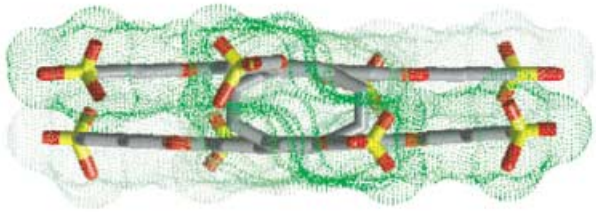
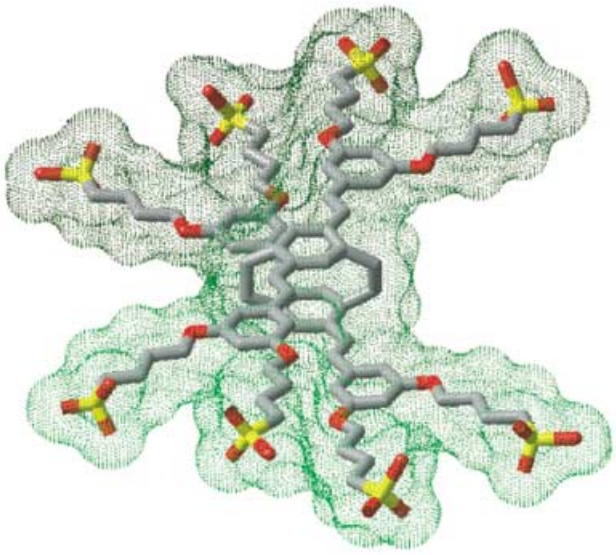
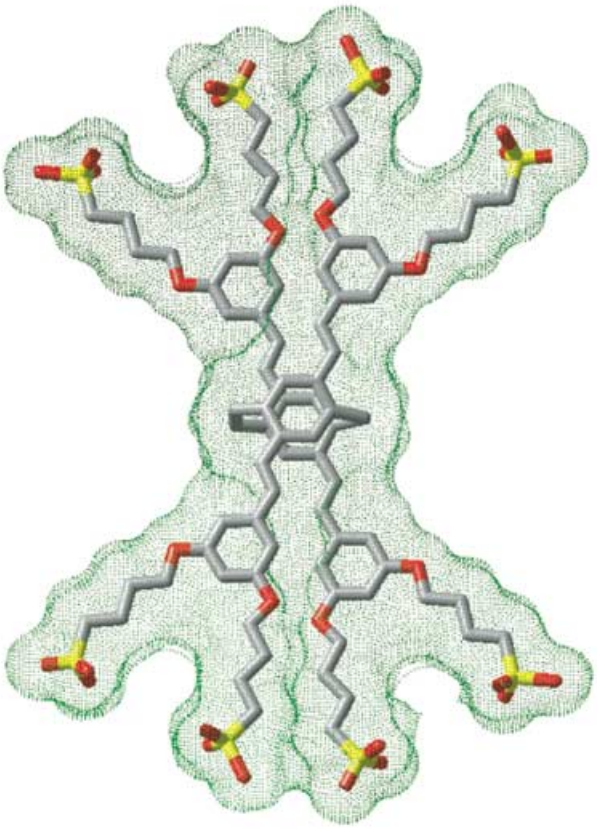
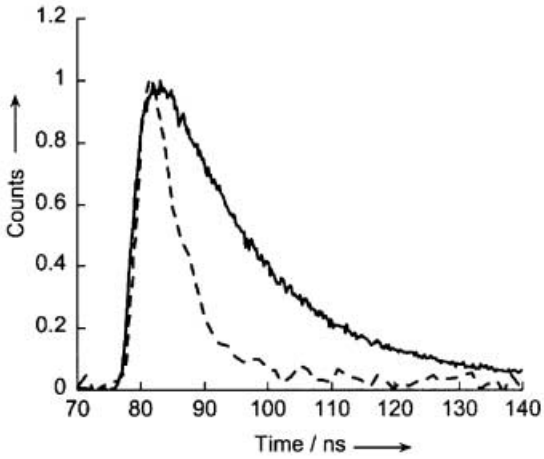
Paracyclophane Bichromophores as Fluorescent Optical Reporters









