as an inseparable mixture of 4-methyltroponeiron tricarbonyl (major) and 5-methyltroponeiron tricarbonyl (minor): IR (CH_2Cl_2) 2045, 1985, 1634 cm^{-1}; ^{1}H NMR of 4-methyltroponeiron tricarbonyl ($CDCl_3$) 6.55 (dd, 1 H, J = 9.2, 12 Hz, H-6), 6.21 (d, J 9.2 Hz, 1 H, H-3), 4.95 (d, J = 12.2 Hz, 1 H, H-7), 2.95 (d, J = 9.2 Hz, 1 H, H-2), 2.66 (d, J = 9.2 Hz, 1 H, H-5), 2.48 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) 209.1 (Fe-CO), 198.98 (C-1), 57.57 (C-2), 90.88 (C-3), 113.03 (C-4), 54.54 (C-5), 148.27 (C-6), 121.84 (C-7); ^{1}H NMR of 5-methyltroponeiron tricarbonyl ($CDCl_3$) 6.95 (1 H, H-6), 6.10 (d, J = 8.3 Hz, 1 H, H-7), 5.32 (d, J = 8.3 Hz, 1 H, H-4), 1.48 (s, 3 H, CH_3). Anal. Calcd for $C_{11}H_8O_4Fe$: C, 50.80; H, 3.08. Found: C, 50.58; H, 3.25.

Preparation of Cycloadduct 34. The mixture of 4-methyl- and 5-methyltroponeiron tricarbonyl (0.095 g, 0.366 mmol) was treated with 1 equiv of TMSOTf at −78 °C in 1 mL of CH_2Cl_2 for 3 h. (η^1-allyl)Fp (0.1355 g, 0.621 mmol) was added neat via syringe, and the reaction was continued for an hour at −78 °C, then allowed to warm to room temperature, and finally heated at reflux for 3 h. Solvent was removed and replaced with 10 mL of THF and 5 mL of saturated aqueous $NaHCO_3$, and the mixture was stirred for 90 min. The reaction was poured into 30 mL of Et_2O and 30 mL of brine. Workup yielded an orange-red residue which was chromatographed on a silica gel preparative plate with 1.5:1 skellysolve-B/EtOAc to give 0.079 g (45%) of product as a yellow oil and as a mixture of diastereomers: IR (CH_2Cl_2) 2080, 1995, 1945, 1635 cm^{-1}; ^{1}H NMR ($CDCl_3$) 5.65 and 5.58 (dd, J = 1.47, 7.33 Hz, 1 H, H-3), 4.77 and 4.75 (s, 5 H, Cp), 3.20–1.40 (m, 9 H); ^{13}C NMR ($CDCl_3$) 210 (C-1), 68.28/66.32 (C-2), 88.65/90.50 (C-3), 107.04/108.1 (C-4), 55.67/55.53 (C-5), 53.03 (C-6), 49.75 (C-7), 16.53 (C-8), 43.48 (C-9), 52.81 (C-10), 23.06/25.36 (C-11), 85.32/85.15 (Cp), 210.08 (Fe-CO), CO 217.4 (Fp-CO). Anal. Calcd for $C_{21}H_{18}O_6Fe_2$: 52.71; H, 3.76. Found: C, 52.46, H, 3.71.

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Lipophobic Effects on Photochemical and Photophysical Behavior of Molecules with Polar Chains in Nonpolar Solvents. Evidence for Intermolecular Aggregation and Self-Coiling

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Abstract: The emission spectra of naphthalene end-labeled poly(ethylene glycol) oligomers (N–P_n–N) in isopentane and hexane at different temperatures have been studied under stationary and nonstationary conditions. The photochemical dimerization of the end naphthalene groups of N–P_n–N has also been investigated. The results reveal that lipophobic interactions force single N–P_n–N chains to coil up at room temperature and push them together to form aggregates below −20 °C. The excimer emission dominates the fluorescence spectra of N–P_n–N at low temperature. The fluorescence depolarization measurements demonstrate the existence of energy migration inside aggregates. The glassy solutions of N–P_n–N in isopentane (77 K) show strong delayed excimer fluorescence and phosphorescence of triplet excimer. The photoirradiation yields both intermolecular and intramolecular dimerization products of the naphthalene groups. This work provides the first example to apply lipophobic interaction to expediting the formation of macrocyclic entities, including a 42-membered-ring product. The conformational difference between singlet and triplet excimers was confirmed by the experiments of formation and cleavage of the photodimers.

Introduction

In aqueous solution substances with nonpolar regions tend to associate so as to diminish the hydrocarbon–water interfacial area. This hydrophobic effect is a principal contributor to substrates binding in micelles or membranes.[1] Recent studies demonstrate that in aquaorgano binary mixtures hydrophobic interactions force molecules with long hydrocarbon chains to aggregate and self-coil.[2] The properties of these aggregates, including aggregation number, microscopic polarity, and microviscosity inside aggregates, have been investigated,[3] and self-coiling has been used to expedite the formation of macrocyclic entities from molecules with flexible chains.[4] Furthermore, it has been recently established that for linear polymers, the conformation of the polymer chain can be affected by hydrophobic interaction.[5] Curiously, "lipophobic effects" on the behavior of molecules with polar regions in nonpolar solvents were scarcely reported. Substances with poly(ethylene glycol) (PEG) chain have been widely used as surfactants. Since PEG chains play a hydrophilic role in surfactant molecules, one might expect that in nonpolar solvents lipophobic interactions could force single PEG chains to coil up or push them together and make them form aggregates. We wish to report that this is indeed the case for PEG oligomers in appropriate temperature ranges.

