Improving the Properties of Organic Dyes by Molecular Encapsulation

Easwaran Arunkumar,[a] Christopher C. Forbes,[a] and Bradley D. Smith*[a]

Keywords: Cyclodextrins / Rotaxanes / Dendrimers / Gels / Host–guest systems

There is a demand for new methods of protecting organic dyes from aggregation effects and photochemical degradation. The purpose of this microreview is to summarize the recent attempts to improve the properties of dyes by molecular encapsulation. Organic dyes have been encapsulated inside inorganic matrices such as molecular sieves, and molecular containers such as cyclodextrins, cucurbiturils, dendrimers, and self-assembled gels. Another strategy is permanent protection of the dye as the thread component in a rotaxane. Molecular encapsulation is an attractive supramolecular strategy because it is inherently flexible and does not necessarily require time-consuming synthetic processes. Indeed, molecular encapsulation is an effective way to recycle familiar dyes that are already well-characterized.
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

1.0 Introduction

Organic chromophores such as cyanines, squaraines, azo dyes and perylenediimide dyes are widely used as pigments in many commercial products. They are active ingredients in semiconducting materials,[1] textile products,[2] laser materials,[3] optical disks,[4] paints,[5] and probes for biological systems.[6] Modern research on organic dyes includes investigations of building blocks for conjugated polymers, hydrogen bonded assemblies, chromogenic sensors, molecular shuttles, solar energy cells, photonics and various approaches to photodynamic therapy.[7–11] A common limitation with organic dyes, especially those with long-wavelength absorption bands, is their susceptibility to chemical and photochemical degradation. The reason for the enhanced reactivity is the inherently small HOMO–LUMO energy gap, which means that the dyes are potentially reactive with both nucleophiles and electrophiles. Another potential drawback with organic dyes is their tendency to aggregate, which induces multichromophoric interactions that alter the color quality and quench the photoluminescence. In principle, these problems can be attenuated by supramolecular encapsulation strategies that isolate the individual dye molecules and prevent self-aggregation or similar interactions with the chemical environment. The purpose of this microreview is to summarize the recent literature on methods to improve the properties of organic dyes by molecular encapsulation. The focus is on relatively "robust" molecular containers and does not include "soft" assemblies like micelles, emulsions or vesicles.

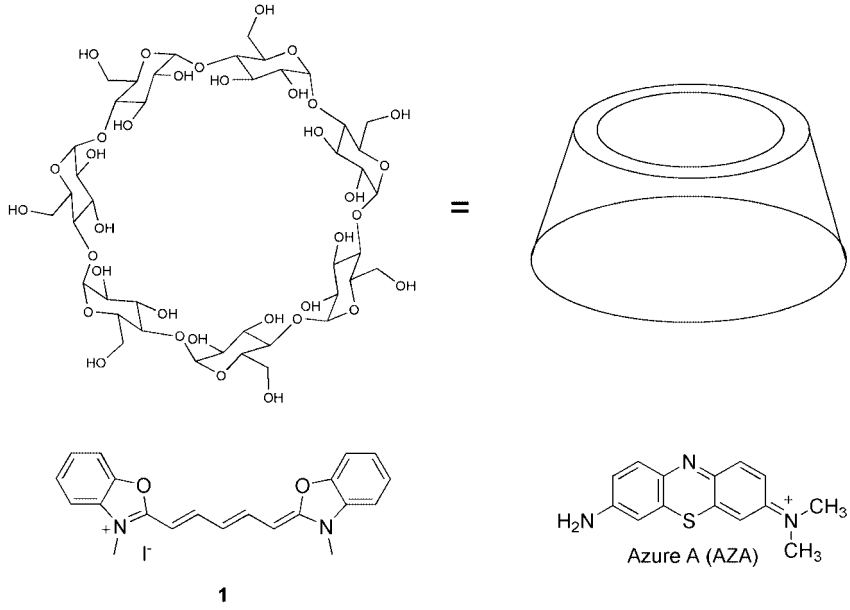
[a] Department of Chemistry and Biochemistry, University of Notre Dame,
Notre Dame, IN 46556, USA
Fax: +1-574-631-6652
E-mail: smith.115@nd.edu

2.0 Cyclodextrin-Encapsulated Dyes

Cyclodextrin (CD) is a fascinating molecule for supramolecular chemists because it has a remarkable ability to incorporate aromatic molecules within its macrocyclic cavity. The different cavity sizes of the three best known CDs are 5.7, 7.8 and 9.5 Å for α-CD, β-CD and γ-CD respectively. One of the earliest examples of dye encapsulation inside a CD was a report by Cramer and co-workers who, in 1967, described the inclusion of an azo dye within the cavity of α-CD.[12] Since then, many groups have used CD as a host to protect dyes from reactive chemicals like water or singlet oxygen.[13] For example, Rao and co-workers studied the supramolecular complexation of cyanine dyes such as **1** (Scheme 1). By characterizing the photophysical behavior of the dyes, they found that the dye-CD inclusion complex typically prevents dye dimerization.[14] Specifically, they observed CD driven conversion of thiacarbocyanine dimer to monomer as indicated by an increase in the red-shifted absorption band at the expense of a higher energy blue-shifted dimer. In some cases, the inclusion process inhibited photodegradation of the chromophore but the effect was dye dependent. Photodecomposition of thiacarbocyanines occurred even after complexing with CD, whereas analogous

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

 DOI: 10.1002/ejoc.200500372 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 1.

indocarbocyanine dyes became more resistant to photobleaching upon CD complexation.