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Through-Space Delocalized Water-Soluble Paracyclophane Bichromophores: New Fluorescent Optical Reporters

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Abstract: Conjugated polymers and oligomers can serve as highly responsive fluorescent reporters for biosensor applications. However, their optical properties in aqueous media are highly dependent upon environmental conditions. The structure of the paracyclophane framework provides a platform for designing optical reporters that show little sensitivity to surfactants, and thus is well-suited for fluorescent assays. The permanent intramolecular delocalization through the paracyclophane core dominates intermolecular perturbations in spontaneously formed aggregates.

Keywords: aggregation · biosensors · conjugated polymers · fluorescence · paracyclophane

Introduction

There is substantial worldwide research effort, in industrial and academic laboratories, focused on developing highly sensitive and selective methods of biosensors useful in medical diagnostics and biomedical research.[1] An efficient biosensor is a reporter that contains a biomolecular recognition element able to detect nanomolar or subnanomolar quantities of one or more target analytes. Optimum biosensors need to operate in a selective manner and provide a "real-time response" in the form of a transduction signal that is easy to detect. Conjugated polymers (CPs) have emerged as a class of materials that provide a highly responsive platform for chemical and biological sensors. These materials may be viewed as a collection of short, conjugated (oligomeric) units kept in close proximity by virtue of the polymer backbone. The delocalization characteristic of their electronic structure allows fast intra- and interchain energy transfer,[2] and enables photoexcitation migration to low energy sites. The emission of a large number of absorbing units is therefore efficiently quenched by photoinduced electron-transfer[3] or by Förster energy-transfer mechanisms.

A complication with water-soluble CPs as optical reporters is that they are sensitive to the environment, namely to the addition of surfactant. The efficiency of CPs is related to aggregate formation in aqueous solution and to the polymer structure. Even for oligomers with well-defined structures the fluorescence quenching efficiencies depend on surfactant concentration and aggregate dimensions. In this contribution we describe the background and our efforts towards the design of well-defined, water-soluble paracyclophane optical reporters that are insensitive to changes in coil conformation and in aggregate formation.

CP-Based Chemical Sensors

In one of the first demonstrations of optical amplification for chemical sensing,[4] a polyreceptor showed amplification (65-fold) in fluorescence quenching by a single cationic receptor *N*,*N*′-dimethyl-4,4′-bipyridinium (MV^{2+}, methyl viologen) relative to the parent monomer structure. The polyreceptor used was a cyclic ether-containing CP, as shown in Figure 1, which displays binding affinity for MV^{2+}.

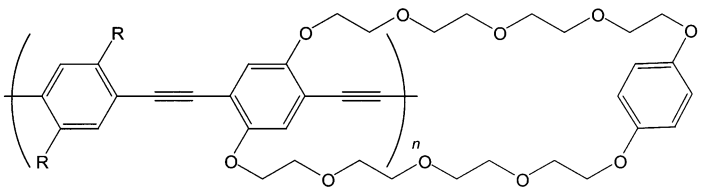

Figure 1. Cyclic-ether-based polymer used for amplification through energy migration.

Optical excitations travel along the polymer backbone and are quenched upon encountering an MV^{2+}-bound receptor. This amplification phenomenon by energy migration, which utilizes the collective response of a polymer, is at the core of CP-based sensors. Conductivity-based sensory devices, which operate on the basis of changes in charge transport, may also be implemented by connecting the modified CP between two electrodes.[5] Cations (such as Na^+, MV^{2+}) can be selectively

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sensed by using this technique, and an array of molecular materials (Figure 2)[5] have been used for this purpose. Polythiophenes and polypyrroles functionalized with polyalkyl ether chains,[6] crown ethers,[7] and aza-crown ethers[8] have been the most abundantly studied. Other structures of CPs functionalized with pyridyl-based ligands,[9] cyclodextrins,[10] and calixarenes[11] have also been developed.