A variety of approaches have been employed to explore and examine the structural and dynamic features of molecular assemblies, including electron micrography, NMR, neutron scat-

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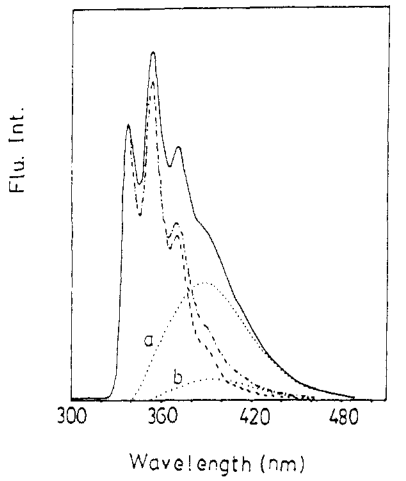

Figure 1. Fluorescence spectra of N–P_3–N (—), BN (– –), and N–M_{10}–N (–••–) in isopentane at room temperature; [N–P_3–N] = [N–M_{10}–N] = 0.5 × [BN] = 1 × 10^{-4} M; curves a and b represent the excimer emission of N–P_3–N and N–M_{10}–N, respectively.

tering, laser Raman and infrared spectroscopies, and luminescence spectroscopy. Fluorescence probe technique, such as steady-state fluorescence spectroscopy, excited-state decay analysis, time-resolved fluorescence spectroscopy, and fluorescence depolarization, have been shown to be quite effective in the investigation of the microscopic environment around a chromophore.[6] Among the many possible fluorescence chromophores pyrene has been extensively used in such techniques due to its unusually long fluorescence lifetime, its ability to form an excimer, and the sensitivity of its structured fluorescence spectrum to the polarity of the environment.[7] We anticipate that fluorescence probe techniques will also be useful in the study of fluorophore end-labeled PEG oligomer–nonpolar solvent systems. However, in these systems pyrene appears not to be a proper candidate as fluorescence probe, since its large bulk might undergo lipophilic interaction which would compensate the lipophobic interaction between the PEG chain and the solvent. Furthermore, for the pyrene end-labeled PEG oligomers, the fluorescence spectra are expected to be dominated by intramolecular excimer emission both in nonpolar and polar solvent with low viscosity because of the long fluorescence lifetime of pyrene and the short chain length of PEG oligomer. Therefore, in the present study we use naphthalene as the probe, which has a relative small bulk, reasonable fluorescence quantum yield, and photochemical reaction potential. The molecules we studied in this work have the following structures and are abbreviated as N–P_n–N: For comparison we also studied

$$N_pCOO{-}(CH_2CH_2O)_n{-}CON_p$$

$$N{-}P_n{-}N\ (n = 2, 3, 4, 5, 6, 7, 12)$$

$$(N_p = 2\text{-naphthyl})$$

the behavior of polymethylene bis(2-naphthoate) (N–M_n–N):

$$N_pCOO{-}(CH_2)_n{-}OCON_p$$

$$N{-}M_n{-}N\ (n = 5, 10)$$

$$(N_p = 2\text{-naphthyl})$$

Through the examination of excimer formation, delayed excimer fluorescence, excimer phosphorescence, fluorescence depolarization, and photochemical dimerization, we obtained the evidences for aggregation and self-coiling of N–P_n–N in nonpolar solvents. We also used aggregation and self-coiling to expedite the inter- and intramolecular photodimerization reactions of the naphthalene groups of N–P_n–N.

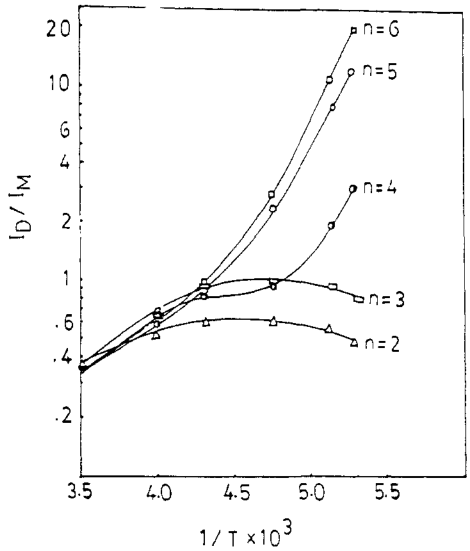

Figure 2. The plot of I_D/I_M of N–P_n–N in isopentane as a function of temperature. [N–P_n–N] = 1 × 10^{-4} M.

Results and Discussion

Fluorescence Spectra. The fluorescence spectrum of N–P_3–N in isopentane at ambient temperature, which is typical of the other naphthalene end-labeled PEG's in nonpolar solvents studied in this work, is shown in Figure 1. The fluorescence spectra of the model compounds, butyl 2-naphthoate (BN) and N–M_{10}–N, are also given in Figure 1. All of the three compounds exhibit the structured fluorescence characteristic of naphthoate monomer with maxima at 337, 352, and 375 nm and a shoulder at 390 nm. N–P_3–N shows, in addition, a long tail extending to lower energies. When the (0, 0) band of the N–P_3–N emission spectrum is normalized to the (0, 0) band of BN fluorescence spectrum and the spectrum of BN is subtracted, a structureless excimer emission band is resolved with a maximum at ca. 400 nm. At concentration below 1 × 10^{-3} M, the ratio of fluorescence intensities of excimer to monomer I_D/I_M is independent of concentration, suggesting that the excimer is intramolecular. Thus the excimer formation is attributed to the self-coiling of the PEG chain which makes the two end chromophores approach each other.

