# Photoinduced Energy and Electron Transfer in Pyrene–Porphyrin, Porphyrin–Benzoquinone Binary Systems and the Pyrene–Porphyrin–Benzoquinone Ternary System†

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Intramolecular energy transfer (from singlet excited pyrene to porphyrin) and electron transfer (from singlet excited porphyrin to benzoquinone and then from ground state pyrene to the porphyrin cation radical) are observed in a covalently bonded pyrene–porphyrin–benzoquinone ternary system.

Recently much effort has been devoted to the study of light-induced charge separation in donor–acceptor systems.[1] The goal of these studies is not only to understand the biological reaction centres, but also to assemble artificial supramolecular systems which can duplicate functions of natural systems.[2] Recently, successful attempts have been reported.[3] In this communication, we report our results in this area. The system we studied is a covalently bonded pyrene–porphyrin–benzoquinone ternary system, which has two advantages compared to systems reported in the literature. First, the synthetic procedure is simpler, and, secondly, the compound is thermodynamically much more stable.

Connolly and Kurley[4] have studied the intermolecular quenching of the fluorescence of *meso*-tetraphenylporphyrin by benzoquinone and observed a dependence of the quenching rate on viscosity of the solvent, consistent with the findings

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† For Part 7 of the series Sensitized Photo-redox Reactions, see X. Liang (H.-K. Leung), G. Wu, M. Hu, Q. Yu, H. Shou, Y. Lin and X. Liang, *Acta Chim. Sinica, Engl. Edn.*, 1989, 277.

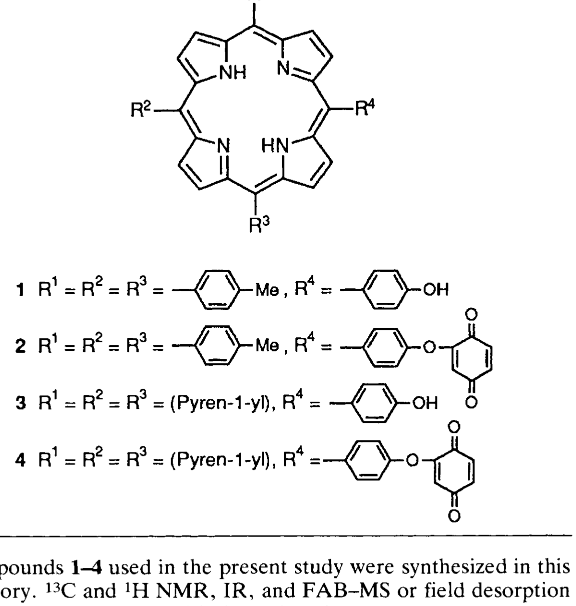
of Schmidt and coworkers[5] that refractive index is an important factor in controlling electron transfer rates. By the procedure developed by Maruyama and coworkers,[6] we synthesized the covalently bonded porphyrin–benzoquinone binary system **2** (TPP–BQ)‡ by photo-induced coupling of the mono-phenolic-TPP **1** with benzoquinone. The absorption spectra of **2** and **1** are similar. Upon irradiation at 420 nm (Soret), **1** gives intense fluorescence bands at 660 and 720 nm, while in **2**, the fluorescence was totally diminated. From data on intermolecular[4] and intramolecular systems,[7] we infer that the quenching of the fluorescence in the TPP–BQ binary system occurs *via* an electron transfer mechanism from the singlet excited porphyrin to the benzoquinone moiety.

The contribution of intermolecular energy transfer from the excited singlet state of pyrene to ground state **1** is not obvious. Shown in Fig. 1 is the fluorescence spectra of a $1.0 \times 10^{-6}$ mol dm$^{-3}$ solution of pyrene with the addition of different quantities of **1**. As the concentration of **1** increases, the emissions (380, 393 nm) of pyrene decrease as the porphyrin emissions increase. However, there is considerable absorption of **1** at 340 nm, the wavelength of excitation. By comparison with data without pyrene, we estimate the contribution of the intermolecular energy transfer process to be less than 3%. Another emission band appears at 440 nm, the nature of which is yet to be identified. The excitation spectrum of this band is exactly the same as the absorption spectrum of pyrene. We suspect this is the emission of the exciplex formed between excited pyrene and **1**. The quenching of the pyrene fluorescence by **1** follows a good Stern–Volmer relationship (coefficient of correlation = 0.993) and the quenching rate constant ($k_q$) is approaching the diffusion control value.

By a modification of the procedure of Adler and coworkers,[8] we synthesized the *meso*-tris-pyrenyl-mono-*p*-hydroxyphenyl-porphyrin **3**. The absorption spectrum indicates that the two chromophores do not interact in the ground state. By excitation at the pyrene absorption band, we observe a fluorescence due to pyrene of negligible intensity, but a very intense emission of the porphyrin, as shown in Fig. 2. (Since there is significant porphyrin absorption at this wavelength also, part of the emission recorded arises from direct excitation of the porphyrin moiety). Taking into consideration the overlap of the emission spectrum of pyrene and the absorption spectrum of porphyrin, we infer that the very efficient quenching of pyrene fluorescence occurs *via* an energy transfer mechanism from the excited singlet state of pyrene to the porphyrin moiety and the efficiency of the intramolecular energy transfer process is estimated to be around 99%, compared to around 5% (at the same concentration of the two chromophores) in the intermolecular process.