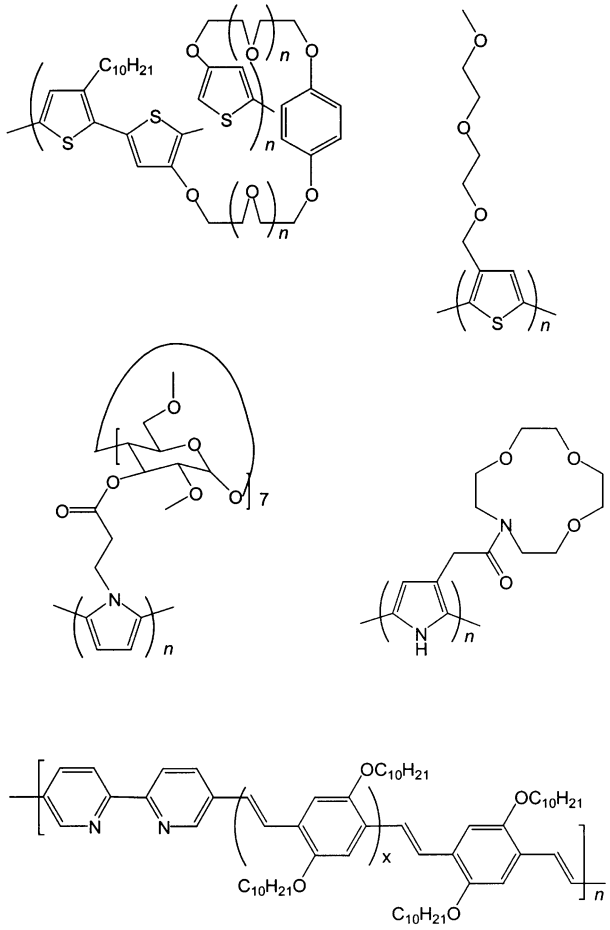


Figure 2. Examples of materials used in chemosensor wires.

The efficiency of CP-based chemosensors is increased in thin-film applications by introducing three-dimensional amplification. Concentrations of vapors of trinitrotoluene (TNT) as low as 10^{-18} M were detected by using thin films of a pentiptycene-containing CP.[12] Studies on ordered films of poly(phenyleneethynylene) materials demonstrated that the modulation of the film thickness induces a transition to a three-dimensional behavior, resulting in more efficient trapping.[13]

CPs as Optical Reporters in Biosensor Designs

Water-soluble CPs are required for the detection of biological targets in homogeneous media. This property is typically achieved by the incorporation of charged functionalities on the polymer backbone.[14] The hydrophobic nature of the conjugated framework results in extensive aggregation in solution.[15] Selected examples of water-soluble CPs used in biosensor applications are shown in Figure 3. Structures include derivatives of poly(*p*-phenylenevinylene) (PPV) with sulfonated pendant groups, such as MPS-PPV,[14] MBL-PPV,[15] and poly[lithium-5-methoxy-2-(4-sulfobutoxy)-1,4-phenylenevinylene]. Cationic derivatives of poly(fluorene) are also useful, such as poly(9,9-bis(6′(*N*,*N*,*N*-trimethylammonium)hexyl)fluorenephenylene).[16]