The ratios of I_D/I_M of N–P_n–N in isopentane have been measured at temperatures ranging from −90 to 45 °C and are shown in Figure 2. All of the measurements were made at constant N–P_n–N concentration (1 × 10^{-4} M). At higher temperatures the fluorescence spectra consist of predominantly monomer emission for all of the compounds. However, at lower temperatures significant differences in the behavior of N–P_n–N with long chains and those with short chains are apparent. The plots for N–P_2–N and N–P_3–N have a "high-temperature region" where I_D/I_M increases with decreasing temperature, a "low-temperature region" where I_D/I_M decreases with decreasing temperature, and an "intermediate-temperature region" where I_D/I_M reaches a maximum. This temperature dependence of I_D/I_M can be well understood by consideration of excimer formation through a dynamic process.[8] The plots for molecules with $n \geq 4$ bear an analogy to that of N–P_3–N in the high-temperature region, but below a particular temperature the ratio of I_D/I_M increases drastically with decreasing temperature. In order to clarify the reason for the intense excimer emission in the low-temperature region we examined I_D/I_M as a function of N–P_n–N concentration. As shown in Figure 3, the plot of I_D/I_M vs [N–P_n–N] displays a break, which is a typical behavior of aggregation. Thus we attribute the increase in the excimer emission at low temperature

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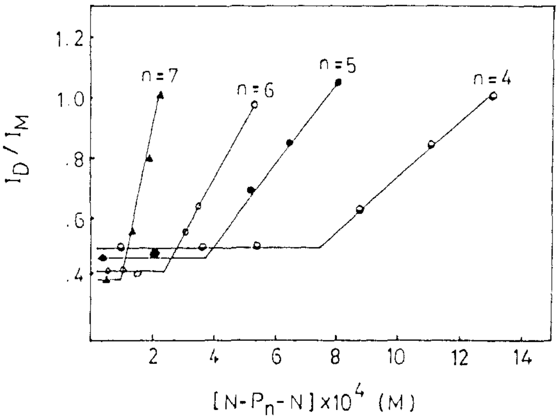


Figure 3. The plot of I_D/I_M of N-P$_n$-N in isopentane as a function of N-P$_n$-N concentration at -23 °C.

to intermolecular aggregation, which induces the enhancement of local chromophore concentration. The concentration corresponding to the break point is defined as the critical aggregation concentration (CAC). At concentration below the CAC N-P$_n$-N exists only in its monomeric form, and the excimer formation is due to self-coiling. Thus I_D/I_M is independent of [N-P$_n$-N] and is defined as R_m. Above the CAC the degree of aggregation increases with [N-P$_n$-N]. At high enough concentration the excimer mainly originates from the aggregate, and its emission dominates the fluorescence spectra.

To get information on the ground-state conformation of the chromophores within the coil and aggregate, the excitation spectra and fluorescence decay of N-P$_n$-N in isopentane solution were measured. As mentioned above, in the high-temperature region the excimer formation is due to self-coiling. The excitation spectra for the N-P$_5$-N excimer and monomer emission are identical, and the maxima correspond to that in the UV absorption spectrum, suggesting the absence of strong interaction between the naphthoate chromophores in the ground state. The emission at 335 nm decays biexponentially with lifetimes of 2 and 10 ns (x^2 = 1.13). The analysis of the decay at 400 nm yields a growth in time which corresponds to the shorter living component of the monomer region and a decay time which has the same values as the longer living component of the monomer. All these results suggest that the excimer is formed through a dynamic process.[8] Obviously N-P$_n$-N in isopentane at room temperature tends to assume the self-coiling conformation, and the two end groups are in proximity but do not associate with each other to form a sandwich pair in the ground state. Similarly, in low temperature with concentration below the CAC the excimer also originates from sefl-coiling, and the excitation spectra and fluorescence decay measurements reveal that the chromophores in the ground state do not form a sandwich pair. It is noticed from Figure 3 that at concentration below the CAC the I_D/I_M values, i.e., R_m, decrease with increasing the PEG chain length. This result is probably due to the fact that the naphthoate groups inside the coil are further diluted by the PEG chain for N-P$_n$-N with a longer chain.

In contrast, in the low-temperature region at concentration above the CAC, the excitation spectra for the monomer and for the excimer are clearly different. Figure 4 shows the excitation spectra of N-P$_5$-N (2.7 × 10^{-4} M) in isopentane solution at -23 °C for monomer and excimer emission, monitored at λ_{em} = 355 and 410 nm, respectively. The general features of the two spectra are similar. However the spectrum for the excimer is slightly but evidently red-shifted. In addition, in the fluorescence decay measurements no rising component can be detected in the excimer decay profile, suggesting that the growth in time is less than 0.2 ns (the time resolution of our instrument). These observations indicate that the excimer originates from pairs of naphthoate groups which exist prior to excitation. In other words, inside the aggregate the chromophores are in the excimer conformation in the ground state. This is confirmed by the fact that N-P$_n$-N (1 × 10^{-4} M) in isopentane glass (77 K), where the rotation of the chromophores is frozen, mainly emit excimer fluorescence.

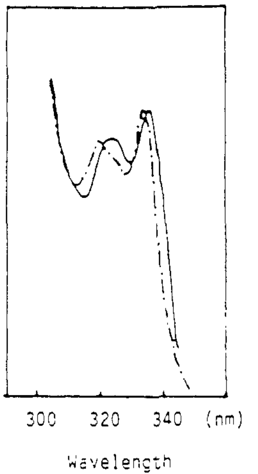


Figure 4. Excitation spectra of N-P$_5$-N in isopentane at -23 °C. [N-P$_5$-N] = 2.7 × 10^{-4} M: (-·-) monitored at 355 nm and (—) monitored at 410 nm.

The driving force for self-coiling and aggregation is probably the lipophobic interaction, since in tetrahydrofuran N-P$_n$-N emits only monomer fluorescence both at high temperature and low temperature. Furthermore, N-M$_5$-N and N-M$_{10}$-N which have the nonpolar chains show exclusively monomer fluorescence in isopentane solution at low temperature and very weak excimer fluorescence at room temperature. The lipophobic interaction occurs only when polar (lipophobic) molecules are dissolved in nonpolar medium. The N-P$_n$-N with longer PEG chains are expected to undergo greater lipophobic force and possess higher aggregating ability. This is supported by the following observations. First, at a given temperature (Figure 3) the N-P$_n$-N with longer chains have smaller CAC values and greater slopes of the lines at concentrations above the CAC. Second, at a given concentration the N-P$_n$-N with longer chains form aggregates at higher temperature (Figure 2).

