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Enhancement of photoinduced intramolecular cross-cycloaddition of α-(9-anthryl)-ω-(1-naphthoyl) end-labeled poly(ethylene glycol) via lipophobic interactions and complexation with metal cations

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Abstract—The fluorescence spectra and photocycloadditions of poly(ethylene glycol) labeled at the chain termini with one 9-anthryl and one 1-naphthoyl group (N-P_n-A) both in non-polar and polar solvents in the presence of alkali-metal cations have been investigated. Lipophobic interactions in non-polar solvents and complexation of the polyether with cations in polar solvents force the two terminal groups of N-P_n-A into proximity, and irradiation of the solutions produces intramolecular photocyclomers to the exclusion of intermolecular products. © 2001 Published by Elsevier Science Ltd.

Although the photocycloaddition of anthracene[1–5] and that of naphthalene[2,3,6–9] have been extensively studied, relatively little has been reported on the cross-photocycloaddition between an anthracene and a naphthalene moiety.[2,3,10–16] The main reason for this is the large difference in the quantum yields between the photocycloaddition of anthracene and the cross-photocycloaddition of anthracene and naphthalene. Thus, bichromophoric molecules with anthryl as one chromophore and naphthyl as another generally undergo intermolecular anthryl-anthryl cycloaddition rather than intramolecular cross-cycloaddition upon photoirradiation.

In the present paper we report preliminary results of a study of the intramolecular photocycloaddition of bichromophoric compounds in which an anthryl and a naphthoyl group are linked by poly(ethylene glycol) chains. The molecules have the following structures and are abbreviated as N-P_n-A ($n = 4$, 5, 6), synthesized by esterification of the corresponding poly(ethylene glycol) with 1-naphthoyl chloride and then with 9-anthracenepropanoic acid.[2] The products were separated and purified by column chromatography.

$$N_p\text{-COO-}(CH_2CH_2O)_n\text{-COCH}_2CH_2\text{-}A_n$$
$$A_n = \text{9-anthryl, Np} = \text{1-naphthyl } n = 4, 5, 6$$

We will demonstrate that one can use lipophobic interactions and the complexation of the polyether chain with cations to overcome the difficulty for synthesis of naphthalene–anthracene cross-photocyclomers.

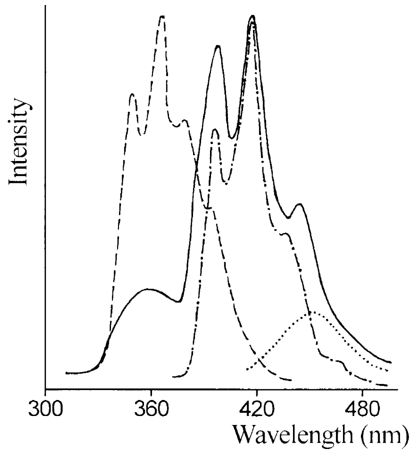

Figure 1. The fluorescence spectra of N-P_4-A (—, 2×10^{-5} M, excitation at 280 nm), N–M (– – –, 3×10^{-5} M, excited at 280 nm) and A–M (–·–·–·, 3×10^{-5} M, excited at 365 nm) in cyclohexane. The dot curve represents the intramolecular exciplex emission of N-P_4-A.

Keywords: α-(9-anthryl)-ω-(1-naphthoyl) end-labeled poly(ethylene glycol); cross-photocycloaddition between an anthracene and a naphthalene moiety; lipophobic interaction; complexation of polyether with alkali-metal ions.