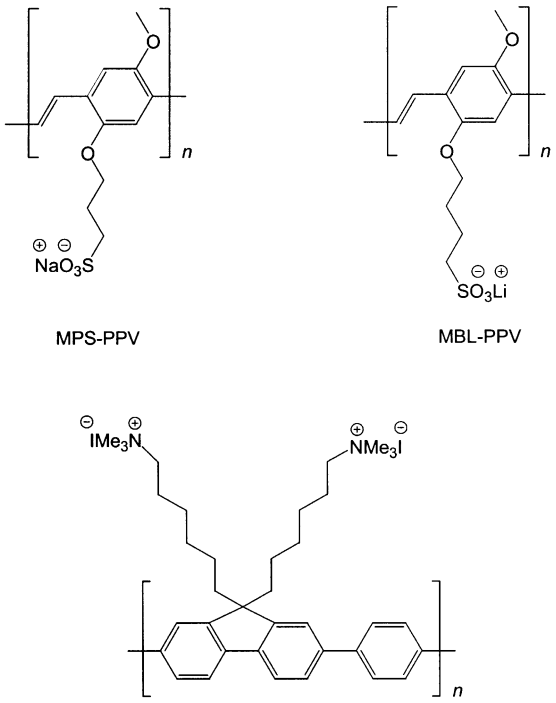


Figure 3. Examples of water-soluble CPs used in biosensor applications.

The photophysical properties of MPS-PPV (molecular weight 1-5 × 10^5, 1000 monomer repeat units) were recently reported.[17] A millionfold amplification of the fluorescence quenching, relative to dilute solutions of the parent stilbene monomer, is observed when small quantities (1 – 5 × 10^{-7} M) of MV^{2+} are added. These numbers must be considered with caution, because in the stilbene case the quenching process is dynamic, whereas for the charged polymer the mechanism involves static quenching. The Stern – Volmer constant K_{sv} gives a quantitative measure of the fluorescence quenching [Eq. (1)]:[18]

$$F^o/F = 1 + K_{sv}[Q] \quad (1)$$

whereby F^o is the intensity of fluorescence in the absence of the quencher Q, F is the intensity of fluorescence in the presence of Q, and [Q] is the concentration of Q. In the above example of MPS-PPV, the quencher is MV^{2+}. Under dilute conditions, the Stern – Volmer plot for quenching by MV^{2+} gave a K_{sv} value of 1.7 × 10^7 M^{-1}. The negatively charged MPS-PPV readily binds in aqueous solution with the quencher to form a weak donor – acceptor complex, thereby increasing the local concentration of the quencher. Close proximity enables photoinduced charge transfer and, due to the large number of

monomers sampled by the photoexcitation, a large amplification takes place.

It was also reported that this highly effective fluorescence quenching of MPS-PPV could be used in a reversible manner in a biosensor application. A short flexible tether attached a viologen derivative to biotin, a specific receptor for the protein avidin. The MV^{2+}–biotin moiety effectively quenches the fluorescence of MPS-PPV. Since avidin and biotin form a strong complex (binding constant, $K_d \sim 10^{-15}$),[17] the addition of avidin to the mixture removes the quencher from MPS-PPV, suppressing the photoinduced electron transfer, and the fluorescence quenching is reversed (see Figure 4).

However, there are additional considerations for using CP fluorescence recovery for the detection of a more diverse class of biologically relevant molecules. Charged analytes might interfere in the quenching efficiency of the polymer by perturbing the electrostatic interaction between the CP and the quencher. The size of the quencher plays an important role in its complexation, since it is likely that the quenching reversal in the polymer–MV^{2+}–biotin system with avidin was partly due to steric effects resulting from the large size of avidin. Therefore, a smaller antigen might be unable to fully remove the quencher from the polymer. Additionally, experiments on a similar anionic polyelectrolyte MBL-PPV demonstrated that addition of different proteins to low concentrations of the polymer resulted in changes in the fluorescence,[9] an indication that nonspecific interactions can complicate the identification of a target analyte when a large number of unknown structures are examined.

The presence of surfactants is often required in biomolecular recognition events. However, surfactants influence the optical properties of polyelectrolytes.[19] In fact, addition of small amounts of dodecyltrimethylammonium bromide (DTA) to aqueous solutions of MPS-PPV increases the fluorescence quantum yield 20-fold, due to change in polymer conformation and/or aggregate breakup.[20] More importantly, in the presence of MV^{2+}, the addition of DTA results in a decrease in K_{sv} by two orders of magnitude, at a DTA/polymer repeat unit ratio of 1:10. This decrease in quenching efficiency eliminates the optical amplification provided by the polymer structure.