Effects of Unlabeled PEG on Excimer Formation of N-P$_n$-N. To provide more evidence for aggregation we studied the effect of unlabeled PEG on the excimer formation of N-P$_n$-N in isopentane. In the low temperature and high concentration region the excimer emission dominates the fluorescence spectrum of N-P$_5$-N (Figure 5). Addition of unlabeled poly(ethylene glycol) with molecular weight of 600 (PEG 600) results in the enhancement of monomer emission and reduction in excimer fluorescence. In the presence of sufficient unlabeled PEG, the fluorescence spectrum is dominated by monomer emission. Addition of unlabeled PEG 400 shows the similar effect. Obviously this is due to the fact that unlabeled PEG coaggregates with N-P$_5$-N, and the chromophores are diluted in the coaggregate.

Fluorescence Depolarization and Singlet Energy Migration. The evidence for aggregation based on excimer formation is further strengthened by fluorescence depolarization measurements. The relative orientations of the absorption dipole and emission dipole of a chromophore in a rigid matrix are fixed, so that if the chromophore absorbs polarized radiation, its emission will retain memory of the excitation polarization. The degree of polarization, P is defined as

$$P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$$

where $I_{\parallel}$ and $I_{\perp}$ stand for the intensities of the emitted light polarized parallel and perpendicular to the polarization of the incident light, respectively. The singlet energy migration from one chromophore to another of different orientation results in depolarization. For randomly oriented chromophores the P values vary from -1/3 to 1/2. Many elegant works have proved that fluorescence polarization measurements are useful in the study of singlet energy migration beween chromophores attached to a polymer chain.[9] Similarly, the mutual chromophore separation in aggregate favors excitation migration, and the fluorescence is

Table I. P Values of N-P_n-N, N-M_n-N, and BN in Isopentane, MTHF, and Ethanol Glasses at 77 K[a]

glass	N-P_2-N	N-P_3-N	N-P_4-N	N-P_5-N	N-P_6-N	N-P_7-N	BN	N-M_5-N	N-M_{10}-N
isopentane	0.70	0.02	0.02	0.05	0.06	0.08	0.34	0.28	0.36
ethanol	0.20	0.24	0.22	0.23	0.26	0.21	0.39	0.27	0.30
MTHF	0.23	0.26	0.25	0.27	0.28	0.26	0.37	0.22	0.20

[a] λ_{em} = 355 nm, λ_{ex} = 337 nm: [N-P_n-N] = [N-M_n-N] = 0.5 × [BN] = 1 × 10^{-4} M.

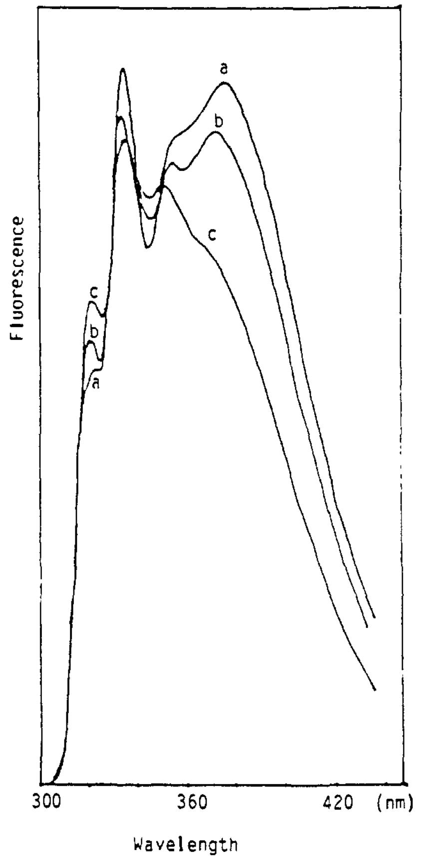


Figure 5. The effect of unlabeled PEG 600 on the fluorescence spectra of N-P_5-N in isopentane at −23 °C. [N-P_5-N] = 2.5 × 10^{-4} M, [PEG 600]: (a) 0 M; (b) 1.0 × 10^{-4} M; (c) 2.0 × 10^{-4}.

expected to be depolarized. As mentioned above, the fluorescence spectra of N-P_n-N in isopentane glass are dominated by excimer emission, but weak monomer fluorescence can still be detected. Representative P values at λ_{em} = 355 nm, λ_{ex} = 337 nm for N-P_n-N, N-M_n-N, and BN in isopentane, 2-methyltetrahydrofuran (MTHF) and ethanol glasses (77 K) are listed in Table I. In ethanol and MTHF glasses all the compounds studied in this work have the P values ranging from 0.20 to 0.39, suggesting no significant energy migration. In isopentane glass while BN and N-M_n-N show almost the same P values as in ethanol and MTHF glasses, the fluorescences of N-P_n-N are significantly depolarized, suggesting the existence of singlet excitation migration. This observation provides additional evidence for aggregate formation.

Intra- and Intermolecular Photodimerization Reactions of the End Naphthalene Groups. Photodimers of naphthalene derivatives have been known since Hammond et al. reported the intermolecular ($4\Pi_s + 4\Pi_s$) photodimerization of 2-methoxynaphthalene.[10] Photoirradiation of alkyl 2-naphthoate resulted in a "cubane-like" photodimer as the unique product (Scheme I) in spite of the fact that six isomeric dimers are formally possible.[11] This selectivity originates from two restrictions. First, the photodimerization occurs only between the substituted rings. Second, in the dimer the substituents are in the head-to-tail orientation. The photoirradiation of a bichromophoric compound, like N-P_n-N, can lead either to intra- or intermolecular reactions. The intramolecular reaction gives macrocyclic ring-closure products, while the intermolecular reaction results in polymers. Self-coiling of the chain linking the two terminal chromophores will increase the intramolecular ring-closure probability, while aggregation will enhance the intermolecular polymerization. Thus study of the photodimerization may provide evidence on self-coiling and aggregation.

