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Photophysical studies on multichromophoric cyclotriphosphazenes. Trinuclear excimer formation in hexakis(2-naphthyloxy)cyclotriphosphazene

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Abstract—Hexakis(2-naphthyloxy)cyclotriphosphazene showed an interesting emission behavior between its monomer and excimer forms, the latter nearly completely dominating in water. Encapsulation studies with β-cyclodextrin in water partially revived the monomer emission.

With a view to understanding the mechanism and dynamics of natural photosynthetic reactors,[1] photophysical studies of multichromophoric scaffolds have gained much current attention. These scaffolds are also useful for harvesting diffused sunlight for potential use in solar energy conversion and in the construction of luminescent biological and trace metal sensors.[2] Early studies on multichromophoric systems were carried out with polymers that were substituted at intervals with chromophoric units.[3] However, due to their inherent flexibility and thus a number of different coiled conformations, these polymers turned out to be poor mimics of the natural photosynthetic reactors. In search of better mimics, Jullien and co-workers recently studied a number of naphthyl substituted β-cyclodextrins (β-CDs) containing up to 14 chromophore units.[4] The structural rigidity of these systems held the naphthyl chromophores in spatially well-defined positions and in close proximity with each other. This led to efficient energy hopping between the naphthyl units in these molecules. Inspired by these results, we initiated a study on new multichromophoric scaffolds as molecular mimics of the natural photosynthetic antennae.

Our initial task was to seek a conformationally rigid multitopic core that could be substituted with multiple chromophoric units. Previous studies from these laboratories have shown that tetraphenylmethane, a centrally rigid tetrahedral scaffold, can be effectively used in this regard.[5] However, tetraphenylmethane can accommodate only four chromophores. While searching for a higher valent core structure, we were attracted to the cyclotriphosphazenes (CTPs), which have hexavalent inorganic cores. In this paper, we describe the unusual excited state photophysical properties of hexakis(2-naphthyloxy)cyclotriphosphazene **3** arising from highly pre-organized trinuclear excimer formation.

Cyclotriphosphazene (CTP) is a well known hexatopic core, which can be easily per-functionalized via substitution reactions on the corresponding hexachloride $(NPCl_2)_3$, especially with heteroatomic nucleophiles.[6] In symmetrically per-substituted CTP derivatives, the inorganic ring is nearly planar, the phosphorus atoms almost tetrahedral (sp^3) and the nitrogen atoms approach an sp^2 geometry.[7] As a result, the geminal substituents on the phosphorus atoms are oriented in a well defined spatial arrangement, one above and one below the CTP ring. Moreover, in homogeneously per-substituted CTPs, the three substituents on either side of the CTP ring are also mutually equidistant. CTP rings are photochemically inert and do not have any low energy absorption band of their own. Hence, they do not interfere with the photophysical properties associated with the attached chromophores. The ease with which

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CTP rings can be per-functionalized (vis-à-vis cyclodextrins) together with the structural rigidity of the products make CTP an attractive core for the construction of multichromophoric scaffolds.

A number of hexakis(aryloxy)cyclotriphosphazenes were prepared from hexachlorocyclotriphosphazene and the corresponding phenol (NaH, THF, reflux).[8] The absorption and emission spectra of those derived from simple phenols (phenol, 4-*tert*-butylphenol) were similar to those of the individual phenols indicating that there were no interactions between the chromophore units either in the ground state or in the excited state. However, hexakis(2-naphthyloxy)cyclotriphosphazene **3**, derived from 2-naphthol (Scheme 1), showed an unexpected emission behavior, entirely different from the hexakis(phenoxy) and the hexakis(4-*tert*-butylphenoxy) derivatives, which attracted our attention for detailed study.

The absorption spectrum of **3** recorded in CH_2Cl_2 is shown in Figure 1 (solid line). The positions of absorption are similar to those of 2-naphthol.[9] The absorption maxima do not show any appreciable solvatochromic shift in solvents of widely different polarities (*n*-heptane, dioxane, CH_2Cl_2, CH_3CN, MeOH, water). However, in contrast to the vibrational structures observed for 2-naphthol,[9] the lower energy bands of **3**, especially the E_2 band (λ_{max} 276 nm with shoulders at 272 and 279 nm), are somewhat broadened. This is obviously caused by the presence of six 2-naphthol units in **3**. From the similarity of the absorption spectrum of **3** to that of 2-naphthol, it may be inferred that there are no ground state interactions between the chromophores in **3**. If at all present, they must be very weak with magnitudes smaller than the optical line width.