The inclusion of phenothiazine dyes, such as azure A (Scheme 1), inside CDs has been studied by Lee and coworkers, who discovered a size correlation.[15] α-CD did not induce any change in the photophysical properties of the dyes; whereas, β-CD efficiently increased the monomer peak in the absorption spectrum and γ-CD induced the opposite effect. Thus, the CD nanocapsule could be used to control dye dimerization and alter the dye's photophysical properties for various applications. In order to improve chromophore orientation in thin films, Laschewsky and coworkers successfully combined the concepts of electrostatic self-assembly with supramolecular encapsulation by forming inclusion complexes of a polymeric, non-linear optically active azo dye and a cationic pyridinium-modified β-CD.[16]

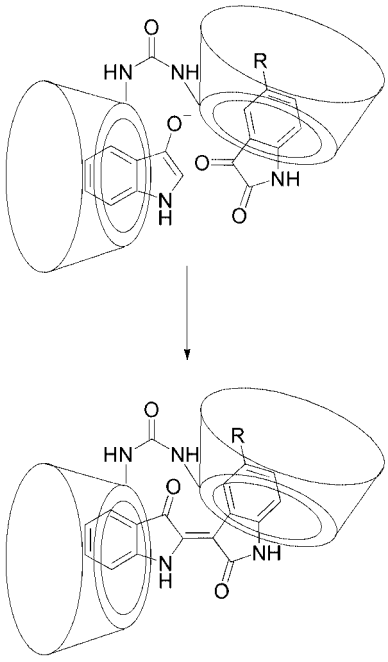
Easwaran Arunkumar earned a Masters degree in organic chemistry from Mahatma Gandhi University, Kottayam, India in 1998 and his Ph.D. degree from University of Kerala [Supervisor: Dr. A. Ajayaghosh, Photosciences and Photonics Division, RRL (CSIR), Trivandrum] India in 2004. He is currently working as a postdoctoral associate in the research group of Professor Bradley Smith at the University of Notre Dame. His present research is focused on development of functional near IR dyes which are stabilized using supramolecular interactions.

Christopher C. Forbes earned his B.S. from the University of Arizona in Tucson, Arizona in 1997 and his Ph.D. from the University of Notre Dame in 2005. In his doctorate work, he studied the supramolecular chemistry of the amide bond in rotaxane forming reactions. He is currently a postdoctoral fellow in the research group of Shahriar Mobashery at the University of Notre Dame and is involved with the study and synthesis of MMP inhibitors as antimetastatic chemotherapy agents.

Bradley D. Smith obtained a B.Sc.(Hons) degree from the University of Melbourne, and a Ph.D. in 1988 from Penn State University. After postdoctoral training at Oxford University and then Columbia University, he moved to the University of Notre Dame in 1991. He is currently a Professor of Chemistry and Biochemistry with research interests in the fields of bioorganic and supramolecular chemistry. One of the aims of his group is to design and synthesize fluorescent molecules that can sense the structure and function of biomembranes.

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

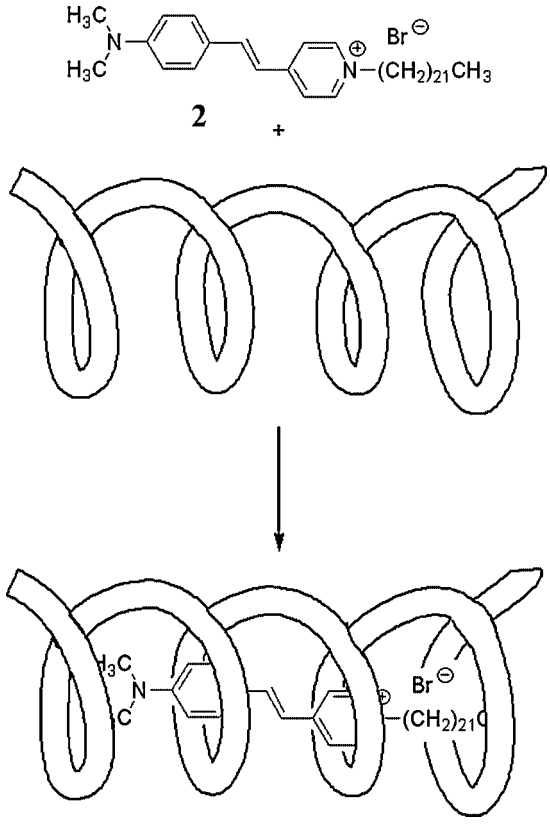
In this approach, the CD inclusion process partially orients the chromophores and prevents their reorientation. Velic and co-workers reported the formation of inclusion complexes between a coumarin dye and thiolated β-CD with the goal of generating a nanostructured layer on a surface.[17] Thiolated β-CD was bound to a gold surface and observed to form a single layer of host–guest complex with modest affinity compared to simple alkylthiols. CDs have also been used to promote dye synthesis. Easton and co-workers discovered that a urea-linked CD dimer behaves as a molecular reactor to favor the formation of specific isomers of indigoid dyes (Scheme 2).[18] For example, inclusion of the reactants inside the CD dimer alters the ratio of indigo to indirubin-5′-sulfonate by a factor of 3500. A final point with CD is that it is a chiral host, and thus has the ability to encapsulate dyes as twisted dimers such that a CD-dye complex can exhibit couplet bands in the circular dichroism spectrum.[19]



Scheme 2.

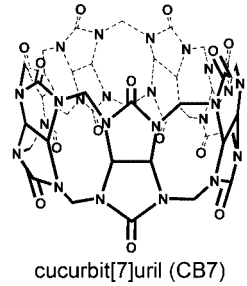
The helical-shaped polysaccharide, amylose, is also known to form inclusion complexes with various types of organic compounds. As with CD, hydrophobic interactions drive guest inclusion, and a rigid-rod supramolecular complex is formed with the chromophore aligned axially inside the amylose helix. This noncentrosymmetric molecular arrangement is an interesting strategy for second-harmonic generation. Kim and co-workers found that thin films composed of the inclusion complex of hemicyanine dye **2** inside amylose (Scheme 3) exhibit improved self-poling and long-term thermal stability.[20]

The past decade has seen renewed interest in cucurbit[*n*]urils as macrocyclic hosts that form inclusion complexes with organic guests in water. In many ways cucurbit[*n*]urils are like CD's; they can be designed to have different cavity sizes with the cyclic heptamer, cucurbit[7]uril (CB7), having



Scheme 3.