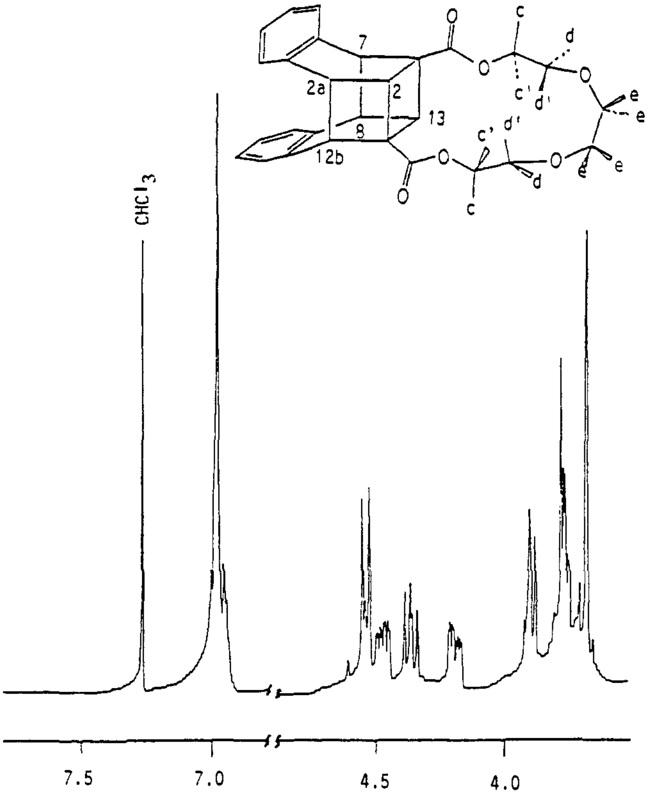
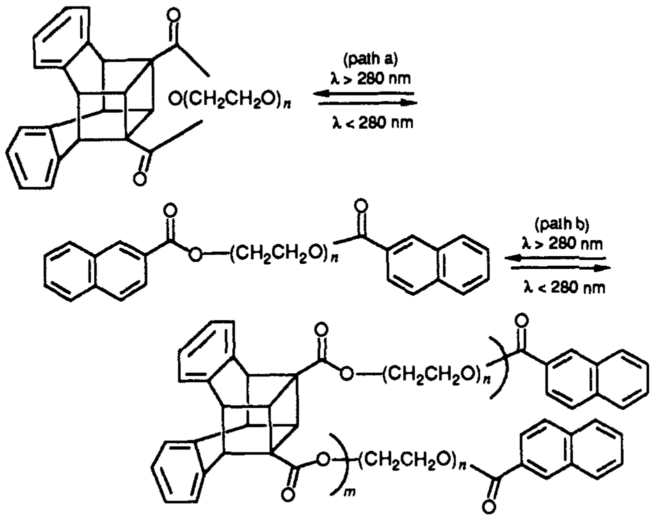


Figure 6. 400-MHz ^{1}H NMR spectrum of D_3 in $CDCl_3$.

Scheme I



Irradiation with λ > 280 nm of 1 × 10^{-4} M solution of N-P_n-N in isopentane at room temperature only leads to formation of

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Table II. Conversion of N-P$_n$-N and N-M$_{10}$-N in Isopentane and Methanol at Room Temperature after Irradiation[a]

solvent	N-P$_2$-N, %	N-P$_3$-N, %	N-P$_5$-N, %	N-P$_{12}$-N, %	N-M$_{10}$-N, %
isopentane	58	51	32	29	5
methanol	30	24	18	5	4

[a] For 0.5 h with a 450 W Hanovia lamp. The concentration of all the sample was ca. 1×10^{-4} M.

intramolecular ring-closure photodimers as shown in Scheme I (path a). No polymerization products (path b) were detected. The yields of the intramolecular products are 100% based on the consumption of the starting materials. The assignment of the intramolecular reaction relies on the observation that the *m/e* values of the molecular ion peak in mass spectra of the products are identical with those of the corresponding starting materials N-P$_n$-N. The structure proposed for the cubane-like photodimer rests mainly on its ^{1}H NMR spectrum which is in close agreement with that reported in the literature.[11] The ^{1}H NMR spectrum for the intramolecular photodimer of N-P$_3$-N is shown in Figure 6, and the spectral details and assignments for the products are given in the Experimental Section. Irradiation of N-P$_n$-N solution in methanol at the same condition gives the same products, but the quantum yields are much lower than those in isopentane. Table II gives the conversions of N-P$_n$-N and N-M$_{10}$-N in these two solvents after irradiation for 0.5 h with a 450-W Hanovia high-pressure mercury lamp in a merry-go-round apparatus. The conversions of all N-P$_n$-N in methanol are smaller than those in isopentane, particularly for N-P$_n$-N with a longer chain. Furthermore, N-M$_{10}$-N, which has a similar length but a nonpolar chain as N-P$_3$-N, shows solvent independent conversion, and the magnitude of the conversions is one order of magnitude smaller than that of N-P$_3$-N in isopentane. Obviously the high yield of N-P$_n$-N in isopentane is attributed to self-coiling of the PEG chains. The above results demonstrate the potential application of self-coiling to the synthesis of macrocyclic entities. The formation of a macrocyclic ring from a flexible chain demands a formidable price in tems of entropy.[12] In general, chemists use energetically highly favored reactions between the end groups to synthesize large-ring compounds.[13] The new approach is to use forces to reduce the entropy expense.[4] To our knowledge, the formation of the intramolecular photodimers of N-P$_n$-N in nonpolar solvents, including the 42-membered-ring photodimer of N-P$_{12}$-N, is the first example of application of lipophobic force to promoting large-ring formation.

