Excimer Phosphorescence of Naphthalene End-labelled Poly(ethylene glycol) observed in a Glass Matrix. Evidence for Aggregate Formation

Chen-Ho Tung* and Yi-Ming Wang

Institute of Photographic Chemistry, Academia Sinica, Beijing 100012, China

Naphthalene end-labelled poly(ethylene glycol) emits excimer phosphorescence and delayed excimer fluorescence in isopentane glass, and the sandwich dimer technique confirms the conformational difference between singlet and triplet excimers.

Although singlet excimers of aromatic hydrocarbons have been extensively studied, until recently relatively little had been reported on triplet excimers. The main reason for this lies with 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[1] and others[2] have observed the weak excimer phosphorescence from fluid solutions of naphthalene and related compounds, using a home-made 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. Hitherto there have been a few cases where the emission observed in a rigid glass was assigned to the triplet excimer, but later was found to originate from an impurity.[3]

We have demonstrated by photochemical and photophysical probes that in nonpolar solvents lipophobic interactions force molecules with polar chains to aggregate.[4] We anticipate that in the aggregate of lumophore-labelled molecules some chromophores may assume a triplet excimer conformation in the ground state. In a glass matrix such a triplet excimer site would show excimer phosphorescence upon excitation. Here we report that this is indeed the case for naphthalene end-labelled poly(ethylene glycol) ($N{-}P_n{-}N$) in isopentane glass (77 K).

$$N_PCOO{-}(CH_2CH_2O)_n{-}OCN_p$$
$$N{-}P_n{-}N \ (n = 2{-}7)$$
$$(N_p = \text{2-naphthyl})$$

Figure 1 shows the emission spectra of $N{-}P_5{-}N$, which is typical of $N{-}P_n{-}N$, and the model compound butyl 2-naph-

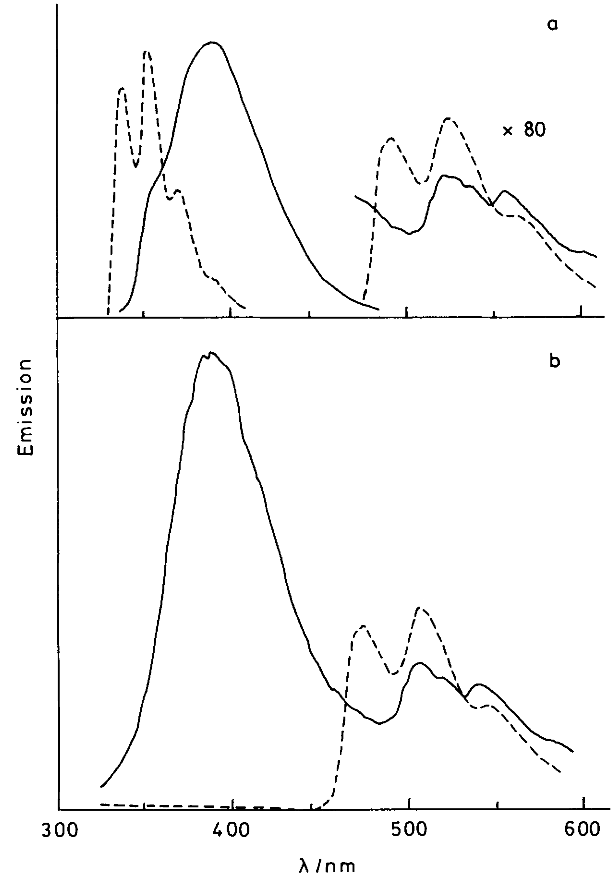
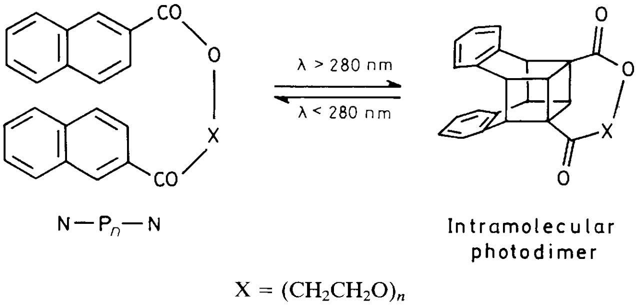


Figure 1. The emission spectra of N–P_5–N (——) and BN (---) in isopentane glass (77 K); (a) prompt fluorescence and phosphorescence; (b) delayed fluorescence and phosphorescence. [N–P_5–N] = 1×10^{-4} M, [BN] = 2×10^{-4} M.

thoate (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 the 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.[1] 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 aggregates the mutual chromophore separation is expected to favour triplet and/or singlet excitation migration. Some chromophores in aggregates might be arranged in a triplet excimer conformation (triplet excimer site), some in a singlet excimer conformation (single 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 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



Scheme 1. Intramolecular photodimerization and dissociation of N–P_n–N at room temperature.

pathways: i, the excitation of the chromophores in singlet excimer sites; ii, the excitation of the chromophores in triplet excimer sites as well as the monomeric conformation, followed by excitation migration. As a result, the excimer fluorescence is much stronger compared with monomer fluorescence in the 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 state 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[1a] that the conformation of the naphthalene triplet excimer is 'L-shaped' rather than the sandwich-pair geometry favoured 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 the conformational difference between triplet and singlet excimers, we carried out the following two experiments. First, irradiation of a solution N–P_5–N in isopentane at room temperature with $\lambda > 280$ nm yielded an intramolecular 'cubane-like' dimer[5] as shown in Scheme 1.[4] The glassy solution (77 K) of the purified dimer in isopentane was subsequently re-irradiated with $\lambda < 280$ nm to re-generate the naphthoates which are in a sandwich-pair arrangement. The glass thus obtained, exhibited delayed excimer fluorescence only (no phosphorescence was detected in the delayed emission spectra). 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 a 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.

This work was supported by the National Science Foundation of China.

Received, 23rd June 1989; Com. 9/02655J

References

1 (a) E. C. Lim, *Acc. Chem. Res.*, 1987, **20**, 8; (b) P. C. Subudhi and E. C.Lim. *J. Chem. Phys.*, 1975, **63**, 5491; (c) *Chem. Phys. Lett.*, 1974, **44**, 479; (d) S. Okajima, P. C. Subudhi, and E. C. Lim, *J. Chem. Phys.*, 1977, **67**, 4611.

2 T. Takemura, H. Baba, and Y. Shindo, *Chem. Lett.*, 1974, 1091; T. Takemura, M. Aikawa, H. Baba, and Y. Shindo, *J. Am. Chem. Soc.*, 1976, **98**, 2205.

3 J. B. Birks, 'Photophysics of Aromatic Molecules,' Wiley–Interscience, London, 1970, pp. 301—371.

4 C.-H. Tung and Y.-M. Wang, 'Lipophobic Effect on the Behavior of Poly(ethylene glycol) Oligomers in Nonpolar Solvents–Evidence for Intermolecular Aggregation and Self-coiling,' to be submitted for publication.

5 P. J. Collin, D. B. Roberts, G. Sugowdz, D. Wells, and W. H. F. Sasse, *Tetrahedron Lett.*, 1972, 321; C. Kowala, G. Sugowdz, W. H. F. Sasse, and J. A. Wunderlich, *ibid.*, 1972, 4721; T. Teitel, D. Wells, and W. H. F. Sasse, *Aust. J. Chem.*, 1976, **29**, 1783.