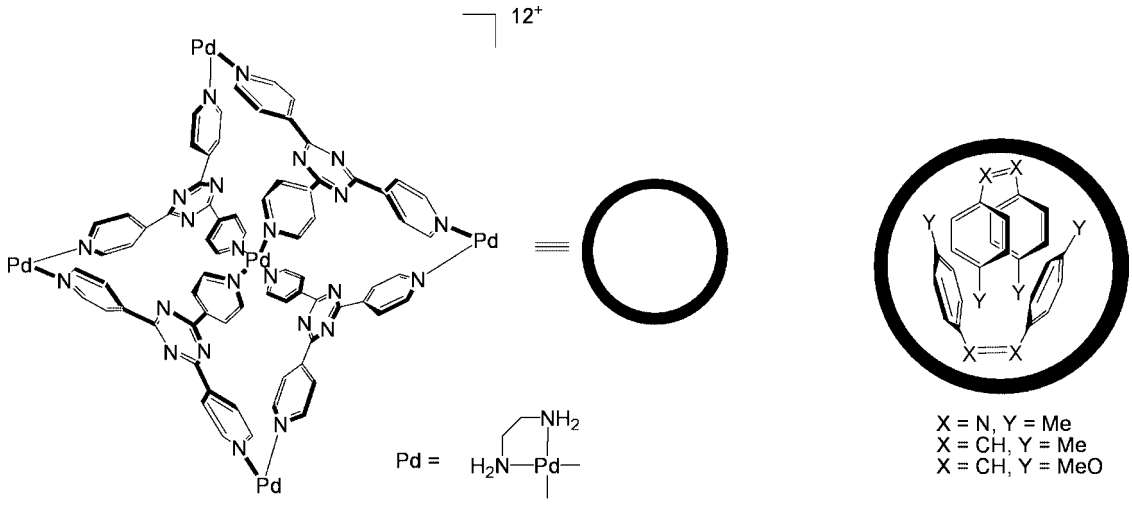
a cavity large enough to accommodate organic dyes.[21] Very recently, Mohanty and Nau reported that CB7 encapsulates the practically important fluorescent dye, rhodamine 6G, with an association constant of $>50{,}000\ M^{-1}$ which is much stronger than the value of $200\ M^{-1}$ observed with CD. The rhodamine-CB7 complex exhibits several improved dye properties such as longer fluorescence lifetime, suppression of dye aggregation, prevention of surface adsorption and decreased photobleaching.[22] It is likely that in the future cucurbit[*n*]urils will become quite useful as dye-containing nanocapsules for various types of biological imaging and screening applications.



cucurbit[7]uril (CB7)

One of the newest methods of encapsulating dyes is to employ self-assembling molecular capsules.[23] For example, Kuzukawa and Fujita have developed a nanoscale coordination cage, (Scheme 4) that selectively encapsulates "C"-shaped molecules. The capsule promotes the "ship-in-bottle" formation of *cis*-azobenzene and *cis*-stilbene derivatives and inhibits *cis*-to-*trans* isomerization.[24] Depending on

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

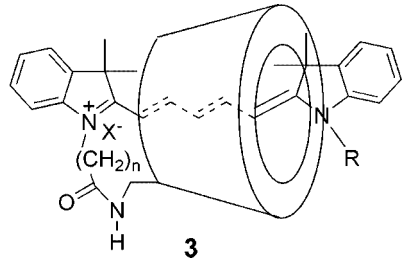


Scheme 4. "Ship-in-bottle" formation of a hydrophobic dimer of *cis*-azobenzene and *cis*-stilbene derivatives in the cavity of a nanoscale coordination cage.

specific substitution pattern, one or two dye molecules are captured and constrained inside the nanocage.

3.0 Rotaxane Dyes

A potential problem with simple inclusion of a dye inside a container molecule like CD is the inherent reversibility of the process. Even in the best cases with association constants of 10^4–10^5 M^{-1} the complex can dissociate at low concentration and release the dye, or the dye can be displaced by a second, high affinity impurity molecule.[25] Thus, there is a need for assembly methods that permanently trap the dye inside the container. An interesting early approach was reported by Guether and Reddington, who conjugated a series of cyanine dyes to β-CD and formed self-threaded structures, **3**, which exhibited enhanced photostabilities in aqueous solution and live cells.[26]