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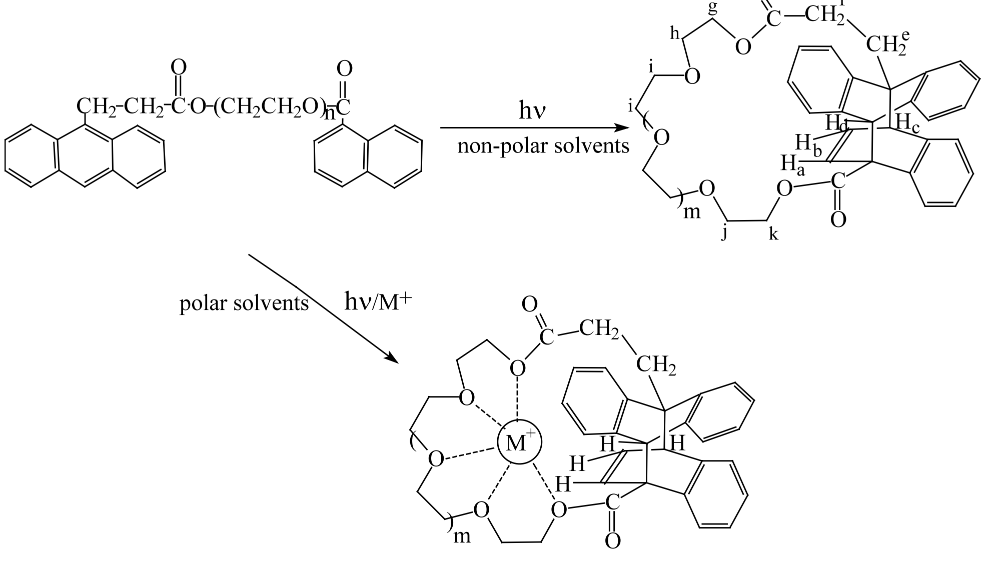
Our first approach to synthesize the cross-photocyclomers involves the use of lipophobic interactions in non-polar solvents to force the polyether chains of N-P$_n$-A to self-coil, thus, increasing the probability of end-to-end encounters.[17] Fig. 1 shows the fluorescence spectrum of N-P$_4$-A (2×10^{-5} M) in cyclohexane, which is typical of the other N-P$_n$-A studied in nonpolar solvents. The fluorescence spectra of the model compounds for anthryl (9-methylanthracene, A–M) and for naphthoyl (methyl 1-naphthoate, N–M) in cyclohexane, upon excitation at 365 and 280 nm, respectively, are also given in Fig. 1. A–M and N–M exhibit their monomer fluorescence with maxima at 395, 420 and 440 nm, and at 337, 352, 375 and 390 nm, respectively. Selective excitation of the naphthoyl chromophore at 280 nm for equimolar mixtures of A–M and N–M at concentrations below 10^{-5} M results in only the fluorescence of N–M, and no emission from anthryl was detected. On the other hand, selective excitation of the naphthoyl group in N-P$_4$-A mainly gives the emission of the anthryl chromophore, although weak fluorescence from the naphthoyl moiety is observed. The excitation spectrum for the anthryl fluorescence corresponds to the UV absorption both of the anthryl and the naphthoyl chromophores. These observations suggest that significant intramolecular energy transfer from naphthoyl to anthryl in N-P$_4$-A occurs. In addition, the fluorescence spectrum of N-P$_4$-A shows a long tail extending to the lower energy. Since the (0,0) band (at 395 nm) of the anthryl emission overlays the fluorescence of the naphthoyl, we normalized the second vibronic band (at 420 nm) of the anthryl fluorescence in N-P$_4$-A to that of A–M. Subtraction of the A–M spectrum from the spectrum of N-P$_4$-A results in the exciplex emission.[10–13] We found that even at very low concentration ($<1\times10^{-5}$ M), N-P$_4$-A shows exciplex emission, suggesting that the exciplex is intramolecular. By contrast, in polar solvents such as tetrahydrofuran, although excitation of the naphthoyl group in N-P$_4$-A resulted in the emission of the anthryl chromophore, the efficiency of the energy transfer is much smaller compared with that in cyclohexane. The ratios of the fluorescence intensities of the anthryl at $\lambda_{em}=420$ nm to the naphthoyl at $\lambda_{em}=360$ nm are 1.4 and 7.8 in tetrahydrofuran and cyclohexane, respectively. In our previous paper,[6] we demonstrated that in non-polar solvents lipophobic interactions induce flexible polar chains to self-coil. Here we attribute the enhanced intramolecular energy transfer and exciplex formation of N-P$_4$-A in cyclohexane to self-coiling of the polyether chain driven by lipophobic interactions.