Photoinduced coupling of benzoquinone with **3** gives the pyrene–porphyrin–benzoquinone ternary system **4** (Py–P–BQ). Shown in Fig. 3 is the absorption spectrum of **4**. Excitation at the absorption band of the pyrene or the porphyrin moiety does not give any emission band of significant intensity. A preliminary study of the transient absorption spectrum indicates that there is an absorption at 460 nm 10 ns after excitation at 532 nm. This absorption is not observed if we increase the delay time to 50 ns. Both pyrene cation radical[9] and triplet porphyrin[10] have an absorption peak in this region. Taking into consideration the fact that under our experimental conditions the triplet porphyrin has a lifetime in the μs time scale[10] and that electron transfer from the excited singlet porphyrin to the benzoquinone moiety is very efficient as demonstrated in the stationary emission study of **2**, we infer that the transient absorption we observed is that of pyrene cation radical.

In conclusion, we have demonstrated that we have produced a covalently bonded pyrene–porphyrin–benzoquinone ternary system. We observed efficient energy transfer from the excited singlet state of pyrene to the porphyrin moiety,



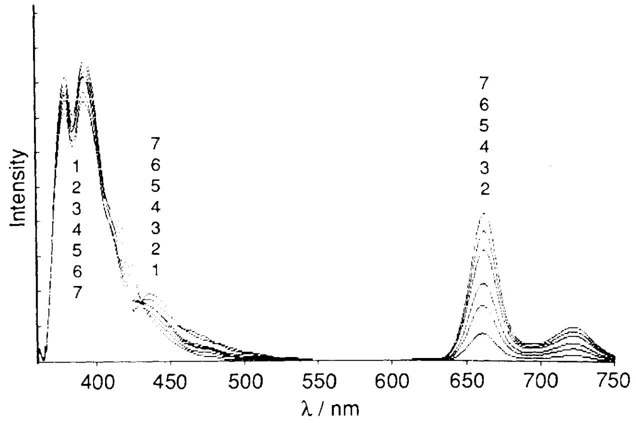


**Fig. 1** The fluorescence spectra of pyrene ($1.0 \times 10^{-6}$ mol dm$^{-3}$) in dichloromethane (excitation at 340 nm) with different concentrations of **1**: 1, 1.0; 2, $2.0 \times 10^{-7}$; 3, $4.0 \times 10^{-7}$; 4, $6.0 \times 10^{-7}$; 5, $8.0 \times 10^{-7}$; 6, $10 \times 10^{-7}$; 7, $12 \times 10^{-7}$ mol dm$^{-3}$

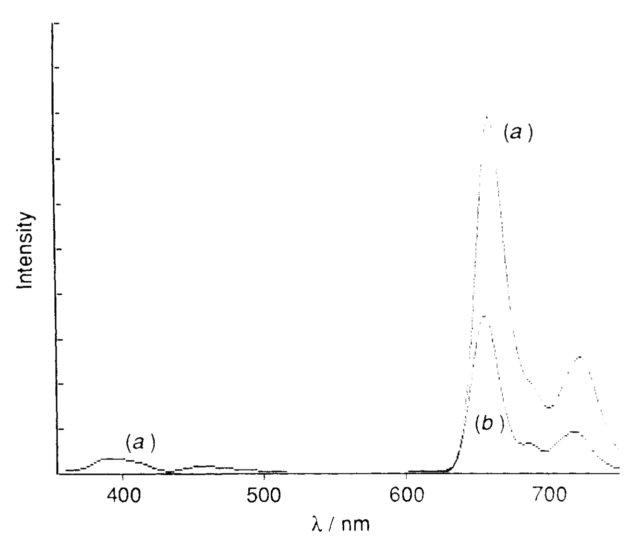


**Fig. 2** The fluorescence spectra of (*a*) compound **3** and (*b*) compound **1**; in dichloromethane ($3.3 \times 10^{-7}$ mol dm$^{-3}$); excitation at 340 nm

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‡ Compounds **1–4** used in the present study were synthesized in this laboratory. $^{13}$C and $^{1}$H NMR, IR, and FAB-MS or field desorption MS studies are in accord with the assigned structures.

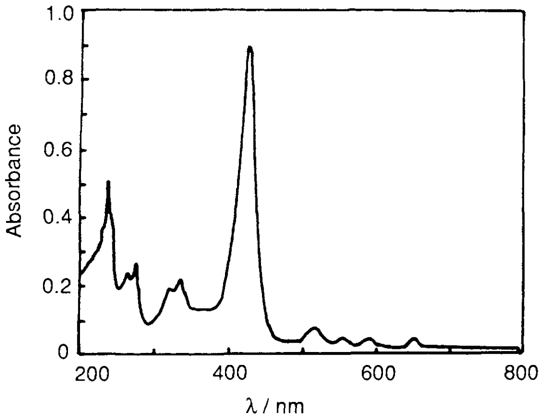

**Fig. 3** Absorption spectrum of the pyrene–porphyrin–benzoquinone ternary system **4** in dichloromethane ($3 \times 10^{-6}$ mol dm$^{-3}$)

and efficient electron transfer from excited singlet state of the porphyrin to the benzoquinone moiety, followed by electron transfer from ground state pyrene to the porphyrin cation radical. We think the easy synthetic accessibility and stability of our system merit further investigation.

We thank the partial support of this work by the National Advanced Materials Committee of China (NAMCC).

*Received, 7th November 1990; Com. 0/05000H*

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