

Triplet exciplexes as energy transfer photosensitisers†

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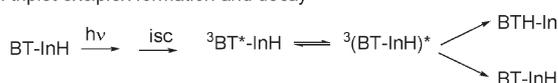
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Experimental evidence is provided for the occurrence of triplet–triplet energy transfer from benzoylthiophene–indole exciplexes to naphthalenes with a remarkable stereodifferentiation; chiral recognition is also observed in the decay of the generated naphthalene triplets.

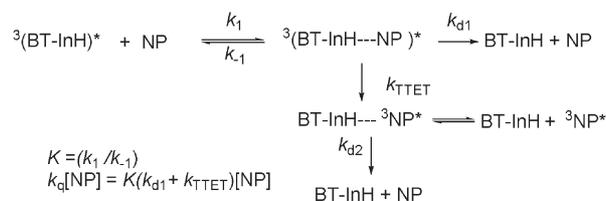
Encounter complexes (exciplexes) are well-established intermediates in emission quenching and in photoreactions such as electron or energy transfer.^{1–3} Thus, Shizuka *et al.* have studied hydrogen-abstraction, electron transfer and bond cleavage in the classical benzophenone–naphthalene (BP–NP) system and postulated the involvement of triplet exciplexes.⁴ Stereodifferentiation in the deactivation of naphthalene triplets in chiral BP–NP bichromophoric systems strongly supports the involvement of intramolecular (BP–NP)* exciplexes.⁵ Formation of exciplexes between π, π^* triplet excited ketones (such as 2-benzoylthiophene, BT) and electron-donating indoles (InHs) has been the subject of recent experimental and theoretical studies.⁶ The triplet lifetime in BT–InH bichromophoric systems **1–4** (Chart 1) is dramatically reduced, and the BTH–In biradicals derived from formal hydrogen abstraction are generated within 50 ns in acetonitrile (Scheme 1a).^{6b}

On the other hand, ternary excited singlet complexes (singlet triplexes) appear to be involved in some photoinduced transformations.^{1b,7–9} In this context, Inoue *et al.*⁹ have advantageously

a) BT–InH triplet exciplex formation and decay



b) sensitised NP triplet formation and induced decay



Scheme 1 Processes involved in the photoexcitation–deactivation of BT–InH bichromophores in the absence or in the presence of naphthalene derivatives.

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employed the formation of intra/intermolecular singlet triplexes in the enantiodifferentiating photoisomerisation of cyclooctene sensitised by optically active aryl benzenepolycarboxylates. In this case, conformational fixation of the chiral alkoxy moiety in the excited sensitizer is achieved through formation of an intramolecular exciplex, which in turn forms a structurally less flexible triplex by interaction with the substrate.

Comparatively, there are few reports on the formation of ternary excited triplet complexes (triplet triplexes).¹⁰ Thus, in the electron transfer from triethylamine (TEA) to the lowest excited triplet states of chloroanthraquinones (XAQ), the influence of TEA concentration on the decay constants of the ${}^3(\text{XAQ-TEA})^*$ exciplex and on the quantum yields of photoreduction has been explained as due to the involvement of triplet ${}^3[\text{XAQ-TEA}]_2^*$ triplexes.^{10a} To our knowledge the involvement of triplexes in triplet–triplet energy transfer (TTET) reactions has not been invoked as yet.

Focused on that target, BT–InH bichromophores **1–4** (which could provide a defined exciplex geometry in the triplet excited state) have been used in the present work as potential photosensitisers to accomplish energy transfer to naphthalene derivatives. In this case, enantio- or diastereo-differentiation phenomena in TTET could in principle be observed due to the chirality of all the reaction partners. This would be expected if triplet triplexes were indeed involved in the energy transfer process.

In addition, enantiomerically pure BT–InH bichromophores, with chiral centers proximal to both the indolic and ketone units (**1** and **2**) or only to one of them (the InH moiety as in **3** and **4**), could also provide insight into the favoured mode of approach of the partners leading to triplex intermediates.

