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Pyrene-benzoylthiophene bichromophores as selective triplet photosensitizers†

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Combination of the pyrene and benzoylthiophene units constitutes an interesting approach to design bichromophoric photosensitizers with increased intersystem crossing quantum yield and enhanced selectivity. The potential of this strategy has been illustrated in the present work by using a model photoisomerization reaction.

The lowest lying triplet excited states of aromatic ketones are usually long lived and can be generated with high quantum yields. In addition, aromatic ketones have triplet energies and redox properties that enable them to induce the transformation of many substrates. Thus, excited aromatic ketones can photosensitize hydrogen abstraction from good hydrogen-donors (*i.e.* alcohols), energy transfer to aromatic compounds and polyenes or oxidation of many substrates (*i.e.* aromatic and aliphatic amines).[1] In this respect, some aspects of the photophysical and photochemical behavior of 2-benzoylthiophenes (BTs) have been previously reported.[2] It has been found that, after excitation, the triplet excited state is generated with a quantum yield close to unity. This excited state abstracts the methine hydrogen atom of isopropyl alcohol, transfers energy to dienes or oxidizes phenols and indoles. However, due to the versatility of aromatic ketones to accomplish so many reactions, on some occasions they can be insufficiently selective as triplet photosensitizers.

By contrast, pyrene has a very low triplet energy ($E_T = 2.10$ eV) and convenient redox properties ($E_{ox} = 1.16$ eV and $E_{red} = -2.09$ eV *vs.* SCE)[3] to act as a more selective triplet photosensitizer. However, though its triplet is long-lived, it is generated with low quantum yield. Therefore, pyrene has been mainly used as a singlet probe, owing to its high fluorescence quantum yield and long singlet lifetime (Φ_f *ca.* 0.65 and $\tau = 650$ ns, in non-polar solvents).[3]

With this background, it appeared of interest to explore the possibility of obtaining selective triplet photosensitizers with low triplet energy, high triplet quantum yield and suitable redox properties to behave as oxidants or reductants *vs.* many substrates. The idea is based on the possibility of enhanced triplet formation *via* exciplex formation.[4] For this purpose, the approach followed in the present work has been to use a combination of the above mentioned chromophores, BT and pyrene, in the same molecule (Fig. 1).

Herein, we wish to report on preliminary studies on the behavior of pyrene-benzoylthiophene bifunctional systems **2** and **3** (Chart 1) as photocatalysts in a typical triplet sensitized reaction: the photoisomerization of (*E*)-stilbene. The results are compared with those obtained for model compounds containing the isolated chromophores, *N*-acetyl-1-pyrenylmethylamine (**1**) and 2-benzoylthiophene (BT, **4**). They clearly show that bichromophoric compounds **2** and **3** behave as more efficient triplet photosensitizers. Time-resolved studies have provided evidence supporting that compounds **2** and **3** have a low lying triplet excited state located in the pyrene moiety, which is obtained with high triplet quantum yield in a non-polar solvent, such as 1,4-dioxane.

Pyrene derivatives [Py-NH-COCH$_3$(**1**), Py-NH-SUP (**2**) and Py-NH-TPA (**3**)] were synthesized by condensation of 1-pyrenemethylamine with the corresponding carboxylic acid [acetic acid, suprofen (SUP) or tiaprofenic acid (TPA)]. The resulting amides were purified by column chromatography and characterized by NMR spectroscopy and Mass spectrometry (see ESI†).

The UV-visible absorption spectra of bichromophoric compounds **2** and **3**, recorded in dioxane, were the composites obtained by adding the spectra of the individual chromophores. Comparison with those of Py-NH-COCH$_3$ agreed with little, if any, electronic interaction between the pyrene and BT chromophores in the ground state and indicated that at wavelength longer than 330 nm more than 99% of the excitation is absorbed by the pyrene moiety (Fig. 2).