At -25 °C irradiation of N-P$_n$-N solution in isopentane at concentration above the CAC results in polymers (path b in Scheme I) in addition to the intramolecular photodimers (path a). The polymers were obtained as a precipitate, which is soluble in tetrahydrofuran. The products were analyzed and fractionated by HPLC and identified by ^{1}H NMR and mass spectroscopies. The ^{1}H NMR spectra of the products show both the phenyl protons and the naphthalene protons in the low field, and from the ratio of these protons the degree of polymerization was determined. Intermolecular dimer and trimer were detected. The absence of a higher polymer in the products is probably due to the insolubility of the dimer and trimer in the reaction solution at the reaction temperature. They precipitated out in the course of irradiation, which prevents them from further growing. Irradiation of N-P$_n$-N solution in methanol at the same condition gives the intramolecular photodimers only, and no polymers were formed. These experimental results confirm that N-P$_n$-N in isopentane form aggregates at low temperature.

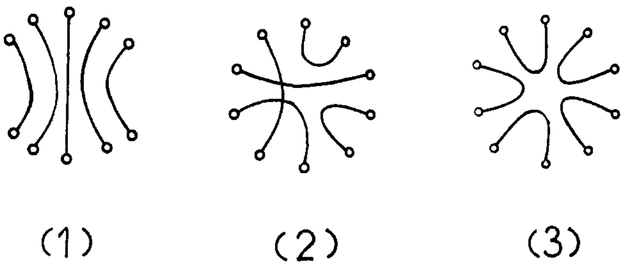

Figure 7. Schematic representation of the proposed structures of the aggregates.

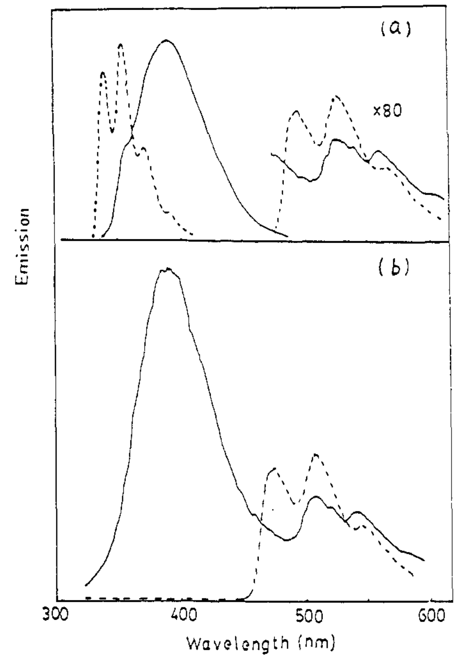

Figure 8. The emission spectra of N-P$_5$-N (—) and BN (--) in isopentane glass (77 K): (a) prompt emission and (b) delayed fluorescence and phosphorescence. [N-P$_5$-N] = 1×10^{-4} M, [BN] = 2×10^{-4} M.

The photodimerization and unlabeled PEG dilution experiments give an insight into the orientation of the molecules within the aggregates. Three plausible aggregates are shown in Figure 7. Both types 1 and 2 are consistent with the PEG dilution effect on excimer formation. However, the irradiation of N-P$_n$-N aggregate solution yielded both the inter- and intramolecular photodimers, as mentioned above. For example, for the solution of N-P$_5$-N (5×10^{-4} M) in isopentane at -25 °C the ratio of intra- to intermolecular products is roughly 1. Although the intramolecular products can be formed by the substrates located in the bulk phase, some of them originate from the aggregates. This observation supports types 3 and 2. Therefore, without further evidence we tentatively prefer type 2.

Delayed Excimer Fluorescence and Triplet Excimer Phosphorescence. Although singlet excimers of aromatic hydrocarbons have been extensively studied, until recently relatively little has been reported on triplet excimers. The main reason for this lies with the experimental difficulties. Formation of an excimer via a dynamic process requires a fluid medium. However, phosphorescence detection of a triplet excimer in fluid solutions is difficult. Lim[14] and Takemura[15] have observed the weak excimer phosphorescence from fluid solutions of naphthalene and related

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compounds, by using a homemade spectrophosphorimeter which combines the high intensity of a repetitively pulsed flash lamp (excitation source) and the high sensitivity of photon counting (detection system). To form a triplet excimer in a rigid matrix the two chromophores have to be arranged in the excimer conformation prior to excitation. Recently Burkhart[16] and Webber[17] reported the excimer phosphorescence from poly(vinylnaphthalene) in solid film and in MTHF glass, respectively.

Figure 8 shows the emission spectra of N–P_5–N, which is typical of the N–P_n–N, and the model compound BN in isopentane glass (77 K). The significant differences in both phosphorescence and fluorescence between N–P_5–N and BN are evident. First, the phosphorescence spectrum of BN is typical of monomer phosphorescence of naphthoate derivatives. The phosphorescence of N–P_5–N shifts to lower energy by about 45 nm, and its general features are analogous to the triplet excimer phosphorescence of naphthalene and related compounds reported by Lim.[14] Secondly, BN emits monomer fluorescence only, and no delayed fluorescence was detected at concentrations below 1×10^{-3} M. On the other hand, for N–P_5–N the excimer fluorescence dominates the fluorescence spectrum, although the monomer fluorescence is still observed as a shoulder. Furthermore, N–P_5–N emits intense delayed excimer fluorescence. These observations are consistent with aggregation of N–P_n–N. In the aggregate the mutual chromophore separation is expected to favor triplet and/or singlet excitation migration. Some chromophores in the aggregate might be arranged in a triplet excimer conformation (triplet excimer site), some in a singlet excimer conformation (singlet excimer site), and others in monomeric form. The singlet and triplet excimer sites may function as an energy trap in singlet and triplet energy migration, respectively. The singlet excited state of the chromophore in a triplet excimer site and monomeric conformation may undergo intersystem crossing, energy migration and give rise to monomer fluorescence. Excitation of the chromophores in singlet excimer sites exclusively leads to excimer fluorescence. Thus the singlet excimer originates from two pathways: (1) the excitation of the chromophores in singlet excimer sites and (2) the excitation of the chromophores in triplet excimer sites as well as the monomeric conformation, followed by excitation migration to a singlet excimer site. As a result, the excimer fluorescence is much stronger compared with monomer fluorescence in the prompt fluorescence emission spectra. Similarly the triplet excimer may originate from the excitation of the chromophores in triplet excimer sites followed by intersystem crossing or from the migration of the monomer triplet state which was generated at the monomeric sites. Since triplet excimer sites act as energy traps in triplet migration, the concentration of these need not be high in order to observe excimer phosphorescence. Their low concentration makes it possible that two triplet states, which are formed by intersystem crossing of singlet excited chromophores in the monomeric conformation, migrate together and annihilate each other with the creation of one singlet excited and one ground state. The resultant singlet excited state may migrate to the singlet excimer site to give rise to delayed excimer fluorescence.