Irradiation with $\lambda>280$ nm of 1×10^{-3} M solution of N-P$_n$-A in tetrahydrofuran gives the intermolecular photocyclomer of two anthryl groups. On the other hand, below 1×10^{-3} M, irradiation results in no photochemical reaction, because the lifetime of the singlet excited state of the anthryl (or naphthoyl) is not long enough to allow it to encounter the other terminal chromophore of the N-P$_n$-A molecule (intramolecular reaction) or a chromophore of another molecule (intermolecular reaction). However, irradiation of a 2×10^{-5} M N-P$_n$-A solution in cyclohexane yields the intramolecular [4π+4π] photocyclomer exclusively (Scheme 1). We have examined the absorption spectra of N-P$_4$-A as a function of irradiation time. These spectra show the absorption of both naphthoyl and anthryl chromophores. Upon irradiation, the absorption of naphthoyl and anthryl decreases concurrently. After 6 h irradiation, the conversion is close to 100%. The products were separated by HPLC. Only the intramolecular photocyclomer was obtained, and no intermolecular photocyclomer was detected. Based on the consumption of the starting material, the yield of the product is 100%. The assignment of the intramolecular reaction relies on the observation that the *m*/*z* value of the molecular ion peak of the product in the mass spectrum is identical to that of the starting material N-P$_4$-A. Furthermore, in the ^{1}H NMR spectrum of the product, no protons assignable to the naphthoyl



Scheme 1.

and anthryl groups were detected. The structure proposed for the head-to-tail (h–t) photocyclomer rests mainly on its ^{1}H NMR spectrum, which is analogous to, but different from that of the h–h photocyclomer of 1-(9-anthryl)-3-(1-naphthyl)-propane reported by Ferguson, Mau and Puza.[11,12] Similar results for the irradiation of N-P$_5$-A and N-P$_6$-A were obtained. The ^{1}H NMR and MS spectral details and assignments for the cyclomers are given in a note.[18] Obviously, the formation of the cross-photocyclomer in non-polar solvents is attributed to self-coiling of the poly(ethylene glycol) chain.

Our second strategy to synthesize intramolecular cross-photocyclomers of N-P$_n$-A involves the complexation of the polyether chain with metal ions in polar solvents. We have demonstrated that poly(ethylene glycol) chain linking two terminal naphthalene groups can complex with cations, thus the two terminal groups approach each other.[19] We expect that such complexation might also occur for N-P$_n$-A. Fig. 2 shows the fluorescence spectra of N-P$_4$-A in diethyl ether/ethanol (1:1, v/v) upon excitation of the naphthoyl chromophore at 280 nm. The structural fluorescence emissions from both naphthoyl and anthryl groups are observed in the absence of metal cations, suggesting that significant energy transfer from excited naphthoyl to anthryl groups occurs. However, the fluorescence spectrum is dominated by the naphthoyl emission. The ratio of the fluorescence intensities of the anthryl to the naphthoyl chromophores is independent of the concentration of N-P$_4$-A, indicating that the energy transfer is intramolecular. Progressive addition of LiCl, NaCl, KCl and CsCl to the solution of N-P$_4$-A in diethyl ether/ethanol (1:1, v/v) resulted in an increase in anthryl emission at the expense of the naphthoyl band, as shown in Fig. 2. These observations suggest that in the presence of a salt, the polyether chain of N-P$_4$-A indeed complexes with the alkali-metal cation. As a result, the two terminal chromophores are in proximity, thus enhancing the intramolecular energy transfer.

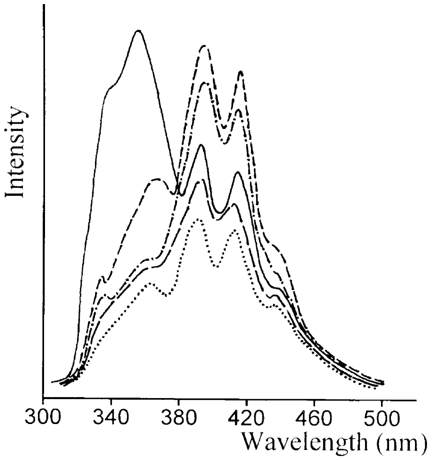


Figure 2. The fluorescence spectra of N-P$_4$-A in diethyl ether/ethanol (1:1, v/v) in the absence and presence of cations (—); ion free; (---), in the presence of LiCl; (–·–·–·), in the presence of NaCl; (– – –), in the presence of KCl; (·········), in the presence of CsCl; [N-P$_4$-A] = 2×10^{-5} M, [MCl] = 1×10^{-4} M; excitation at λ = 280 nm.