Irradiation ($\lambda > 330$ nm) of deaerated dioxane solutions containing (*E*)-stilbene (**5**) (0.04 M) and a catalytic amount of photosensitizer **1–3** (5%) led to photostationary mixtures with 84% of (*Z*)-stilbene in all cases (Fig. 3). After 2.5 h the photoequilibrium was nearly achieved with **2** or **3** (77% and 81% (*Z*)-stilbene, respectively). The photoreaction was terminated after an additional 1.5 h of irradiation. However, with the simple pyrenyl model **1**, 21 h were needed to obtain a 79% (*Z*)-stilbene. The composition

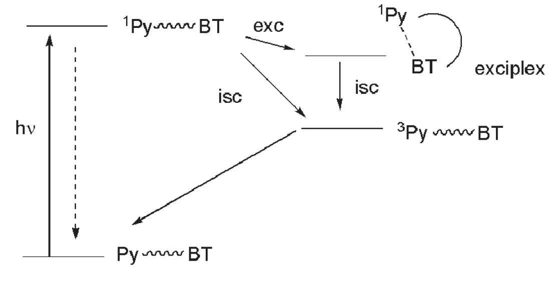

Fig. 1 Processes involved in the photoactivation–deactivation of pyrene-benzoylthiophene bichromophores. exc: exciplex formation, isc: intersystem-crossing.

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† Electronic supplementary information (ESI) available: NMR, IR, elemental analysis or HRMS and MS data for **1–3**. Also, emission spectra for **1–3** (1×10^{-3} M). See DOI: 10.1039/b510880b

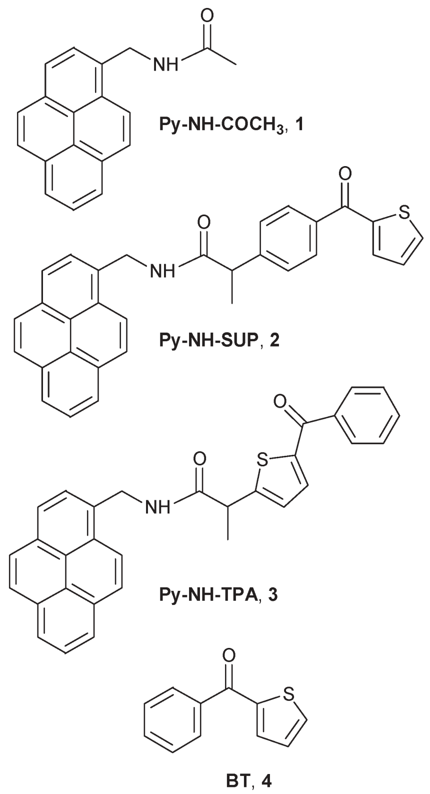


Chart 1 Photosensitizers used in the present study.

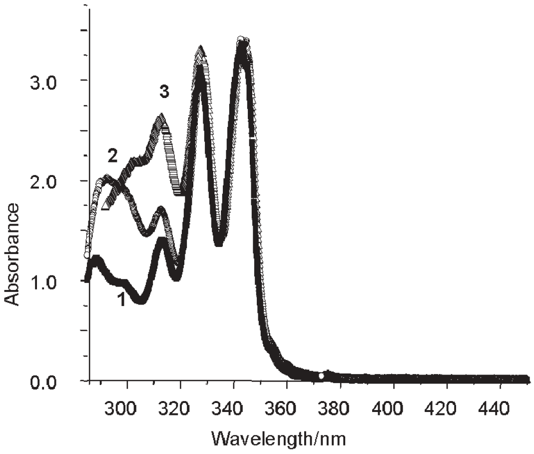


Fig. 2 Absorption spectra of **1–3** in the concentration range of 0.2 × 10^{-5}–1.2 × 10^{-5} M in dioxane.

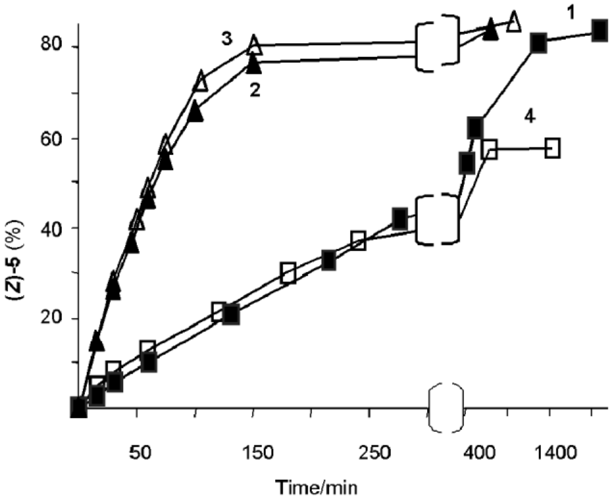
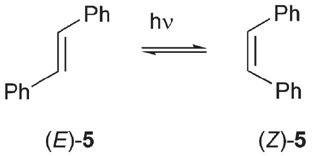


Fig. 3 A: Time-course of the *E*/*Z* isomerization of stilbene in dioxane photosensitized by bichromophores **2** (▲) and **3** (△), compared with the reference compounds **1** (□) and **4** (■).