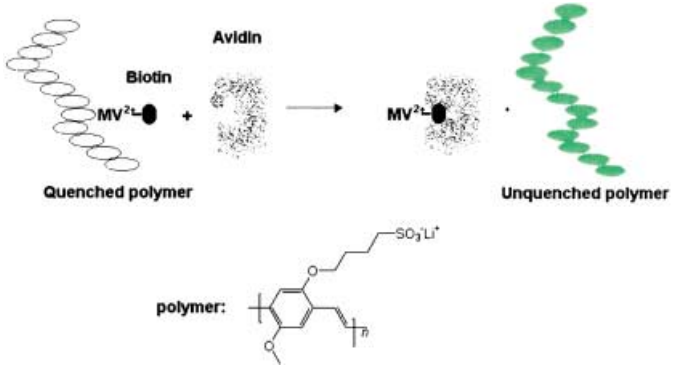
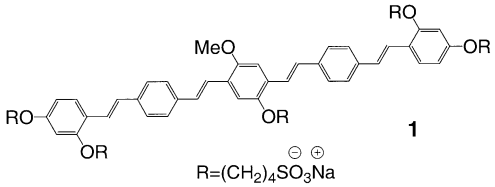


Figure 4. Representation of a fluorescence-recovery-based biosensor. The fluorescence of the polymer is quenched by the MV^{2+}–biotin moiety. The addition of avidin effectively removes the quencher from the proximity of the polymer; this allows the polymer to fluoresce, thus signaling the binding event of biotin to avidin.

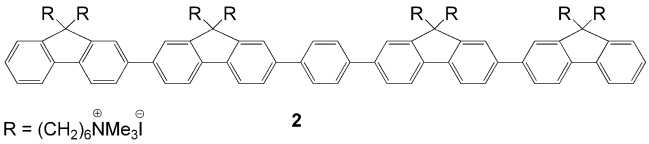
The fluorescence intensity observed from CPs is influenced by the molecular structure of the polymer. The statistical distribution of the polymeric chains, batch-to-batch variability, and variations in polymer conformation and aggregate formation in aqueous solution make structure–property relationships difficult to deconvolute. To gain a better understanding and control of the structural factors governing the optical properties of CPs, the water-soluble phenylenevinylene oligomer **1** was designed and synthesized, and its fluorescence properties examined.[21]



Light-scattering experiments demonstrate that **1** self-assembles into aggregates with a root-mean-squared radius of $\sim$190 nm within a concentration range of 3.7 to 7.1×10^{-5} M. The K_{sv} value ($4.5 \times 10^5\,M^{-1}$) with MV^{2+} in water indicates a static-quenching regime, favored by ion pairing between **1** and MV^{2+}. This value is fifty times lower than that obtained for MPS-PPV/MV^{2+} under similar conditions. However, upon addition of the surfactant DTA, the fluorescence quenching in **1**/MV^{2+} increases in efficiency. Indeed, it is possible to obtain a greater amplification of the quenching of **1**/MV^{2+} relative to MPS-PPV. It is suspected that the formation of smaller aggregates upon DTA addition allows for stronger interactions between **1** and MV^{2+} and that there is facile energy migration within these aggregates. These results indicate that the spontaneous formation of aggregates in well-defined chromophores such as **1** can be advantageously used to provide a superior quenching efficiency, relative to polymer-based counterparts.

Additional studies[22] have shown that the aggregation of oligomers also influences the efficiency of Förster energy transfer. When **1** was mixed with a fluorene-based water-soluble oligomer, such as **2**,[16] energy transfer from **2** to **1** was observed. Under dilute conditions, static quenching by formation of ion pairs dominates, and the K_{sv} value ($\sim 1 \times 10^7\,M^{-1}$) obtained from the linear portion of the Stern–Volmer plot is consistent with efficient quenching.