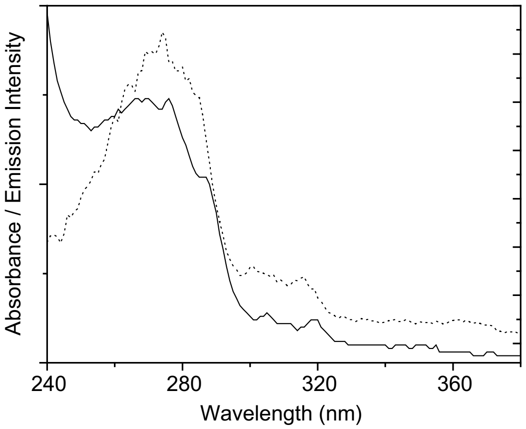
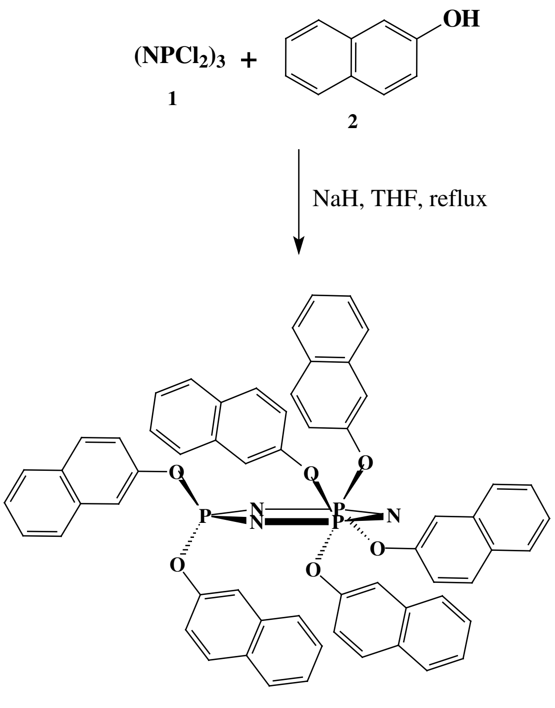


Figure 1. Absorption (solid line) and excitation (dotted line) spectra of **3** in CH_2Cl_2.



3 (65%)

Scheme 1.

The emission spectra of **3** (λ_{exc} 280 nm) recorded in different solvents are shown in Figure 2. Two emission bands were observed, one centred at λ_{max} 340 (structured) and the other at 386 nm (broad and unstructured) with red tailing up to 500 nm. In comparison, the emission spectrum of 2-naphthol (10^{-6} M in CH_2Cl_2, λ_{exc} 274 nm) showed structured bands consisting of a maximum at 347 nm with a shoulder at 340 nm. Thus the appearance of the 386 nm band in **3** was somewhat unexpected. Moreover, the emission spectrum of **3** was found to be highly dependent on solvent polarity. Thus, on increasing the solvent polarity (*n*-heptane→dioxane→CH_3CN→MeOH→water), the intensity of the 386 nm band gradually increased at the expense of the 340 nm band. In a highly polar solvent such as water, the 386 nm band was practically the sole peak. Based on these observations, we assigned the 386 nm band in **3** as that arising from excimer formation whereas the shoulder at 340 nm represented emission from the unassociated form. The excitation spectrum of **3** monitored

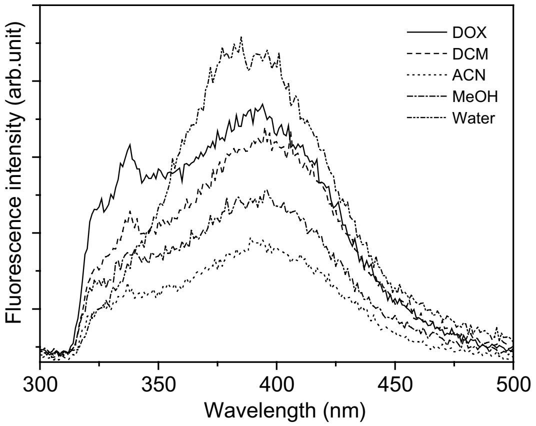


Figure 2. Emission spectra of **3** (λ_{exc} 280 nm) in different solvents (DOX = 1,4-dioxane, DCM = CH_2Cl_2, ACN = CH_3CN).

at 386 nm (Fig. 1, dotted line) was found to be similar to its absorption spectrum. Such correlation was also found in other solvents, irrespective of the solvent polarity. Since the excitation spectra of **3** were insensitive to the solvent polarity and therefore, independent of the relative proportions of the 386 nm and the 340 nm bands, the former band is more likely due to excimer formation than any ground state interactions.

