer to dimer upon inclusion within CB[8]. Given that the hydrophobicity of the dye molecules investigated here is not all the same and the structures are slightly different, not all are expected to respond to CB[8] in an identical manner. In fact, careful examination of the figures reveals that amounts of CB[8] required to quantitatively convert monomers into dimers are different. Quantitative measurement of binding constants would be useful, which is planned for the future.

The most important aspect of the study was concerned with understanding the factors involved in binding of the dyes to OA relative to CB[8]. Examination of Figures 7–9 reveals that even after the addition of excess OA (10 times the concentration of CB[8]), almost 50% of the dye molecules remained within CB[8]. This suggests that given a chance, the dye molecules prefer CB[8] over OA. This could be due to the fact that inclusion within CB[8] is favored by hydrophobic interaction in addition to cation–dipolar interaction. Interaction with OA is facilitated only by Coulombic interaction, and when attached to the exterior of OA, the hydrophobic dye will be exposed to the aqueous exterior. We are aware that quantitative measurements of binding constants are essential to fully understand the forces that hold the dye molecules within CB[8] and on the surface of OA. With data in hand, any speculation would be premature and risky. Quantitative measurements of relative binding are planned for the future.

■ CONCLUSIONS

Organic dye molecules absorbing in the visible region have a great potential as sensitizers during visible light photocatalysis, a topic of considerable current interest. Water-soluble OA with a well-defined internal cavity has been established to include a variety of structurally diverse, reactive organic molecules. The current study was undertaken to establish the feasibility of bringing a water-soluble organic dye closer to an OA-encapsulated organic molecule so that selective photoreaction could be conducted through visible light activation. The results presented here have established that water-soluble cationic dye molecules can be adsorbed on the exterior of OA molecules. By controlling the ratio of dye and OA molecules, it should be possible to have the dyes as monomers at the exterior of OA.

Figure 8. (a) UV–visible absorption spectra of TA in the presence of CB[8] and OA. Absorption spectra of TA upon addition of CB[8] = 560 nm and (b) on subsequent addition of OA. See Figure S5 for details. (c) UV–visible absorption spectra of AB upon addition of CB[8] and (d) on subsequent addition of OA. See Figure S8 for details.
Coulombic attraction between the negatively charged OA and the positively charged dye is likely the driving force for the attraction. More importantly, at low dye-to-OA ratios, the dye molecules are adsorbed as monomers. The photophysically active monomeric dye molecules can thus serve as sensitizers to initiate photoreactions within OA through energy- and electron-transfer processes. We plan to exploit this feature in our studies on visible light-catalyzed supramolecular chemistry.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00433.

Absorption and emission spectra of TA, AO, TBO, and AB in water in the presence of various concentrations of hosts OA and cucurbituril (PDF)

**AUTHOR INFORMATION**

*E-mail: murthy1@miami.edu.

**ORCID**

V. Ramamurthy: 0000-0002-3168-2185

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

V.R. is thankful to the National Science Foundation (CHE-1411458), USA, for financial support.

**REFERENCES**

(1) Law, K. Y. Effect of Dye Aggregation on the Photogeneration Efficiency of Organic Photoconductors. *J. Phys. Chem.* 1988, 92, 4226−4231.

(2) Mustroph, H.; Stollenwerk, M.; Bressau, V. Current Developments in Optical Data Storage with Organic Dyes. *Angew. Chem., Int. Ed.* 2006, 45, 2016−2035.

(3) Schäfer, F. P. Organic Dyes in Laser Technology. *Angew. Chem., Int. Ed. Engl.* 1970, 9, 9−25.

(4) Schäfer, F. P. *Dye Lasers*; Springer-Verlag: Berlin Heidelberg, 1973; Vol. 1.

(5) Yang, G.; Tang, Y.; Li, X.; Ågren, H.; Xie, Y. Efficient Solar Cells Based on Porphyrin Dyes with Flexible Chains Attached to the Auxiliary Benzo thiadiazole Acceptor: Suppression of Dye Aggregation and the Effect of Distortion. *ACS Appl. Mater. Interfaces* 2017, 9, 36875−36885.

(6) Koyumura, N.; Wang, Z.-S.; Mori, M.; Miyashita, M.; Suzuki, E.; Hara, K. Alkyl-Functionalized Organic Dyes for Efficient Molecular Photovoltaics. *J. Am. Chem. Soc.* 2006, 128, 14256−14257.
(7) Matsuzaki, H.; Murakami, T. N.; Masaki, N.; Furube, A.; Kimura, M.; Mori, S. Dye Aggregation Effect on Interfacial Electron-Transfer Dynamics in Zinc Phthalocyanine-Sensitized Solar Cells. *J. Phys. Chem. C* 2014, 118, 17205–17212.

(8) Reddy, K. S. K.; Chen, Y.-C.; Wu, C.-C.; Hsu, C.-W.; Chang, Y.-C.; Chen, C.-M.; Yeh, C.-Y. Cosensitization of Structurally Simple Porphyrin and Anthracene-Based Dye for Dye-Sensitized Solar Cells. *ACS Appl. Mater. Interfaces* 2018, 10, 2391–2399.