The quenching efficiency for **1**/**2** mixtures is also perturbed by the concentration of surfactant (sodium dodecylsulfate, SDS). An evaluation of the influence of surfactant on K_{sv} can be provided by correlating the ratio of SDS equivalents against the number of charged units (CU). In the range for which [SDS]/[CU] = 0–0.75, there is little change in the K_{sv} value (between 1 and $5 \times 10^6\,M^{-1}$); at [SDS]/[CU] = 1, a



pronounced increase is observed and a maximum value of $4 \times 10^7\ \text{M}^{-1}$ is reached. A progressive decrease in K_{sv} values is then observed with further addition of SDS.

The complications given above, namely the dependence of MPS-PPV and oligomer fluorescence on surfactant, and therefore other solutes that influence aggregation, make it highly desirable to design a "stable" reporter for biosensor applications. Specifically, one would like to design water-soluble molecules with delocalized electronic structures that are insensitive to changes in coil conformation and in aggregate dimensions.

Three-Dimensional Electronic Delocalization Within Paracyclophane-Based Bichromophores

Our initial motivation for studying paracyclophane (pCp) derivatives arose from the desire to model interchromophore contacts. Previous work with pCp molecules shows that the pCp core acts as a bridge to bring two individual chomophores into close contact, at a distance shorter than van der Waals distance.[23] This contact provides a key junction to model interchromophore through-space delocalization.[24] By having this pCp contact, permanent chromophore – chromophore through-space delocalization is established in a well-defined way. Synthetic control makes it possible to examine how chain length, orientation and different functionalities affect the electronic coupling between the two subunits.

The characteristics of pCp bichromophores derive mainly from two states: the "chromophore" state, which is the state characterized by through-bond (TB) delocalization along the parent chromophore, and the "phane" state, which is characterized by through-space (TS) delocalization across the pCp core.[25, 26] The electronic characteristics of a pCp dimer results from the mixing of these two states. Taking this into consideration, one encounters three different electronic structures, depicted in Figure 5.

Class A encompasses molecules such as **3**, in which "monomer" units with restricted conjugation length are connected by the pCp core at their termini.[27] In such molecules, there is very little mixing of the two states, and the first excited state (S_1) can be described as mostly phane in character, whereas the second excited state (S_2) can be described as mostly chromophore in character. Since the phane state has a vanishing oscillator strength, the chromophore state acts as an antenna, and absorption leads to excitation directly to the S_2 state. Internal conversion leads to the lower energy S_1 state, and emission occurs from there (Figure 5, A). Molecules of this class are characterized by longer fluorescence lifetimes relative to their monomeric counterparts.

Molecules such as **4** typify the class B.[27] For these molecules S_1 is mostly chromophore in character. Since this transition is allowed, both the absorption and emission derive most directly from the chromophore state. As expected, the absorption and emission spectra are very similar to those of the parent monomer chromophore (Figure 5, B).

For classes A and B, the pCp core connects the chromophores at their termini. Electronic calculations for the parent chromophores show that with an increase in conjugation length, terminal rings participate less strongly in the description of the HOMO and the LUMO.[28] One can therefore expect diminishing through-space delocalization between the chromophores with increasing conjugation length.

Molecules such as **5**, in which the center ring of each parent distyrylbenzene chromophore is connected by the pCp core, form the third class of paracyclophane dimers (Figure 5, C).[27] Since the central ring is a more active participant in the molecular orbitals of the parent chromophore, there is better mixing of the chromophore and phane states, and neither state dominates the absorption or emission spectra. Excitation leads to full delocalization within the entire molecule.

Water-Soluble Paracyclophane Chromophores as Stable Optical Platforms for Fluorescent Biosensors

We looked to bypass the complications by aggregation and self-quenching encountered with **1**. As stated previously, the