Irradiation of N-P$_4$-A solution in methanol at concentrations below 1×10^{-3} M results in no photochemical reaction as in the case in tetrahydrofuran. However, irradiation of a 2×10^{-5} M solution of N-P$_4$-A in methanol in the presence of salts leads to an intramolecular photocyclomer as the unique product (Scheme 1). The assignment of the intramolecular photocyclomer relies mainly on the MS and ^{1}H NMR spectra as mentioned above. The quantum yield of the photocyclomer is dependent on the cation size. Table 1 gives the relative quantum yields of the cross-photocycloaddition of N-P$_4$-A in methanol in the presence of various alkali-metal cations. The quantum yield in the presence of Li$^+$ is arbitrarily defined as 1.0. Evidently, Na$^+$ and K$^+$ are more effective than Li$^+$ and Cs$^+$ for enhancing the intramolecular photocycloaddition. We proposed that the polyether chain of N-P$_4$-A complexes the cations, and the size of the polyether chain in N-P$_4$-A matches Na$^+$ and K$^+$ much better than Li$^+$ and Cs$^+$. A good match between the length of the polyether chain and the size of the cation effectively makes the two chromophoric groups associate with each other and promotes the intramolecular cross-photocycloaddition.

In summary, we have successfully synthesized the anthracene–naphthalene cross-photocyclomers from bichromophoric compounds with poly(ethylene glycol) chains by using lipophobic interactions in non-polar solvents, and complexation of polyether chain with cations in polar solvents. In both cases the two terminal chromophores of N-P$_n$-A are in proximity, thus enhancing intramolecular photocycloadditoin.

Acknowledgements

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Table 1. The relative quantum yields of cross-photocycloaddition of N-P$_4$-A in methanol in the presence of alkali-metal cations. The quantum yield in the presence of LiCl is arbitrarily defined as 1.0

	In the absence of cation	Li$^+$	Na$^+$	K$^+$	Cs$^+$
N-P$_4$-A	No reaction	1.00	1.24	1.16	0.84

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18. **N-P$_4$-A**: ^{1}H NMR (CDCl$_3$), (ppm): 7.46–8.93 (16H, m, ArH), 4.54 (2H, t, NpCOOC$\underline{\mathrm{H}}_2$CH$_2$O-), 4.26 (2H, t, AnCH$_2$CH$_2$COO-C$\underline{\mathrm{H}}_2$-CH$_2$O-), 3.96 (2H, t, AnC$\underline{\mathrm{H}}_2$-), 3.86 (2H, t, NpCOOCH$_2$C$\underline{\mathrm{H}}_2$O-), 3.60 (2H, t, AnCH$_2$-CH$_2$COO-CH$_2$-C$\underline{\mathrm{H}}_2$O-), 3.64–3.75 (8H, m, -OCH$_2$-), 2.81 (2H, t, -AnC$\underline{\mathrm{H}}_2$CH$_2$COO-). MS: *m*/*z* 580 (M$^+$), 250 (AnCH$_2$CH$_2$COOH$^+$), 191 (AnCH$_2^+$), 172 (NpCO$_2$H$^+$), 155 (NpCO$^+$), 127 (Np$^+$).

    Cyclomer of N-P$_4$-A: ^{1}H NMR (CDCl$_3$), (ppm): 6.60–7.50 (12H, m, ArH), 6.20 (1H, d, H$_a$), 6.10 (1H, m, H$_b$), 5.25 (1H, s, H$_d$), 5.10 (1H, m, H$_c$), 4.35 (2H, t, H$_k$), 4.16 (2H, t, H$_g$), 3.85 (2H, t, H$_j$), 3.56–3.74 (8H, m, H$_i$), 3.54 (2H, t, H$_h$), 2.95 (2H, t, H$_e$), 2.78 (2H, t, H$_f$). (MS: *m*/*z* 580 (M$^+$), 250 (AnCH$_2$CH$_2$COOH$^+$), 191 (AnCH$_2^+$), 172 (NpCO$_2$H$^+$), 155 (NpCO$^+$), 127 (Np$^+$).