Herein, we report experimental evidence supporting the occurrence of TTET from BT–InH exciplexes to naphthalenes. The relative quenching rate constants found for the BT–InH⋯NP

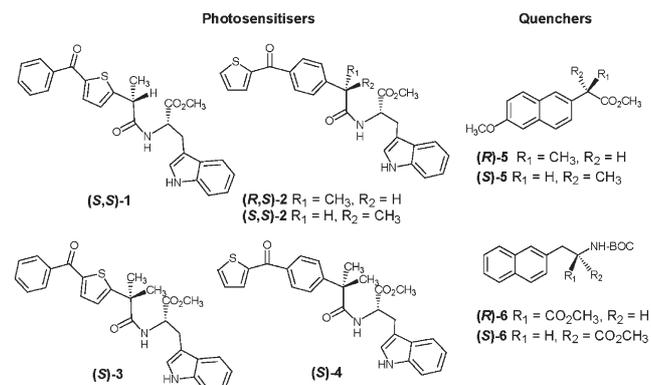


Chart 1 Structures of the BT–InH photosensitisers and NP quenchers.

diastereoisomeric pairs indicate a remarkable enantio- or diastereo-differentiation in the formation of triplet naphthalenes. Interestingly, chiral recognition is also observed for the decay of the naphthalene triplets in the diastereomeric pairs.

The known BT–InH bichromophoric compounds **1–4** were used as triplet sensitizers in triplet naphthalene formation. Laser flash photolysis (Nd:YAG, 355 nm, 10 ns pulse) of deaerated acetonitrile solutions of **1–4** ($0.7\text{--}1.1 \times 10^{-3}$ M), in the presence of increasing amounts of NP derivatives **5** or **6**, was performed at room temperature. These experiments revealed that $^3(\text{BT-InH})^*$ exciplex (E_T ca. 58 kcal mol $^{-1}$)^{6c} sensitises a relatively slow formation of NP triplet ($\lambda_{\text{abs}} = 430$ nm, E_T ca. 61 kcal mol $^{-1}$),¹¹ to the detriment of BTH–In biradical formation (see Fig. 1 for the (*R,S*)-**2**–(*R*)-**6** combination).

Kinetic traces obtained under identical conditions (room temperature, same absorbance of the sensitizer, quencher concentration, etc.) for two diastereomeric pairs, such as (*S,S*)-**1**/(*S*)-**5** and (*S,S*)-**1**/(*R*)-**5** or (*R,S*)-**2**/(*S*)-**5** and (*R,S*)-**2**/(*R*)-**5**, were compared in order to detect a possible chiral recognition in the energy transfer process. As a matter of fact, a significant diastereodifferentiation in the efficiency of NP triplet formation was observed ($\Delta A_R > \Delta A_S$). This is shown in Fig. 2 for (*R,S*)-**2**/(*S*)-**5** and (*R,S*)-**2**/(*R*)-**5** and in ESI† for other diastereomeric pairs.

To ascertain whether the stereocenter close to the ketone unit plays an essential role in the configurational dependence of NP triplet formation, similar studies were performed using (*S,S*)-**2**. In this case, a smaller effect was observed, but NP triplet formation was more efficient for (*S*)-**5** (see inset in Fig. 2). In addition, bichromophoric compound (*S*)-**4**, lacking the chiral center close to the ketone moiety, exhibited negligible enantiodifferentiation when quenched by both enantiomers of **5** at room temperature (Fig. 3b). At first sight, this appears to suggest that the approach of NP to the BT–InH exciplex is taking place mainly from the ketone side. However, it is not uncommon to find temperature dependent stereodifferentiation, which has been attributed to a significant contribution of the entropy factor in the process.^{1a} Thus, the apparent lack of configurational dependence in the (*S*)-**4**–(*S*)-**5** and (*S*)-**4**–(*R*)-**5** diastereomeric pairs is only due to the coincidence

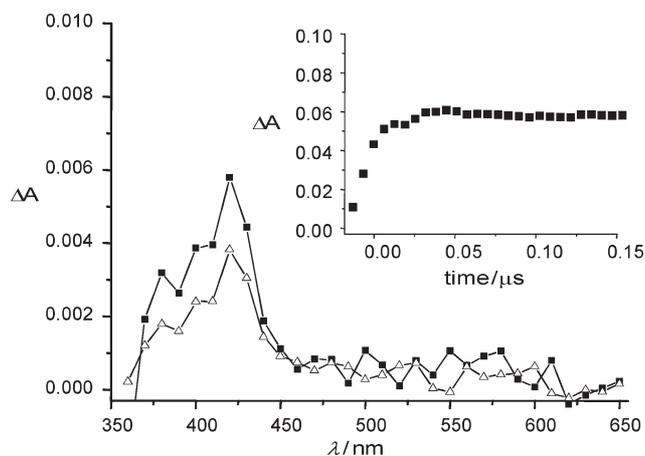


Fig. 1 Transient absorption spectra of a deaerated solution of (*R,S*)-**2** (0.7 mM) and (*R*)-**6** (9.9 mM) in acetonitrile 0.035 μs (■) and 1.0 μs (△) after the laser pulse (355 nm). Inset: transient kinetic traces recorded at 430 nm following 355 nm laser excitation, recorded at short times.