Scheme 1 Photoisomerization of (*E*)-stilbene.

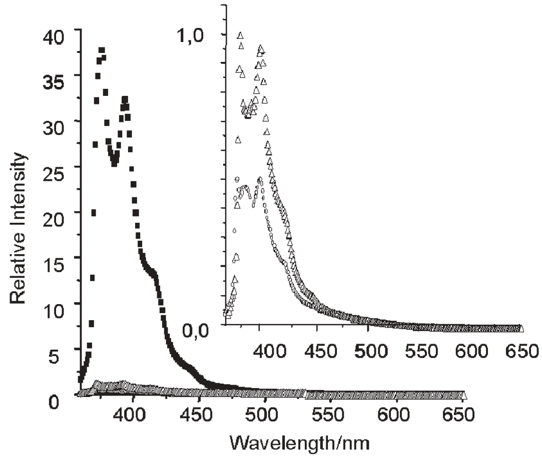


Fig. 4 Fluorescence emission spectra of **1** (■), **2** (○) and **3** (△) in nitrogen-saturated dioxane at λ_{exc} = 355 nm. Inset: magnification of the spectra for **2** and **3** above 380 nm. The concentration range was of 0.2 × 10^{-5}–1.2 × 10^{-5} M.

of the equilibrium mixture was different (57/43 *Z*/*E*) when using 2-benzoylthiophene as photocatalyst.

Steady-state fluorescence and transient absorption measurements were performed in order to explain the photobehaviour of pyrenyl compounds **1–3** as photocatalysts. The emission spectra (Fig. 4) obtained in dioxane after excitation at 355 nm showed a remarkably smaller intensity for the bichromophoric compounds, Py-NH-SUP and Py-NH-TPA, than for Py-NH-COCH$_3$, even when the absorption of the samples was adjusted to the same value (absorbance 0.3 at 355 nm). The fluorescence quantum yields were determined by a comparative method, using recrystallized quinine sulfate in 0.5 M H_2SO_4 (Φ_f = 0.546)[5] as the reference standard (Table 1). Even at the higher concentrations used for the preparative experiments on photoisomerization of (*E*)-**5**, formation of excimers was nearly negligible (see Figure S1 in ESI†).

Since the 2-benzoylthiophene chromophore, a substructure shared by SUP and TPA, has a singlet energy 0.4 eV higher than that of pyrene,[2b,6] such emission quenching cannot be attributed to singlet–singlet energy transfer from the pyrene to the BT chromophore. The free energy change, ΔG^0_{ET}, for the intramolecular electron transfer process in dioxane was estimated using the known half-wave reduction potential of BT (around −1.6 eV *vs*

Table 1 Values of ΔG^0_{ET}, ΔG^0_{ex}, quantum yields and triplet lifetimes for **1–3**

	1	**2**	**3**
ΔG^0_{ET}/eV	n.a.[a]	0.47	0.47
ΔG^0_{ex}/eV	n.a.[a]	−0.22	−0.22
Φ_{f}	0.67	0.012	0.020
Φ_{T}	0.18	0.79	0.91
τ_{T}/μs	46.5	5.0	14.4

[a] n.a.: not applicable.

SCE)[2] and half-wave oxidation potential of pyrene in the Rehm–Weller relationship[7] (eqn 1).

$$\Delta G^0_{\mathrm{ET}} = E_{\mathrm{ox}}(\mathrm{D/D^+}) - E_{\mathrm{red}}(\mathrm{A^-/A}) - E_{0,0}{}^* + 2.6\ \mathrm{eV}/\varepsilon - 0.13\ \mathrm{eV} \qquad (1)$$

where $E_{0,0}{}^*$ is the singlet energy of the pyrene chromophore (3.34 eV)[3] and ε is the dielectric constant of the solvent ($\varepsilon = 2.21$ for dioxane).

The ΔG^0_{ET} values indicate that photoelectron transfer between pyrene and BT is not thermodynamically feasible in dioxane (Table 1). However, exciplex formation (ΔG^0_{ex}) in this solvent would be favourable in the bichromophoric systems **2** and **3**, as estimated by eqn 2 using an average value of 0.75 eV for μ^2/ρ^3.[8]

$$\Delta G^0_{\mathrm{ex}} = E_{\mathrm{ox}}(\mathrm{D/D^+}) - E_{\mathrm{red}}(\mathrm{A^-/A}) - E_{0,0}{}^* - \mu^2/\rho^3\{[(\varepsilon - 1)/(2\varepsilon + 1)] - 0.19\} + 0.38\ \mathrm{eV} \qquad (2)$$

Transient absorption studies were performed for the bichromophoric compounds, and data were compared with those obtained for the simpler model (Py-NH-COCH$_3$).