Notably, the emission spectrum of a concentrated solution of 2-naphthol (10^{-2} M in CH_2Cl_2), where intermolecular excimer formation is favored, showed a maximum at 352 nm with a shoulder at 376 nm. While the appearance of this 376 nm peak is due to excimer formation and closely matches the position of the excimer peak of **3** (λ_{max} 386 nm), excimer formation with 2-naphthol occurred only in very concentrated solutions. In contrast, excimer emission from **3** was obtained in dilute solutions (10^{-6} M) suggesting that the excimer formation in **3** is intramolecular, rather than intermolecular, in nature. The positive solvatochromic shift observed in **3** together with the large difference in its excimer and monomer emissions (3500 cm^{-1}) point towards intramolecular excimer formation. Semi-empirical AM1 calculations (Hyperchem 5.01) on **3** showed that the central inorganic ring was almost planar with a near perpendicular O–P–O bond angle.[10] The six naphthalene units are highly pre-organized, three on either side of the central CTP ring. The three naphthalene rings on either side are oriented in a propeller type arrangement. Perhaps, due to the rigid geometry of the central CTP ring,[8c] which orients the chromophores (three on either side of the CTP ring) in close proximity, strong π-stacking interactions can operate between the naphthyl rings on either side of the CTP ring favoring intramolecular excimer formation. The average interplanar distance between the naphthyl rings on either side of the CTP plane is ~4.5 Å, which is well within the geometric limits for intramolecular exchange interaction to take place. Therefore, trinuclear excimer formation between the three naphthyl units on either side of the CTP plane is expected to be a facile process. In comparison, hexaphenoxycyclotriphosphazene showed only monomer emission (λ_{max} 290 nm) with no excimer formation. Perhaps, due to their smaller size, the phenol rings in the latter do not reach the proximal distance for excimer formation. Since energy trapping by preformed excimers is an irreversible process and excimer emission dominates in **3**, we conclude that energy migration between the naphthyl chromophores should be very fast. However, at this stage, we cannot comment on the possibility of interfacial energy transfer across the CTP ring in **3**.

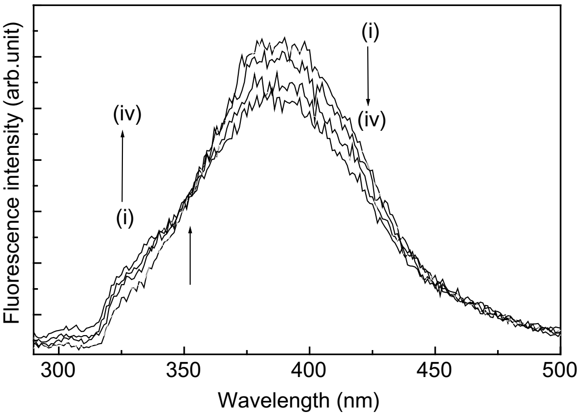


Figure 3. Emission spectra of **3** in water (2 μM) in the presence of β-cyclodextrin (i: 0 mM, ii: 3.9 mM, iii: 7.8 mM, iv: 11.7 mM). Isoemissive point at λ 351 nm.

Cyclodextrins (CD) can encapsulate various organic chromophores in their hydrophobic cavity and have been widely used as probes to investigate excimer formation in aqueous solutions.[11] Addition of β-CD to an aqueous solution of **3** led to a gradual reappearance of the monomer emission band at 340 nm along with a concomitant decrease in the intensity of the excimer band (Fig. 3). Reappearance of the monomer emission upon β-CD addition indicated that excimer formation in **3**, which completely dominated in water, is somewhat inhibited since some of the naphthyl chromophores are trapped inside the β-CD cavity and hence, cannot participate in intramolecular charge transfer. An isoemissive point was obtained at 351 nm indicating a 1:1 complexation between the naphthyl rings of **3** and β-CD. This is in agreement with the reported complexation behavior of 2-naphthol and β-CD.[11b] Addition of α-CD, however, had no effect on the emission spectrum of **3** in water. The different effects of α- and β-CD can be rationalized by comparing the cavity sizes of the two types of cyclodextrins and the molecular dimension of the naphthyl units. Semi-emipirical AM1 calculations show that the naphthyl units in **3** have a diameter of ~7.2 Å. The size of the cavities for α- and β-CD are 4.5 and 7.8 Å, respectively. Thus, α-CD, with a smaller cavity size cannot encapsulate the naphthyl units of **3** and hence, does not have any effect on its excimer emission. On the other hand, the cavity size of β-CD matches favorably with the molecular diameter of the naphthyl units leading to strong binding and consequently, partial inhibition of the excimer emission. However, even in the presence of β-CD, the excimer emission of **3** was only partially quenched. This may be due to the fact that all the naphthyl rings in **3** were not encapsulated, even with a large excess of β-CD, due to steric hindrance. The energy minimized structure of **3**[10] clearly indicates that encapsulation of all six naphthyl rings with large CD rings would lead to severe steric hindrance.

In conclusion, we have shown that cyclotriphosphazene can be used as a rigid hexavalent scaffold for constructing multichromophoric modules having unusual and interesting photophysical properties. When a relatively large chromophore is used, as in **3**, the structural rigidity of the CTP ring leads to a preferred conformation in which three chromophores reside on either side of the CTP plane forcing them into close proximity. Such a pre-organization leads to facile intramolecular charge transfer in the excited state and a near complete trinuclear excimer formation. Taking advantage of this conformational bias, we are currently preparing other hexachromophoric CTP derivatives for light harvesting studies.

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