(9) Son, H.-J.; Kim, C. H.; Kim, D. W.; Jeong, N. C.; Prasittichai, C.; Luo, L.; Wu, J.; Farha, O. K.; Wasielewski, M. R.; Hupp, J. T. Post-Assembly Atomic Layer Deposition of Ultrathin Metal-Oxide Coatings Enhances the Performance of an Organic Dye-Sensitized Solar Cell by Suppressing Dye Aggregation. *ACS Appl. Mater. Interfaces* 2015, 7, 5150–5159.

(10) Li, X.; Kim, C.-Y.; Lee, S.; Chung, H.-M.; Kim, G.; Heo, S.-H.; Kim, C.; Hong, K.-S.; Yoon, J. Nanostructured Phthalocyanine Assemblies with Protein-Driven Switchable Photoactivities for Biophotonic Imaging and Therapy. *J. Am. Chem. Soc.* 2017, 139, 10880–10886.

(11) Tang, Y.; Chen, H.; Chang, K.; Liu, Z.; Wang, Y.; Qu, S.; Xu, H.; Wu, C. Photo-Cross-Linkable Polymer Dots with Stable Sensitizer Loading and Amplified Single Oxygen Generation for Photodynamic Therapy. *ACS Appl. Mater. Interfaces* 2017, 9, 3419–3431.

(12) Hamer, F. M. The Cyanine Dyes and Related Compounds; John Wiley & Sons: New York, 1964.

(13) Meier, H. Photochemistry of Dyes. In *The Chemistry of Synthetic Dyes*, Venkataraman, K., Ed.; Academic Press: New York, 1971; Vol. 4, pp 389–515.

(14) Kasha, M. Energy Transfer Mechanisms and the Molecular Exciton Model for Molecular Aggregates. *Radiat. Res.* 1963, 20, 55–70.

(15) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. The Exciton Model in Molecular Spectroscopy. *Pure Appl. Chem.* 1965, 11, 371–392.

(16) Spano, F. C. The Spectral Signatures of Frenkel Polaron in H- and J-Aggregates. *Acc. Chem. Res.* 2010, 43, 429–439.

(17) Spano, F. C.; Hestand, N. J. Molecular Aggregate Photophysics Beyond the Kasha Model: Novel Design Principles for Organic Materials. *Acc. Chem. Res.* 2017, 50, 341–350.

(18) Calzaferri, G.; Bossart, O.; Brühlweiler, D.; Huber, S.; Leggerner, C.; Van Veen, M. K.; Ruiz, A. Z. Light-Harvesting Host–Guest Antenna Materials for Quantum Solar Energy Conversion Devices. *C. R. Chim.* 2006, 9, 214–225.

(19) Pauchard, M.; Devaux, A.; Calzaferri, G. Dye-Loaded Zeolite I. Sandwiches as Artificial Antenna Systems for Light Transport. *Chem.—Eur. J.* 2000, 6, 3456–3470.

(20) D’Alfio, L.; Martellini, A. Toluidine Blue: Aggregation Properties and Structural Aspects. *Modell. Simul. Mater. Sci. Eng.* 2006, 14, 581–595.

(21) Arunkumar, E.; Forbes, C. C.; Smith, B. D. Improving the Optical Properties of Organic Dyes by Molecular Encapsulation. *Eur. J. Org. Chem.* 2005, 4051–4059.

(22) Bujdáč, J. Effect of the Layer Charge of Clay Minerals on Optical Properties of Organic Dyes. A Review. *Appl. Clay Sci.* 2006, 34, 58–73.

(23) Bujdáč, J.; Iyi, N. Optical Properties of Molecular Aggregates of Oxazine Dyes in Dispersions of Clay Minerals. *Colloid Polym. Sci.* 2009, 287, 157–165.

(24) Calzaferri, G.; Maas, H.; Pauchard, M.; Devaux, A. Supramolecularly Organized Luminescent Dye Molecules in the Channels of Zeolite I. John Wiley & Sons, Inc., 2002; Vol. 27, pp 1–50.

(25) Florea, M.; Nau, W. M. Strong Binding of Hydrocarbons to Cucurbituril Probed by Fluorescent Dye Displacement: A Supramolecular Gas-Sensing Ensemble. *Angew. Chem., Int. Ed.* 2011, 50, 9338–9342.

(26) Koner, A. L.; Nau, W. M. Cucurbituril Encapsulation of Fluorescent Dyes. *Supramol. Chem.* 2006, 19, 55–66.

(27) Douza, R. N.; Pischel, U.; Nau, W. M. Fluorescent Dyes and Their Supramolecular Host-Guest Complexes with Macrocycles in Aqueous Solution. *Chem. Rev.* 2011, 111, 7941–7980.
in Anisotropic and Isotropic Solvents. *Spectrochim. Acta, Part A* 2007, 66, 717−725.

(49) Gibb, C. L. D.; Gibb, B. C. Well-Defined, Organic Nano-environments in Water: The Hydrophobic Effect Drives Capsular Assembly. *J. Am. Chem. Soc.* 2004, 126, 11408−11409.