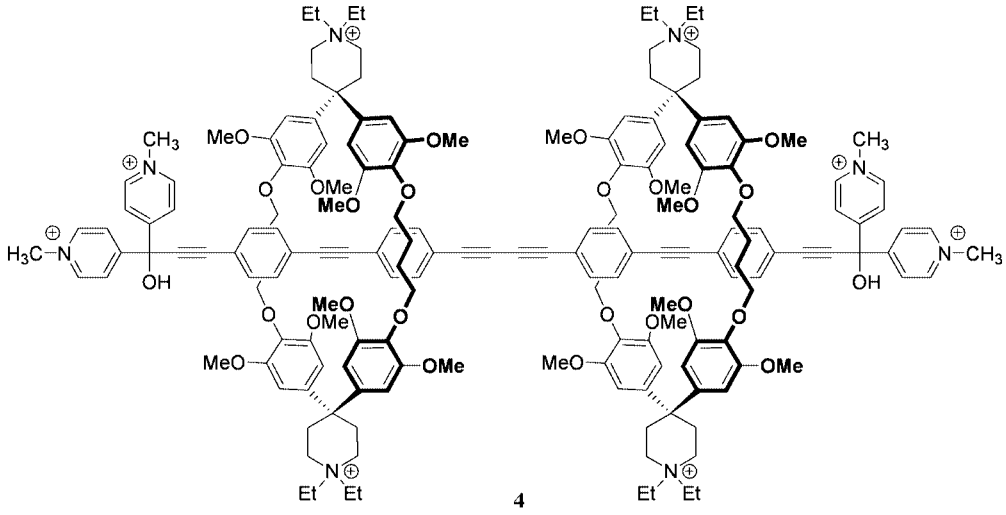
3

An alternative way to form a permanently encapsulated chromophore is to construct an interlocked structure known as a rotaxane. In its simplest form, the rotaxane involves a macrocycle surrounding a dumb-bell shaped dye molecule. Not only does the macrocycle provide steric protection, but it allows the environment around the chromophore to be precisely controlled which provides fine-tuning of the photochemical properties. The pioneering example, reported by Anderson and co-workers, is rotaxane **4** with two encapsulating cyclophane macrocycles around a conjugated phenyleneacetylene.[27] The hydrophobic effect was used to induce pseudo-rotaxane formation followed by capping to produce the rotaxane. The cyclophane macrocycles increase the fluorescence efficiency of the π-conjugated thread by hindering quenching and increasing the kinetic stability of the excited state. It was observed that rotaxane fluorescence emission was around six times higher than the unprotected conjugated thread. Rotaxanes are able to effectively separate cofacial π-systems by a distance that is determined by the thickness of the surrounding macrocycle.

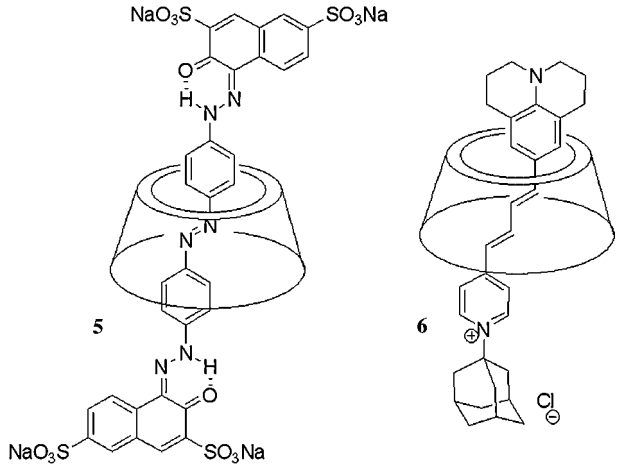
In a concurrent study, the Anderson group prepared water-soluble rotaxanes (**5**), where the chromophore of an azo-dye thread is encapsulated inside the cavity of a CD (Scheme 5).[28] They synthesized a range of water-soluble azo-dye rotaxanes, again using the hydrophobic effect to direct rotaxane formation. All of the rotaxanes were more soluble than the dye threads, and they exhibited a decreased tendency to aggregate. Subsequent publications describe the crystal structure of an azo-dye rotaxane and isolation of azo-dye rotaxane as a single isomer.[29]

The same group employed a capping synthesis to prepare rotaxanes with unsymmetrical cyanine dyes threaded through CD, a synthetic method that results in two stereoisomeric rotaxanes that can be separated by chromatography.[30] The steroisomer **6** exhibits increased fluorescence in nonaqueous solvents which is attributed to the reduced flexibility of the encapsulated chromophore. Rotaxane **6** is also more resistant to photobleaching which the authors attribute to a decreased rate of singlet oxygen formation. Electrochemical studies demonstrated that the rotaxane structure increases the kinetic stability of the cyanine redox system.[31] The highly conjugated cyanine dyes have inherently small HOMO–LUMO band gaps making them easy to oxidize or reduce. Typically, the inclusion of a redox-active guest inside CD hinders the redox chemistry, however, in this case the redox reversibility is enhanced. In another report, a chlorotriazine-functionalized azo dye was threaded through a CD, which dramatically increased the dye's resistance to bleaching. The dye-cyclodextrin complex

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



4



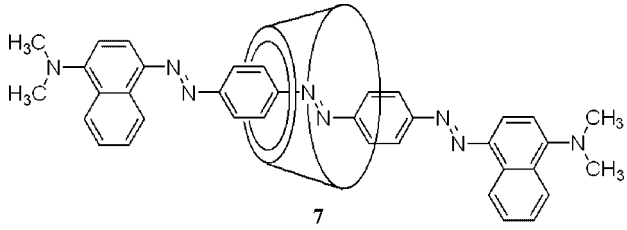
5 6

Scheme 5.

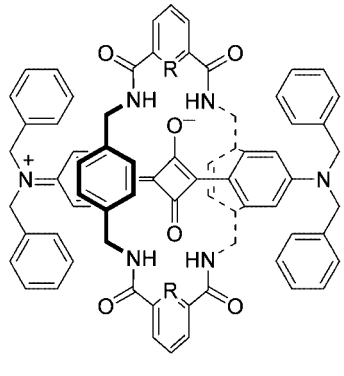
was attached to cellulose through the reactive chlorotriazine moiety.[32] In the presence of aqueous sodium dithionite, the unprotected chlorotriazine dye was completely destroyed in 15 minutes, but the rotaxane dye retained 90% of its absorption after 9 hours. In a more recent report, the Anderson group describe the threading of conjugated poly(p-araphenylene), poly(4,4′-diphenylenevinylene) or polyfluorene through CDs.[33] These new complexes show diminished tendency to aggregate, and increased luminescence efficiency with blue shifted emission.

A separate example of a dye-CD rotaxane was reported by Haque and co-workers who employed the dye-threaded rotaxane **7** to functionalize the surface of a TiO_2 semiconductor.[34] The encapsulating CD limits the interaction between the nanocrystalline TiO_2 and the sensitizer dye, and extends the lifetime of the photogenerated charge separation.

Our group has contributed to this topic by designing a different type of dye-rotaxane architecture, namely, the amide-based rotaxane **8**.[35] The thread component is a squaraine dye which emits potentially useful near-IR fluorescence, however, two drawbacks are the dye's susceptibility to nucleophilic attack[36] and aggregate formation.[37] These problems were rectified by converting the dye into a rotaxane. The rotaxane was produced by hydrogen bond-templated macrocyclization around an appropriate squaraine thread with bulky end groups. The rotaxanes exhibited the same excellent photophysical properties as the precursor squaraines, but the encapsulating macrocycle greatly increased the dye's chemical stability. For example, in aqueous solution, the unprotected squaraine loses its blue color within 48 hours while the rotaxanes retain their color for several weeks. In addition, the surrounding macrocycle diminishes absorption band broadening by inhibiting interchromophoric interactions both in solution and solid state.