It is well established[14a,18] that the conformation of the naphthalene triplet excimer is "L-shaped" or "butterfly-shaped" rather than a sandwich-pair geometry favored by the singlet excimer. In the "L-shaped" triplet excimer the long axes of the two naphthalene rings are very nearly parallel, but the short axes are highly nonparallel. To demonstrate this conformational difference between triplet and singlet excimers we carried out the following two experiments. First, we prepared an isopentane solution of the photodimer of N–P_5–N, i.e., D_5, obtained in the previous section. The solution was cooled to 77 K and subsequently reirradiated with $\lambda = 250$ nm to regenerate the naphthoates which are in sandwich-pair arrangement. The glass exhibits delayed excimer fluorescence only (no phosphorescence was detected). This observation suggests that the naphthoate groups in a sandwich-pair arrangement do not form a triplet excimer. In the second experiment, the glassy solution of N–P_5–N in isopentane (77 K) was thoroughly irradiated with $\lambda > 280$ nm so that all naphthoate groups in the sandwich-pair arrangement are transformed to the dimerization product. The resultant glass showed only triplet excimer phosphorescence and weak monomer fluorescence (no delayed excimer fluorescence was observed). These experimental results confirm that some naphthoate groups in the aggregate are in sandwich-pair arrangement, some in an L-shaped conformation, and others in a monomeric conformation, which give delayed excimer fluorescence, triplet excimer phosphorescence, and delayed monomer fluorescence, respectively.

Table III. ^{1}H NMR Data of D_2, D_3, D_5, and D_{12}[a]

δ, ppm	split	*J*, Hz	I	H
		D_2		
6.90–7.00	m		8 H	Ar
4.67	dddd		2 H	H_c
4.62	d	$J_{2a,12b} = J_{8,7}$ $= 11.5$ Hz	2 H	H_7, H_{12b}
4.32	dd	$J_{2a,12b} = J_{8,7}$ $= 11.5$ Hz $J_{2a,2} = J_{8,13}$ $= 7.2$ Hz	2 H	H_{2a}, H_8
3.97	dddd		2 H	H_c'
3.82–3.87	m		4 H	H_d, H_d'
3.79	d	$J_{2,2a} = J_{8,13}$ $= 7.2$ Hz	2 H	H_2, H_{13}
		D_3		
6.93–6.97	m		8 H	Ar
4.62	d	$J_{2a,12b} = J_{8,7}$ $= 11.7$ Hz	2 H	H_7, H_{12b}
4.46	dddd		2 H	H_c
4.32	dd	$J_{2a,12b} = J_{8,7}$ $= 11.7$ Hz $J_{2a,2} = J_{8,13}$ $= 7.7$ Hz	2 H	H_{2a}, H_8
4.18	dddd		2 H	H_c'
3.88	d	$J_{2,2a} = J_{8,13}$ $= 7.7$ Hz	2 H	H_2, H_{13}
3.82–3.87	m		4 H	H_d, H_d'
3.67	s		4 H	H_e
		D_5		
6.95–6.99	m		8 H	Ar
4.52	d	$J_{2a,12b} = J_{8,7}$ $= 11.8$ Hz	2 H	H_7, H_{12b}
4.39	dd	$J_{2a,12b} = J_{8,7}$ $= 11.8$ Hz $J_{2a,2} = J_{8,13}$ $= 7.6$ Hz	2 H	H_{2a}, H_8
4.25	m		4 H	H_c', H_c
3.86	d	$J_{2,2a} = J_{8,13}$ $= 7.6$ Hz	2 H	H_2, H_{13}
3.61–3.79	m		16 H	H_d, H_d', H_e
		D_{12}		
6.95–6.99	m		8 H	Ar
4.52	d	$J_{2a,12b} = J_{8,7}$ $= 11.8$ Hz	2 H	H_7, H_{12b}
4.39	dd	$J_{2a,12b} = J_{8,7}$ $= 11.8$ Hz $J_{2a,2} = J_{8,13}$ $= 7.6$ Hz	2 H	H_{2a}, H_8
4.30	m		4 H	H_c', H_e
3.86	d	$J_{2,2a} = J_{8,13}$ $= 7.6$ Hz	2 H	H_2, H_{13}
3.60–3.82	m		44 H	H_d, H_d', H_e

[a] Measured in $CDCl_3$, 400 MHz.

Experimental Section

Materials. Commercial ethylene glycol, diethylene glycol, triethylene glycol, poly(ethylene glycol) with molecular weights of 200 (PEG 200), 400 (PEG 400), and 600 (PEG 600), 1,5-pentanediol, 1,10-decanediol, and 2-naphthoic acid (Beijing Chemical Work) were used. 2-Naphthoyl chloride was prepared by reaction of 2-naphthoic acid with thionyl

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chloride and distilled at reduced pressure. Spectral-grade isopentane, hexane, methanol, ethanol, and tetrahydrofuran were used without further purification for emission spectrum measurements.