Laser excitation (LFP) at 355 nm (Nd : YAG, 10 ns laser pulse) of deaerated dioxane solutions showed for all the pyrenyl compounds the typical transient absorption spectrum of the pyrene triplet (λ_{max} at 420 and 520 nm)[9] (see Fig. 5A for **3**).

Intersystem crossing quantum yields were determined for all the pyrenyl compounds by a comparative method using a deaerated acetonitrile solution of pyrene ($\Phi_{\mathrm{T}} = 0.38$)[3] with the same absorbance at the excitation wavelength. The obtained values were higher for the bichromophoric compounds than for **1** (Φ_{T}, Table 1) and the triplet quantum yield for **3** approached the unity. Since in dioxane photoelectron-transfer is thermodynamically disfavoured, exciplex formation seems to enhance nonradiative intersystem crossing to the pyrene triplet.

In addition, decay traces were monitored at 520 nm; they exhibited pseudo-first order kinetics. The triplet lifetime of the bichromophores were shorter than that of the simple pyrenyl derivative **1** (Table 1). Moreover, the intramolecular quenching rate constants were estimated using eqn 3

$$k_{\mathrm{q}}{}^{\mathrm{T}} = (1/\tau_{\mathrm{T}} - 1/\tau_{\mathrm{T}}{}^0) \qquad (3)$$

where τ_{T} and $\tau_{\mathrm{T}}{}^0$ are the pyrene triplet lifetimes in the bichromophoric compounds or in Py-NH-COCH$_3$, respectively. A remarkable regiodifferentiation was found in the triplet decay (Fig. 5B), being the quenching rate constants ratio $k_{\mathrm{q}}{}^{\mathrm{T}}{}_{(\mathrm{Py\text{-}NH\text{-}SUP})}/k_{\mathrm{q}}{}^{\mathrm{T}}{}_{(\mathrm{Py\text{-}NH\text{-}TPA})}$ of 3.8/1.

In summary, the combination of the pyrene and benzoylthiophene units as found in compounds **2** and **3** constitutes an interesting approach to design new bichromophoric photosensitizers with increased intersystem crossing quantum yield and enhanced selectivity. The potential of this strategy has been illustrated in the present work by using a test reaction as a proof of the concept.

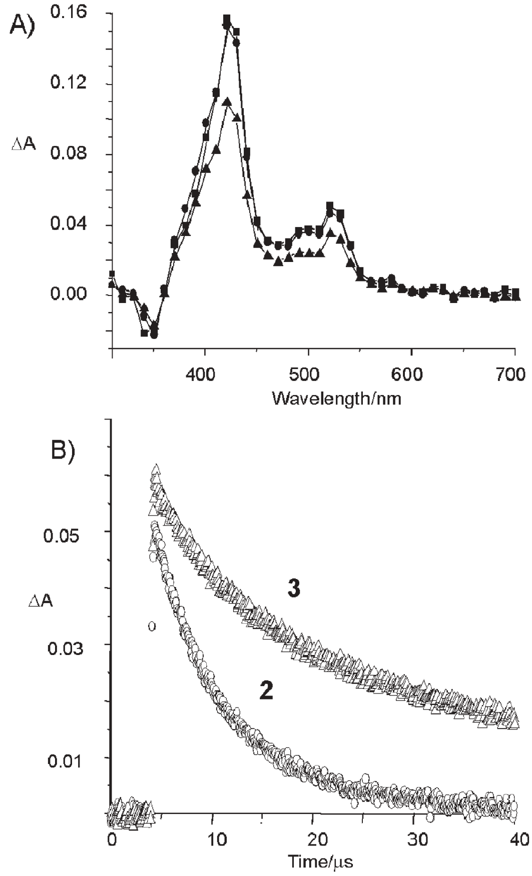


Fig. 5 A: Transient absorption spectra of **3** in deaerated dioxane (A) recorded 0.13 (■), 0.70 (●) and 3.87 (▲) μs after the laser pulse. B: Triplet decay traces (λ_{exc} = 355 nm, λ_{obs} = 520 nm) of **2** (○) and **3** (△) in deaerated dioxane.

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