7



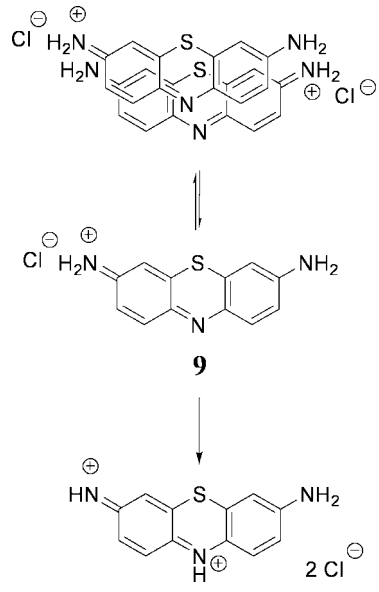
8

4.0 Dendrimer Encapsulated Dyes

Dendrimers are branched polymeric molecules with a tendency to adopt spherical or globular shapes in solu-

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

tion.[38] Most dendrimers have porous interiors, so they can act like unimolecular micelles and trap guest molecules.[39] The supramolecular properties of these macromolecular hosts have been studied extensively by various research groups. For example, Meijer and co-workers used poly(propyleneimine) dendrimers to extract anionic xanthene dyes from water into organic solvents.[40] Similarly, Cooper and co-workers used fluorinated dendrimers to extract methyl orange from water into super critical CO_2.[41] Finally, Smith reported that dendritic peptides, each with a carboxylic acid at the focal point of its structure, can extract polybasic aromatic dyes.[42] For example, UV/Visible spectroscopy showed that the dendrimers can solubilize solid proflavine hydrochloride dye in apolar CH_2Cl_2 solution. In the future, dendrimers are likely to be investigated further as capsules that reversibly trap and release dyes, and they also may have utility as energy capture devices.



Scheme 6.

5.0 Encapsulation of Dyes in Organized Media

5.1 Inorganic Matrices

Inorganic molecular sieves with three-dimensional lattices and layered materials with two-dimensional networks have utility as porous encapsulation matrices. They possess well-defined internal networks of uniform cages, cavities, and channels. They also have high mechanical, chemical, and thermal stabilities, and they are compatible with many types of photochemical experiments.[43] Attempts have been made by various research groups to encapsulate dyes within molecular sieves with the goal of enhancing the dye's stability towards external stimuli.[44] An early demonstration of the ability of zeolites to control dye aggregation was reported by Ramamurthy and co-workers, who found that the aggregation equilibria depend on a number of factors.[45] For example, the monomer–dimer equilibrium for **9** (Scheme 6) was sensitive to the amount of co-adsorbed water within the zeolites.

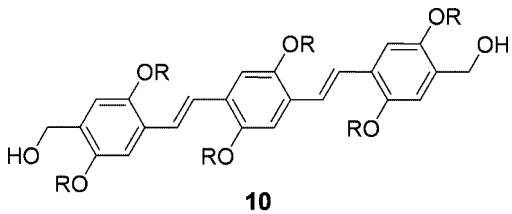
Wöhrle and Schulz-Ekloff reported that dyes incorporated inside molecular sieves exhibit higher stabilities towards photobleaching by O_2 in comparison to solution samples or dyes adsorbed on the exterior of the molecular sieves.[46] The lower reactivity was attributed to the molecular sieves deactivating the energy transfer from dye triplet state to O_2. In 1995, Monte and Levy encapsulated near-IR dyes such as oxazine and cyanine dyes in sol-gel matrices and produced dye-doped glasses. They prepared and characterized a wide variety of glasses using different reaction conditions and observed that the dye in the final material had high chemical stability. Various strategies were shown to increase the chemical stability of the dye inside the sol-gel including high-density matrices and mixed-composition matrices.[47] At around the same time, Jin and Chon reported that dye encapsulation in molecular sieves can induce a structural transformation.[48] Upon encapsulation of methylene blue and perylene dyes, the researchers observed that the molecular sieve, VPI-5, with large, circular pores, underwent a novel structural transformation into the molecular sieve, $AlPO_4$-8, with small, elliptical pores. More recently, Jin and co-workers prepared a new group of highly luminescent and photostable nanoparticles generated by doping a luminescent bipyridyl ruthenium complex inside silica.[49] After the doping process, the dye showed an increase in luminescence, as well as decreased susceptibility to oxidation. The potential utility of the doped nanoparticles was demonstrated in various bio-detection strategies. Similarly, Prasad and co-workers encapsulated a two-photon dye within a silica nanobubble.[50] Photobleaching studies indicated that the silica shell provides a barrier to oxygen penetration, thereby increasing the dye's photostability. Gabelica and co-workers reported that azo dyes encapsulated in Ca-aluminosilicate mesoporous substrates exhibit enhanced stability against color fading.[51] The enhanced resistance to fading was attributed to an optimized Ca–dye interaction which was produced by a controlled heating of $Ca(OH)_2$-loaded mesoporous precursors. The groups of Behrens and Langhals have investigated composites of perylene chromophores and layered double hydroxides (sometimes referred to as anionic clays). The chromophore molecules are stacked in J-type aggregates in the galleries between the hydroxide layers which increases chemical and photostability.[52] Penner and co-workers stabilized the J-aggregates of cyanine dyes at the molecular level by appending them to a polylysine backbone and constructing layer-by-layer assemblies with inorganic clay sheets. These three-dimensional structures have potential applications as layered systems for optical energy transfer and antenna systems.[53]

5.2 Gel Matrices and Energy Transfer

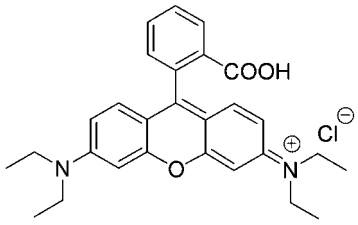
Oligophenylenevinylene's (OPVs), such as **10** (Scheme 7), are promising new materials for light-emitting diodes[54] and photovoltaic cells.[55] The research group of Ajay-

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

aghosh was the first to observe the self-assembly of OPVs. to form three dimensional gel networks in nonpolar solvents.[56] Later, these researchers described the encapsulation of rhodamine B (**11**), within the gel's three-dimensional network for the purpose of light harvesting studies.[57] They demonstrated thermoreversible fluorescence-resonance energy transfer (FRET) from OPV-based gels to the encapsulated dye.