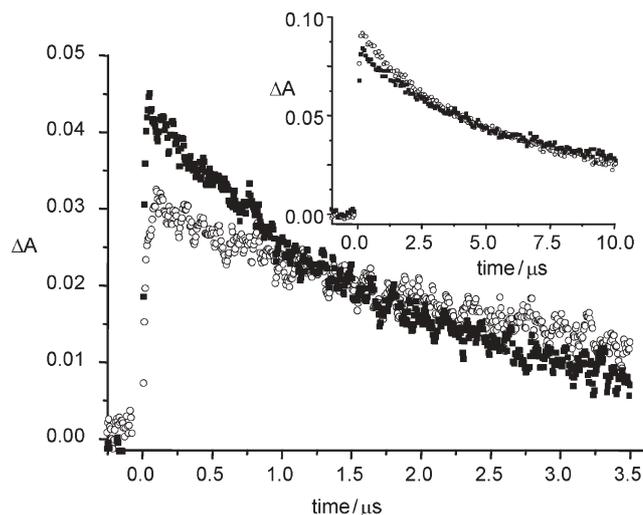


Fig. 2 Transient kinetic traces observed at 430 nm after laser flash photolysis (355 nm) of a deaerated solution of (*R,S*)-**2** (0.7 mM) containing 9.9 mM of (*R*)-**5** (■) and (*S*)-**5** (○) in acetonitrile. Inset: similar experiment with (*S,S*)-**2** and (*R*)-**5** (■) and (*S*)-**5** (○).

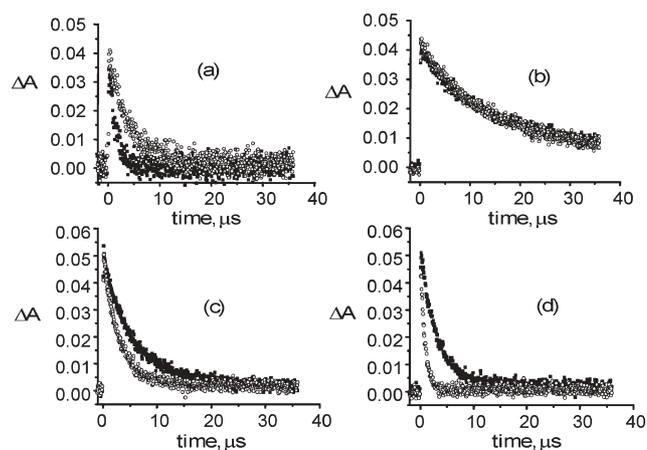


Fig. 3 Transient kinetic traces observed at 440 nm after laser flash photolysis (355 nm) of a deaerated solution of (*S*)-**4** (1.6 mM) containing 9.9 mM of (*R*)-**5** (■) and (*S*)-**5** (○) in acetonitrile at 4 °C (a), 25 °C (b) 45 °C (c) and 55 °C (d).

between room temperature and the equipodal value. Indeed, experiments performed at different temperatures confirmed such behaviour (Fig. 3a–3d).

Kinetic evaluation of the quenching process at room temperature was performed by measuring the end-of-pulse absorbance at 430 nm as a function of NP concentration. These data were plotted against each other in a double reciprocal form, according to eqn. (1), where ΔA_{430} is the absorbance of naphthalene triplets before significant decay takes place (which is proportional to the quantum yield for their formation), $k_q\tau_c$ is the Stern–Volmer parameter, and ΔA_{total} is the absorbance that would be observed if all triplets of the sensitizer were quenched by naphthalene (a constant for each diastereomeric pair).

$$1/\Delta A_{430} = 1/\Delta A_{\text{total}} + (1/\Delta A_{\text{total}}k_q\tau_c[\text{NP}]) \quad (1)$$

Table 1 Data (ΔA_{total} , $k_{\text{q}\tau_{\text{e}}}$) extracted from kinetic evaluation of naphthalene triplet formation sensitised by BT–InH bichromophores 1–4 at room temperature

BT–InH	NP	ΔA_{total}	$k_{\text{q}\tau_{\text{e}}}$	$k_{\text{q}(S)}/k_{\text{q}(R)}$
(S,S)-1	(S)-5	0.034 ± 0.001	252 ± 27	1.4
	(R)-5	0.057 ± 0.002	176 ± 11	
(S,S)-1	(S)-6	0.063 ± 0.001	232 ± 7	1.8
	(R)-6	0.077 ± 0.005	130 ± 15	
(R,S)-2	(S)-5	0.037 ± 0.001	359 ± 20	1.6
	(R)-5	0.063 ± 0.004	220 ± 20	
(R,S)-2	(S)-6	0.059 ± 0.003	245 ± 18	1.7
	(R)-6	0.099 ± 0.007	146 ± 7	
(S)-3	(S)-5	0.042 ± 0.002	145 ± 12	1.1
	(R)-5	0.040 ± 0.02	137 ± 11	
(S)-3	(S)-6	0.042 ± 0.002	267 ± 23	0.9
	(R)-6	0.040 ± 0.001	296 ± 13	
(S)-4	(S)-5	0.040 ± 0.003	260 ± 37	0.9
	(R)-5	0.039 ± 0.002	306 ± 64	
(S)-4	(S)-6	0.062 ± 0.003	177 ± 15	1.3
	(R)-6	0.071 ± 0.005	133 ± 16	

Stern–Volmer plots showed a linear dependence of $1/\Delta A_{430}$ on $1/[\text{NP}]$ at concentrations between 0.1 and 9.9 mM (see ESI† for all sensitiser–quencher combinations). The slopes provided the second-order rate constant of exciplex quenching by NP multiplied by the exciplex lifetime ($k_{\text{q}}\tau_{\text{e}}$). Table 1 lists the data obtained from the kinetic evaluation performed for all pairs.

The existence of enantio- or diastereo-differentiation becomes evident from comparison of the quenching rate constants (see $k_{\text{q}(S)}/k_{\text{q}(R)}$ ratio in Table 1) and the absorbances (ΔA_{total} , Table 1).

The significant configurational dependence is in agreement with the involvement of intermediate ternary complexes in the formation of NP triplet. Thus, quenching of the triplet excited state of bichromophoric compounds 1–4 by NPs 5 or 6 must occur in two steps: ternary ${}^3(\text{BT–InH}\cdots\text{NP})^*$ complex formation followed by decay of this intermediate to the ground state or to the localised excited NP triplet (Scheme 1b). Thus, the second-order quenching rate constant (k_{q}) must be a composite of the pre-equilibrium constant ($K = k_1/k_{-1}$) and the decay process (intrinsic energy-transfer rate constant, k_{TRET} , and decay to the ground state, k_{d1}).

A plausible explanation for the dependence of triplet naphthalene formation on the configuration of both stereocenters is provided by theoretical (DFT) calculations previously performed on this type of BT–InH exciplex.^{6c,12} Those studies support a certain degree of charge transfer from indole to BT, as well as geometries where the aromatic rings of the donor and the acceptor skew away from each other. Therefore, the quencher should approach parallel to the indole and at the same time close to the BT, establishing a BT \cdots InH \cdots NP interaction (see ESI†).

Besides, an interesting observation was that the NP triplet lifetime clearly depended on the presence of the BT–InH bichromophore. Related phenomena have been previously reported for naphthalene–benzophenone bichromophores.^{4,5}

Remarkably, chiral recognition was evident in the NP triplet decay even in those cases where the sensitiser does not have a stereocenter close to the ketone. This is very interesting taking into

account the lack of influence of indole in the quenching of NP triplet. Finally, the enantiodifferentiation factor in the decay of triplet NP 5 induced by bichromophoric compound (S)-4 was found to depend on the temperature. The lifetime ratios ($\tau_{\text{R}}/\tau_{\text{S}}$) were 0.1 (4 °C), 1.0 (25 °C), 1.8 (45 °C) and 3.9 (55 °C). The switching of enantiodifferentiation with the temperature and the higher recognition at elevated temperatures have been previously attributed to the entropy contribution.

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