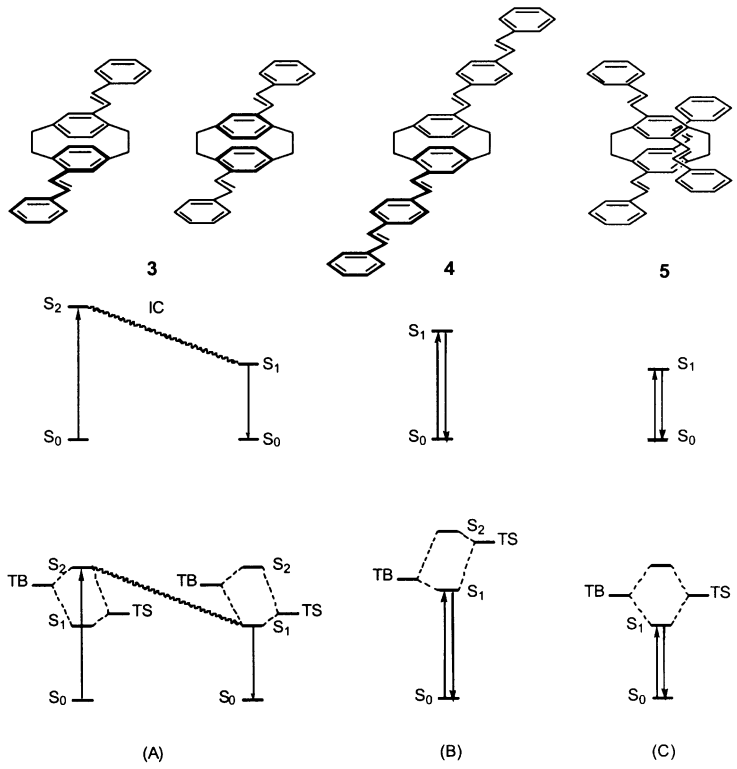
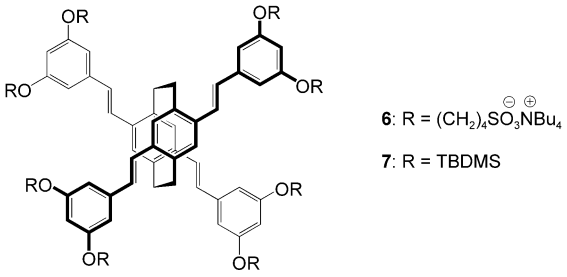


Figure 5. Three different electronic structures of pCp bichromophoric molecules and their corresponding absorbing and emitting states.

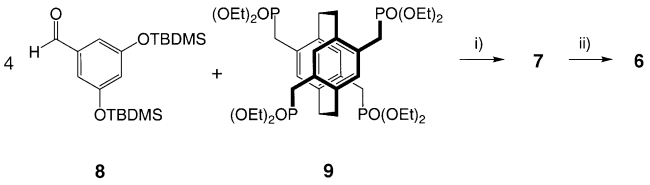
addition of DTA to a solution of **1** increased photoluminescence and enhanced K_{sv}. Drawing upon our previous work with pCp molecules, we decided to model a sensor based upon the framework of **5**, creating a molecule that would contain strong, prebuilt chromophore–chromophore interactions. We anticipated that interchromophore interactions within the aggregate would be superceded by the stronger, permanent intramolecular delocalization.[29]

Our target was molecule **6**, a bichromophoric paracyclophane made water-soluble by sulfonate functionalities. The synthesis of **6** began by the preparation of the neutral



precursor **7** by a Horner–Emmons coupling of **8** with **9** (Scheme 1). The target **6** was produced by deprotection of **7** with *tert*-butylammoniumtriphenyldifluorosilicate (TBAT) and in situ quenching with butane sultone. This latter sequence is a novel method for generating charged groups in one step from neutral precursors.

Figure 6 compares the effect of DTA on the optical properties of **1** and **6**. As shown, the photoluminescence and quenching ability of MV^{2+} are virtually unchanged for **6**. At DTA/SO_3^- ratios of up to 1:1, K_{sv} decreased by less than 8%



Scheme 1. i) KO*t*Bu, toluene. ii) TBAT, butane sultone, DMF.

and the quantum yield, Φ_{PL}, decreased by less than 4%. Substantial changes in the properties of **1** are evident. Also significant is that light scattering over a concentration range of 1.9×10^{-5} to 4.5×10^{-4} M shows that aggregation of **6** occurs in water to form particles with a root-mean-squared radius of 31 nm and an average molecular weight of 1.35×10^5 g mol^{-1}. Thus, 30–40 molecules of **6** are contained in each aggregate. The data from Figure 6 imply that modification of these aggregates by DTA is of little influence on the photoluminescence intensity. The permanent, intrachromophore delocalization within the dimers brought about by the pCp bridge takes precedence over interchromophore interactions.