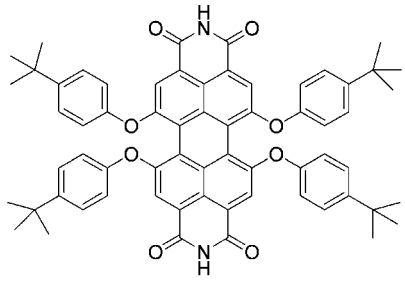
10



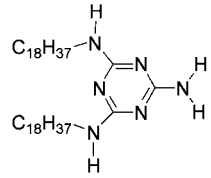
11

Scheme 7.

Collective and hierarchical self-assembly of a binary mixture of functional dyes, such as OPV and perylene bisimide, into chiral fibers has been reported by the groups of Schenning and Würthner who also observed photo-induced electron transfer.[58] Circular dichroism, UV/Vis, and fluorescence spectroscopy were used to prove that the direction of electron transfer was from OPV to the perylene chromphore. Morgado and co-workers have reported a Förster-type energy transfer to a porphyrin chromophore after it was blended with a poly[1,4-phenylenevinylene] derivative.[59] A mechanistic study of excitation energy transfer has been reported by Brunner and co-workers using a similar dye-doped phenylenevinylene system.[60] They found that efficient transfer of excitation energy from a disordered polymer to a dye can only occur if the polymer-to-dye exciton transfer rate is higher than the intrapolymer exciton migration rate at a given energy. Khokhlov and co-workers investigated complexes of cationic hydrogels and oppositely charged organic dyes such as alizarin, naphthol blue black, and rhodamine.[61] The stabilities of the dye-gel complexes were studied in salt solutions and found to increase with the charge density of the polymer network. Hydrogen-bonded dye assemblies were reported by Thalacker and Würthner with perylene bisimide dyes, such as **12**, stacked in between micellar aggregates of melamine **13**.[62] Even at low dye concentration, islands of strongly aggregated perylene bisimides were formed that exhibited exciton-coupled circular dichroism effects. In subsequent work the same group has demonstrated that it is possible to alter the photophysical properties of imide containing chromophores by hydrogen-bonded self-assembly with various types of melamines.[63]



12



13

6.0 Conclusions

Dye chemistry has been studied for well over a century, and although it can be considered a mature field of synthetic research, there is still a demand for new types of dyes with improved chemical and photophysical properties. A major driving force for this need is the continued development of frontier research areas like nanotechnology, biotechnology and materials science. An important topic that will likely attract much synthetic interest over the next few years is the production of new families of near-IR dyes, and dyes that can be excited by two-photon spectroscopy. There is also a need for methods of protecting the dyes from undesired aggregation and adsorption, as well as inhibiting photochemical degradation. Molecular encapsulation is an attractive strategy because it is inherently flexible and does not necessarily require time-consuming synthetic processes. Indeed, molecular encapsulation is an effective way to recycle familiar dyes that are already well-characterized. Future efforts that build on the supramolecular strategies that are described in this article will likely produce dye-based materials with technically important properties.

Acknowledgments

We are grateful for funding support form the NIH (USA) and the Philip Morris External Technology Research Program.

[1] a) W. West, P. B. Gilman, in: *The Theory of the Photographic Process* (Ed.: T. J. James), Macmillian: New York, **1977**, p. 277; b) C. Chen, B. Zhou, D. Lu, G. Xu, *J. Photogr. Sci.* **1995**, *43*, 134.

[2] O. Ozdemir, B. Armagan, M. Turan, M. S. Celik, *Dyes Pigm.* **2004**, *62*, 49.

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[3] a) J. M. Lanzafame, A. A. Muenter, D. V. Brumbaugh, *Chem. Phys.* **1996**, *210*, 79; b) J. M. Lanzafame, L. Min, R. J. D. Miller, A. A. Muenter, B. A. Parkinson, *Mol. Cryst. Liq. Cryst.* **1991**, *194*, 287; c) D. Möbius, *Adv. Mater.* **1995**, *7*, 437; d) N. Tyutyulkov, J. Fabian, A. Mehlhorn, F. Dietz, A. Tadjer, *Polymethine Dyes*, Kliment Ohridski University Press: Sofia, **1991**; e) J. Arden, G. Deltau, V. Huth, U. Kringel, D. Peros, K. H. Drexhage, *J. Lumin.* **1991**, *48–49*, 352.

[4] a) R. Kietzmann, A. Ehret, M. Spitler, F. Willig, *J. Am. Chem. Soc.* **1993**, *115*, 1930; b) B. Trösken, F. Willig, K. Schwarzburg, A. Ehret, M. Spitler, *J. Phys. Chem.* **1995**, *99*, 562.

[5] K. Saito, H. Yokoyama, *Thin Solid Films* **1994**, *234*, 526.

[6] a) S. A. Soper, Q. L. Mattingly, *J. Am. Chem. Soc.* **1994**, *116*, 3744; b) M. Z. Hossain, L. A. Ernst, J. L. Nagy, *Neurosci. Lett.* **1996**, *184*, 183; c) L. Strekowski, M. Lipowska, G. Patonay, *J. Org. Chem.* **1992**, *57*, 4578; d) S. Das, K. G. Thomas, K. J. Thomas, P. V. Kamat, M. V. George, *J. Phys. Chem.* **1994**, *98*, 9291.