    N-P$_5$-A: ^{1}H NMR (CDCl$_3$), (ppm): 7.43–8.90 (16H, m, ArH), 4.52 (2H, t, NpCOOC$\underline{\mathrm{H}}_2$CH$_2$O-), 4.25 (2H, t, AnCH$_2$CH$_2$COO-C$\underline{\mathrm{H}}_2$-CH$_2$O-), 3.96 (2H, t, AnC$\underline{\mathrm{H}}_2$-), 3.87 (2H, t, NpCOOCH$_2$C$\underline{\mathrm{H}}_2$O-), 3.59 (2H, t, AnCH$_2$CH$_2$COO-CH$_2$-C$\underline{\mathrm{H}}_2$O-), 3.64–3.75 (12H, m, -OCH$_2$-), 2.82 (2H, t, -AnC$\underline{\mathrm{H}}_2$CH$_2$COO-). MS: *m*/*z* 624 (M$^+$), 250 (AnCH$_2$CH$_2$COOH$^+$), 191 (AnCH$_2^+$), 172 (NpCO$_2$H$^+$), 155 (NpCO$^+$), 127 (Np$^+$).

    Cyclomer of N-P$_5$-A: ^{1}H NMR (CDCl$_3$), (ppm): 6.61–7.52 (12H, m, ArH), 6.22 (1H, d, H$_a$), 6.14 (1H, m, H$_b$), 5.23 (1H, s, H$_d$), 5.13 (1H, m, H$_c$), 4.35 (2H, t, H$_k$), 4.17 (2H, t, H$_g$), 3.86 (2H, t, H$_j$), 3.60–3.72 (12H, m, H$_i$), 3.53 (2H, t, H$_h$), 2.92 (2H, t, H$_e$), 2.79 (2H, t, H$_f$). MS: *m*/*z* 624 (M$^+$), 250 (AnCH$_2$CH$_2$COOH$^+$), 191 (AnCH$_2^+$), 172 (NpCO$_2$H$^+$), 155 (NpCO$^+$), 127 (Np$^+$).

    N-P$_6$-A: ^{1}H NMR (CDCl$_3$), (ppm): 7.45–8.94 (16H, m, ArH), 4.52 (2H, t, NpCOOC$\underline{\mathrm{H}}_2$CH$_2$O-), 4.25 (2H, t, AnCH$_2$CH$_2$COO-C$\underline{\mathrm{H}}_2$-CH$_2$O-), 3.95 (2H, t, AnC$\underline{\mathrm{H}}_2$-), 3.86 (2H, t, NpCOOCH$_2$C$\underline{\mathrm{H}}_2$O-), 3.57 (2H, t, AnCH$_2$CH$_2$COO-CH$_2$-C$\underline{\mathrm{H}}_2$O-), 3.62–3.76 (16H, m, -OCH$_2$-), 2.81 (2H, t, -AnC$\underline{\mathrm{H}}_2$CH$_2$COO-). MS: *m*/*z* 668 (M$^+$), 250 (AnCH$_2$CH$_2$COOH$^+$), 191 (AnCH$_2^+$), 172 (NpCO$_2$H$^+$), 155 (NpCO$^+$), 127 (Np$^+$).

    Cyclomer of N-P$_6$-A: ^{1}H NMR (CDCl$_3$), (ppm): 6.62–7.54 (12H, m, ArH), 6.26 (1H, d, H$_a$), 6.18 (1H, m, H$_b$), 5.25 (1H, s, H$_d$), 5.13 (1H, m, H$_c$), 4.36 (2H, t, H$_k$), 4.19 (2H, t, H$_g$), 3.86 (2H, t, H$_j$), 3.60–3.78 (16H, m, H$_i$), 3.56 (2H, t, H$_h$), 2.90 (2H, t, H$_e$), 2.80 (2H, t, H$_f$). MS: *m*/*z* 668 (M$^+$), 250 (AnCH$_2$CH$_2$COOH$^+$), 191 (AnCH$_2^+$), 172 (NpCO$_2$H$^+$), 155 (NpCO$^+$), 127 (Np$^+$).
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