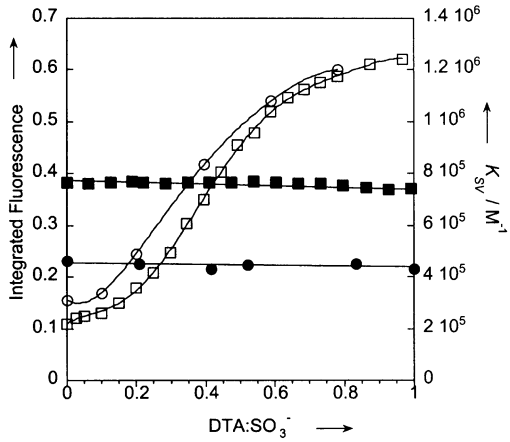


Figure 6. The effect of DTA concentration on: a) the normalized integrated fluorescence intensity of **1** (□) and **6** (■) as a function of the DTA/SO_3^- ratio; b) K_{sv} for **1** (○) and **6** (●) quenched by MV^{2+} as a function of DTA/SO_3^- ratio.

The fluorescence lifetimes (τ_f) of **6** in water and **7** in toluene are 12.5 and 2 ns, respectively (Figure 7). At a concentration of 4.0×10^{-6} M, the absorption and emission maxima of **6** are 399 and 511 nm, respectively. At a similar concentration, the

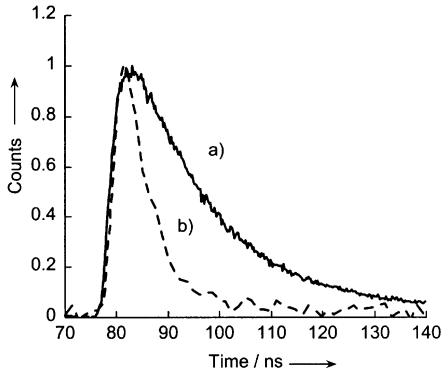


Figure 7. Fluorescence lifetime measurements of compounds a) **6** and b) **7**.

absorption of **7** is nearly identical to that of **6**, but the emission maximum is blue-shifted by 45 nm. Φ_{PL} values[30] are 0.38 for **6** in water and 0.52 for **7** in toluene. The long fluorescence lifetime of **6** is indicative of emission from a state that has a greater contribution from the phane state than that of **7**,[25a] suggesting that the higher dielectric medium lowers the energy of the phane state relative to the chromophore state.

Complementary insight is gained by examining the natural lifetime, τ_N, of the molecules.[18] The value of τ_N is related to the measured lifetime, τ_{meas} and Φ_{PL} by Equation (2):

$$\tau_N = \tau_{meas}/\Phi_{PL} \quad (2)$$

From the measured lifetimes and quantum yields of **6** and **7**, we obtain τ_N values of 33 and 4 ns, respectively. The longer τ_N of **6** is again consistent with a larger contribution from the phane state, relative to **7**. These data and observations are best described by a switch in molecular characteristics from class C to class A (in Figure 5), induced by the higher dielectric constant in water.[31] For comparison, the τ_N for their

distyrylbenzene counterparts are 5 ns (for the monomeric version of **6**) and 3 ns (for the monomeric version of **7**).

Summary

In summary, we have shown that it is possible to design molecules such as **6** that may be considered unimolecular aggregates, and that the strong delocalization within these molecules makes perturbations from adjacent molecules less important. Future efforts will be directed towards the application of such chromophores in biosensor applications.

Acknowledgement

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