[7] a) C. R. Chenthamarakshan, A. Ajayaghosh, *Tetrahedron Lett.* **1998**, *39*, 1795; b) C. R. Chenthamarakshan, J. Eldo, A. Ajayaghosh, *Macromolecules* **1999**, *32*, 5846; c) A. Ajayaghosh, *Chem. Soc. Rev.* **2003**, *32*, 181 and references cited therein.

[8] a) T. van der Boom, R. T. Hayes, Y. Zhao, P. J. Bushard, E. A. Weiss, M. R. Wasielewski, *J. Am. Chem. Soc.* **2002**, *124*, 9582; b) A. Sautter, C. Thalacker, F. Würthner, *Angew. Chem. Int. Ed.* **2001**, *40*, 4425; c) F. Würthner, *Chem. Commun.* **2004**, 1564.

[9] a) A. Ajayaghosh, E. Arunkumar, J. Daub, *Angew. Chem. Int. Ed.* **2002**, *41*, 1766; b) E. Arunkumar, P. Chithra, A. Ajayaghosh, *J. Am. Chem. Soc.* **2004**, *126*, 6590; c) E. Arunkumar, A. Ajayaghosh, J. Daub, *J. Am. Chem. Soc.* **2005**, *127*, 3156.

[10] Q. Wang, D. Qu, J. Ren, K. Chen, H. Tian, *Angew. Chem. Int. Ed.* **2004**, *43*, 2661.

[11] a) D. Ramaiah, I. Eckert, K. T. Arun, L. Weidenfeller, B. Epe, *Photochem. Photobiol.* **2002**, *76*, 672; b) D. Ramaiah, I. Eckert, K. T. Arun, L. Weidenfeller, B. Epe, *Photochem. Photobiol.* **2004**, *79*, 99.

[12] F. Cramer, W. Saenger, H.-Ch. Spatz, *J. Am. Chem. Soc.* **1967**, *89*, 14.

[13] A. Mishra, R. K. Behera, P. K. Behera, B. K. Mishra, G. B. Behera, *Chem. Rev.* **2000**, *100*, 1973.

[14] T. V. S. Rao, J. B. Huff, C. Bieniarz, *Tetrahedron* **1998**, *54*, 10627.

[15] C. Lee, Y. W. Sung, J. W. Park, *J. Phys. Chem. B* **1999**, *103*, 893.

[16] P. Fisher, M. Koetse, A. Laschewsky, E. Wischerhoff, L. Jullien, A. Persoons, T. Verbiest, *Macromolecules* **2000**, *33*, 9471.

[17] D. Velic, M. Knapp, G. Köhler, *J. Mol. Struct.* **2001**, *598*, 49.

[18] J. B. Harper, C. J. Easton, S. F. Lincoln, *Tetrahedron Lett.* **2003**, *44*, 5815.

[19] V. Buss, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 869.

[20] a) O. K. Kim, L. S. Choi, *Langmuir* **1994**, *10*, 2842; b) O. K. Kim, L. S. Choi, J. Y. Zhang, X. H. He, Y. H. Shih, *J. Am. Chem. Soc.* **1996**, *118*, 12220.

[21] C. Marquez, F. Huang, W. M. Nau, *IEEE Trans. Nanobiosci.* **2004**, *3*, 39.

[22] J. Mohanty, W. M. Nau, *Angew. Chem. Int. Ed.* **2005**, *44*, 3750.

[23] a) L. C. Palmer, J. Rebek Jr., *Org. Biomol. Chem.* **2004**, *2*, 3051; b) D. M. Rudkevich, J. Rebek Jr., *Eur. J. Org. Chem.* **1999**, 1991.

[24] T. Kusukawa, M. Fujita, *J. Am. Chem. Soc.* **1999**, *121*, 1397.

[25] H. Yonemura, H. Saito, S. Matsushima, H. Nakamura, T. Matsuo, *Tetrahedron Lett.* **1989**, *30*, 3143.

[26] R. Guether, M. V. Reddington, *Tetrahedron Lett.* **1997**, *38*, 6167.

[27] S. Anderson, H. L. Anderson, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1956.

[28] S. Anderson, T. D. W. Claridge, H. L. Anderson, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1310.

[29] a) S. Anderson, W. Clegg, H. L. Anderson, *Chem. Commun.* **1998**, 2379; b) M. R. Craig, T. D. W. Claridge, M. G. Hutchings, H. L. Anderson, *Chem. Commun.* **1999**, 1537.

[30] J. E. H. Buston, J. R. Young, H. L. Anderson, *Chem. Commun.* **2000**, 905.

[31] J. E. H. Buston, F. Marken, H. L. Anderson, *Chem. Commun.* **2001**, 1046.

[32] M. R. Craig, M. G. Hutchings, T. D. W. Claridge, H. L. Anderson, *Angew. Chem. Int. Ed.* **2001**, *40*, 1071.

[33] F. Cacialli, J. S. Wilson, J. J. Michels, C. Daniel, C. Silva, R. H. Friend, N. Severin, P. Samori, J. P. Rabe, M. J. O'Connel, P. N. Taylor, H. L. Anderson, *Nature Mater.* **2002**, *1*, 160.

[34] S. A. Haque, J. S. Park, M. Srinivasarao, J. R. Durrant, *Adv. Mater.* **2004**, *16*, 1177.

[35] E. Arunkumar, C. C. Forbes, B. C. Noll, B. D. Smith, *J. Am. Chem. Soc.* **2005**, *127*, 3288.

[36] a) J. V. Ros-Lis, B. García, D. Jiménez, R. Martínez-Máñez, F. Sancenón, J. Soto, F. Gonzalvo, M. C. Valldecabres, *J. Am. Chem. Soc.* **2004**, *126*, 4064; b) J. V. Ros-Lis, R. Martínez-Máñez, J. Soto, *Chem. Commun.* **2002**, 2248.