Naphthalene End-Labeled Poly(ethylene glycol) Oligomer (N–P$_n$–N) and Polymethylene Bis(2-naphthoate) (N–M$_n$–N). A series of poly(ethylene glycol) oligomers having a pair of 2-naphthoate groups as the chain terminals were synthesized by esterification of 2-naphthoyl chloride with poly(ethylene glycol) oligomers. For example, N–P$_3$–N was prepared as follows. To a solution of 2-naphthoyl chloride (4 g, 21 mmol) in dry benzene (20 mL) was added first triethylene glycol (1.5 g, 10 mmol) and then pyridine (2 mL) over a period of 30 min. The mixture was refluxed for 10 h and then cooled. The resulting pyridine hydrochloride was removed by filtration. Evaporation of the solvent afforded a yellow oily product. The product was purified by column chromatography on silica eluted with petroleum ether/diethyl ether (25/75, in volume), yield 3.4 g (75%). Anal. Calcd for $C_{28}H_{26}O_6$: C, 73.39; H, 5.66. Found: C, 73.39; H, 5.70. N–P$_2$–N was prepared by the same procedure as N–P$_3$–N. N–P$_4$–N and N–P$_5$–N were obtained first as a mixture from the reaction of 2-naphthoyl chloride with PEG 200 and then separated by chromatography on silica plate eluted with petroleum ether/diethyl ether (25/75). N–P$_6$–N, N–P$_7$–N, and N–P$_{12}$–N were prepared similarly from 2-naphthoyl chloride and PEG 400 and PEG 600, respectively. All of the obtained compounds were identified by IR, MS, and ^{1}H NMR spectra. They showed the same characteristic spectra: IR (KBr) 1715 (C=O), 1285 (C–O) cm^{-1}; ^{1}H NMR (CDCl$_3$) (ppm) 3.7 (m, 4(n–1)H, CH_2OCH_2–), 4.5 (t, 4 H, $CO_2CH_2CH_2$), 7.4–8.5 (m, 14 H, aromatic H). The MS spectra of all the N–P$_n$–N showed corresponding molecular ion peaks and similar fragments: 199 ($N_pCOOC_2H_4^+$), 172 ($N_pCO_2H^+$), 155 (N_pCO^+), 127 (N_p^+). N–M$_5$–N and N–M$_{10}$–N were synthesized from 1,5-pentanediol, 1,10-decanediol, and 2-naphthoyl chloride, respectively, as previously reported.[19]

Instrumentation. ^{1}H NMR spectra were recorded either at 60 MHz with a Varian EM360L or at 400 MHz with a Varian XL-400 spectrometer. MS spectra were run either on a Finigan 4021C spectrometer or on a VG ZAB spectrometer. UV spectra were measured with a Hitachi UV-340 spectrometer. Steady-state fluorescence and phosphorescence spectra were run either on a Hitachi EM 850 or a Hitachi MPF-4 spectrofluorimeter. Fluorescence decay measurements were made with a Horiba NAES-1100 single photon counting nanosecond fluorescence spectrometer. Photoirradiation products were separated by using a Varian VISTA 5500 liquid chromatograph with a Lichrosorb RP18 column. For temperature-dependent fluorescence studies the samples were thermostated by a liquid nitrogen–organic solvent slush bath.[20] Photoirradiation was carried out either at ambient temperature or in a Forma Science Circulating Bath at ca. −25 °C.

Fluorescence Measurements. The samples were purged with nitrogen for at least 30 min before measurements. The excitation wavelength was 280 nm. The spectra were fully corrected for instrumental response. Of particular interest was the excimer-to-monomer intensity ratio, I_D/I_M, calculated from the peak heights at 410 and 335 nm for excimer (I_D) and monomer (I_M), respectively. The peak heights and peak areas were proportional. For polarization measurements relatively small excitation spectral bandwidths were used. Under these excitation conditions, delayed fluorescence was less than 5% of the total fluorescence of N–P$_n$–N.

Photoirradiation and Product Analysis. Photoirradiation was carried out in a quartz reactor, and the samples were purged with nitrogen. A 450-W Hanovia high-pressure mercury lamp was used as the excitation source. Neat toluene and a K_2CrO_4 (0.1% NaOH) solution were used as filters for photodimerization and decomposition of the photodimers, respectively. After irradiation the solvents were evaporated under reduced pressure. The products were separated by using HPLC, with methanol/water (95/5) as the eluting solvent. The intra- and intermolecular products were identified by ^{1}H NMR and mass spectroscopies. The spectral details and assignments for the products of N–P$_2$–N, N–P$_3$–N, N–P$_5$–N, and N–P$_{12}$–N are given in Table III. D$_n$ refers to the intramolecular photodimer of N–P$_n$–N. It is noticed that for D$_n$ with $n \leqslant 3$ and those with $n \geqslant 4$, the NMR data for the chain protons are quite different, although the aryl and bridged protons show the similar chemical shifts and coupling constants. H$_c$ and H$_{c'}$, and H$_d$ and H$_{d'}$ in D$_2$ and D$_3$ are not magnetically equivalent, because the small ring prevents the chain from rotation, and the protons are subject to different field shielding of the carbonyl group. In a larger dimer, the chain can rotate freely, and these protons become magnetically equivalent.

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Registry No. N-P$_2$-N, 127566-71-6; N-P$_3$-N, 127580-12-5; N-P$_4$-N, 127580-11-4; N-P$_5$-N, 127288-02-2; N-P$_6$-N, 128055-76-5; N-P$_7$-N, 128055-77-6; BN, 3007-89-4; N-M$_5$-N, 85191-87-3; N-M$_{10}$-N, 100852-72-0; N-P$_{12}$-N, 128083-53-4.

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