[37] a) A. J. McKerrow, E. Buncel, P. M. Kazmaier, *Can. J. Chem.* **1995**, *73*, 1605; b) H. Chen, M. S. Farahat, K.-Y. Law, D. G. Whitten, *J. Am. Chem. Soc.* **1996**, *118*, 2584; c) J. Qu, J. Zhang, A. C. Grimsdale, K. Müllen, F. Jaiser, X. Yang, D. Neher, *Macromolecules* **2004**, *37*, 8297.

[38] a) C. J. Hawker, R. Lee, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1991**, *113*, 4583; b) J. M. J. Fréchet, *Science* **1994**, *263*, 1710; c) J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijkens, D. M. Grove, G. van Koten, *Nature* **1994**, *372*, 659.

[39] a) G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendritic Molecules: Concepts, Syntheses, Perspectives*, VCH, Weinheim, **1996**; b) S. Stevelmans, J. C. M. van Hest, J. F. G. A. Jansen, D. A. F. J. van Boxtel, E. M. M. de Brabander-van den Berg, E. W. Meijer, *J. Am. Chem. Soc.* **1996**, *118*, 7398; c) C. J. Hawker, K. L. Wooley, J. M. J. Fréchet, *J. Chem. Soc. Perkin Trans. I* **1993**, 1287.

[40] a) S. Stevelmans, J. C. M. van Hest, J. F. G. A. Jaansen, D. A. F. J. van Boxtel, E. M. M. de Brabander-van den Berg, E. W. Meijer, *J. Am. Chem. Soc.* **1996**, *118*, 7398; b) M. W. P. L. Baars, P. E. Froehling, E. W. Meijer, *Chem. Commun.* **1997**, 1959.

[41] A. I. Cooper, J. D. Londono, G. Wignall, J. B. McClain, E. T. Samulski, J. S. Lin, A. Dobrynin, M. Rubinstein, A. L. C. Burke, J. M. J. Fréchet, J. M. DeSimone, *Nature* **1997**, *389*, 368.

[42] D. K. Smith, *Chem. Commun.* **1999**, 1685.

[43] a) K. Kalyanasundaram, *Photochemistry in Microheterogenious Systems*, Academic Press, New York, **1987**; b) V. Ramamurthy, R. G. Weiss, G. S. Hammond, *Adv. Photochem.* **1993**, *18*, 67; c) M. L. Cano, F. L. Cozens, M. A. Esteves, F. Márquez, H. García, *J. Org. Chem.* **1997**, *62*, 7121.

[44] G. Schulz-Ekloff, D. Wöhrle, B. van Duffel, R. A. Schoonheydt, *Micropor. Mesopor. Mater.* **2002**, *51*, 91.

[45] V. Ramamurthy, D. R. Sanderson, D. F. Eaton, *J. Am. Chem. Soc.* **1993**, *115*, 10438.

[46] D. Wöhrle, G. Schulz-Ekloff, *Adv. Mater.* **1994**, *6*, 875.

[47] F. Del Monte, D. Levy, *Chem. Mater.* **1995**, *7*, 292.

[48] Y. M. Jin, H. Chon, *Chem. Commun.* **1996**, 135.

[49] W. Lian, S. A. Litherland, H. Badrane, W. Tan, D. Wu, H. V. Baker, P. A. Gulig, D. V. Lim, S. Jin, *Anal. Biochem.* **2004**, *334*, 135.

[50] M. Lal, L. Levy, K. S. Kim, G. S. He, X. Wang, Y. H. Min, S. Pakachi, P. N. Prasad, *Chem. Mater.* **2000**, *12*, 2632.

[51] Z. Gabelica, S. Valange, M. Shibata, H. Hotta, T. Suzuki, *Micropor. Mesopor. Mater.* **2001**, *44–45*, 645.

[52] J. Bauer, P. Behrens, M. Speckbacher, H. Langhals, *Adv. Funct. Mater.* **2003**, *13*, 241.

[53] I. Place, J. Perlstein, T. L. Penner, D. G. Whitten, *Langmuir* **2000**, *16*, 9042.

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[54] J. H. Bourroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. MacKay, R. H. Friend, P. L. Burn, A. B. Homes, *Nature* **1990**, *347*, 539.
[55] N. S. Sariciftsi, L. Smilowitz, A. J. Heeger, F. Wudl, *Science* **1992**, *258*, 1474.
[56] A. Ajayaghosh, S. J. George, *J. Am. Chem. Soc.* **2001**, *123*, 5148.
[57] A. Ajayaghosh, S. J. George, V. K. Praveen, *Angew. Chem. Int. Ed.* **2003**, *42*, 332.
[58] A. P. H. J. Schenning, J. V. Herrikhuyzen, P. Jonkheijm, Z. Chen, F. Würthner, E. W. Meijer, *J. Am. Chem. Soc.* **2002**, *124*, 10252.
[59] J. Morgado, F. Cacialli, R. Iqbal, S. C. Moratti, A. B. Holmes, G. Yahioglu, L. R. Milgrom, R. H. Friend, *J. Mater. Chem.* **2001**, *11*, 278.
[60] K. Brunner, J. A. E. H. Van Haare, B. M. W. Langeveld-Voss, H. F. M. Schoo, J. W. Hofstraat, A. van Dijken, *J. Phys. Chem. B* **2002**, *106*, 6834.
[61] C. H. Jeon, E. E. Makhaeva, A. R. Khokhlov, *J. Poly. Science Part B: Polymer Physics.* **1999**, *37*, 1209.
[62] C. Thalacker, F. Würthner, *Adv. Funct. Mater.* **2002**, *12*, 209.
[63] a) C. Thalacker, A. Miura, S. De Feyter, F. C. De Schryver, F. Würthner, *Org. Biomol. Chem.* **2005**, *3*, 414; b) F. Würthner, S. Yao, *J. Org. Chem.* **2003**, *68*, 8943.

Received: May 24, 2005
Published Online: August 12, 2005

 © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim