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Pyrene–Benzoylthiophene Exciplexes as Selective Catalysts for the [2+2] Cycloaddition between Cyclohexadiene and Styrenes

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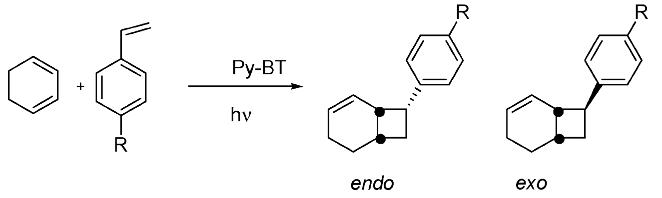
ABSTRACT



Efficient intramolecular fluorescence quenching in pyrene–benzoylthiophene systems leads to formation of exciplexes. These species interact with 1,3-cyclohexadiene (or styrenes), leading to reactive excited triplexes. The overall process affords [2+2] cross-cycloadducts with an average yield of 57%.

Cross-cycloaddition is a well-established synthetic methodology for creation of two new carbon−carbon bonds, leading to the formation of four- ([2+2]) or six-membered ([4+2]) rings. In general, these reactions are inefficient when using electron-rich dienes and olefins.[1−3]

In the reaction between cyclohexadienes (CHDs) and styrene (Sty) derivatives,[4] both [2+2] and [4+2] cross-cycloaddition, as well as olefin and diene dimerization, are usually competitive processes. The use of singlet photocatalysts ($^1C^*$), such as cyanoarenes,[4] leads mainly to the [4+2] cross-cycloadducts; their formation has been postulated to occur via ^{1}(C−Sty−CHD)* ternary excited-state complexes (singlet triplexes). Alternatively, electron-transfer photocatalysts such as triarylpyrylium salts have proved selective toward [2+2] cross-cycloaddition, upon restricted solvent election (THF), albeit with low yield (18%) and accompanied by a considerable degree of dimerization (24%).[4b] By contrast, both benzophenone triplet photosensitization and thermal treatment lead exclusively to CHD dimerization.[4a]

The pyrene (Py) chromophore is characterized by a high fluorescence quantum yield and a long singlet lifetime (ca. 0.65 and 650 ns, respectively, in nonpolar solvents).[5] Its triplet is long-lived and has a very low energy (E_T = 2.1 eV), but it is generated with low quantum yield (Φ_T ca. 0.2),[6]

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[1] Interesting exceptions of [2+2] cross-cycloadditions are: (a) photocycloaddition involving O-, N-, or S-substituted ethenes: Akbulut, N.; Schuster, G. B. *Tetrahedron Lett.* **1988**, *29*, 5125. Mattay, J.; Vondenhof, M.; Denig, R. *Chem. Ber.* **1989**, *122*, 951. Pabon, R. A.; Bellvile, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 2730. (b) The photochemical cycloaddition of C_{60} to alkyl-substituted 1,3-butadienes: Vassilikogiannakis, G.; Chronakis, N.; Orfanopoulos, M. *J. Am. Chem. Soc.* **1998**, *120*, 9911. (c) The 2-acetonaphthanone photosensitized formation of [2+2] cycloadducts of cyclohexadiene with ethylene at pressures above 10 bar: Mirbach, M. F.; Mirbach, M. J.; Saus, A. *Z. Naturforsch. B. Anorg. Chem. Org. Chem.* **1977**, *32B*, 47.

[2] Interesting exceptions of [4+2] cross-cycloadditions are the direct or photosensitized irradiation using alkoxy-substituted 1,3-butadienes or olefins: (a) Mikami, K.; Matsumoto, S.; Okubo, Y.; Fujitsuka, M.; Ito, O.; Suenobu, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **2000**, *122*, 2236. (b) Akbulut, N.; Hartsough, D.; Kim, J.-I.; Schuster, G. B. *J. Org. Chem.* **1989**, *54*, 2549.

[3] Some thermal Diels−Alder reactions are metal-catalyzed processes: Hilt, G.; Smolko, K. I. *Synthesis* **2002**, 686.

[4] (a) Hartsough, D.; Schuster, G. B. *J. Org. Chem.* **1989**, *54*, 3. (b) Martiny, M.; Steckhan, E.; Esch, T. *Chem. Ber.* **1993**, *126*, 1671.

[5] Murov, S.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1993.

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especially in nonpolar solvents. However, the covalent linking of pyrene and benzoylthiophene (BT) units leads to Py−BT bichromophoric compounds such as **3** (Figure 1).

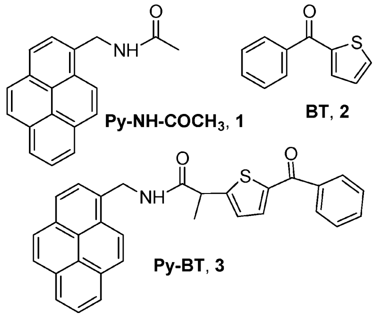
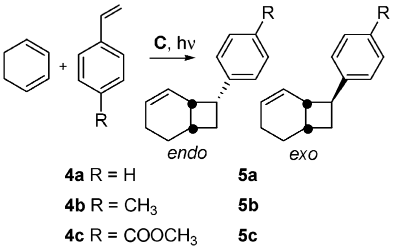


Figure 1. Photocatalysts.

Their lowest-lying triplet excited state, located in the pyrene, is generated with an enhanced quantum yield ($\Phi_T = 0.91$ in 1,4-dioxane). This has been explained by exciplex formation between the pyrene singlet excited state and the benzoylthiophene ground state.

With this background, it seemed of interest to explore whether (Py−BT)* intramolecular exciplexes could be quenched by unsaturated compounds, such as 1,3-cyclohexadiene (CHD) and styrenes (**4a**−**c**), and, if so, whether they can be used as catalysts in cycloaddition processes. We wish to report here on the preliminary results obtained with bichromophore **3** in solvents of different polarity, such as dioxane and dichloromethane (Scheme 1, Table 1). Interestingly, it will be shown that **3** photoinduces formation of the [2+2] cross-cycloadducts without competitive formation of dimers. Conversely, model compounds containing the isolated chromophores, *N*-acetyl-1-pyrenylmethylamine (**1**) and 2-benzoylthiophene (**2**) (Figure 1), lead exclusively to polymeric mixtures.

Scheme 1. Photocatalyzed [2+2] Cross-Cycloaddition between 1,3-Cyclohexadiene and Styrenes



The UV−visible absorption spectra of **3**, in dichloromethane (Figure S1 in Supporting Information) and dioxane, indicated that at a wavelength longer than 320 nm more than 99% of the excitation energy is absorbed by the pyrene moiety.

Irradiation (320 nm > λ > 360 nm) of deaerated solutions containing CHD (0.04 M), **4a**−**c** (0.1 M), and a catalytic amount of **3** (5×10^{-4} M) led to [2+2] cycloadducts **5a**−**c** (exo/endo ratio close to 2:1) as the only observable products (see Scheme 1 and Table 1 and Figure S2 in Supporting Information).[7] However, when **3** was replaced by the model compounds **1** or **2**, polymerization was extensive and only trace amounts of [2+2] cycloadducts were detected by GC. Likewise, cycloadduct formation was not observed in the absence of the photocatalyst.

Table 1. [2+2] Cross-Cycloaddition between Styrenes **4a**−**c** and 1,3-Cyclohexadiene, Photocatalyzed by Bichromophore **3**

styrene	solvent	time (h)	[2+2] cycloadduct	yield (%)
4a	dioxane	6	**5a**	45
4a	dioxane	15	**5a**	45
4b	dioxane	6	**5b**	55
4b	dioxane	15	**5b**	60
4c	dioxane	15	**5c**	40
4a	CH_2Cl_2	15	**5a**	61
4b	CH_2Cl_2	6	**5b**	68
4c	CH_2Cl_2	6	**5c**	64

Scheme 2. Processes Involved in the Photoexcitation−Deactivation of Py−BT in the Presence of CHD and **4a**

$$\begin{array}{lr}
\text{Py-BT} \xrightarrow{h\nu} {}^{1}\text{Py*-BT} & \text{(i)} \\
{}^{1}\text{Py*-BT} \xrightarrow{k_f} \text{Py-BT} & \text{(ii)} \\
{}^{1}\text{Py*-BT} \xrightarrow{k_{intra}} \text{(Py---BT)*} \longrightarrow {}^{3}\text{Py*---BT} & \text{(iii)} \\
{}^{1}\text{Py*-BT} + \text{CHD} \xrightarrow{k_{q1}} \text{Py-BT} + \text{CHD} & \text{(iv)} \\
{}^{1}\text{Py*-BT} + \mathbf{4a} \xrightarrow{k_{q2}} \text{Py-BT} + \mathbf{4a} & \text{(v)} \\
\text{CHD} + \text{(Py---BT)*} \longrightarrow \text{CHD---(Py---BT)*} & \text{(vi)} \\
\mathbf{4a} + \text{(Py---BT)*} \longrightarrow \mathbf{4a}\text{---(Py---BT)*} & \text{(vii)} \\
\begin{array}{c} \text{CHD---(Py---BT)*} + \mathbf{4a} \\ \text{or} \\ \mathbf{4a}\text{---(Py---BT)*} + \text{CHD} \end{array} \longrightarrow \mathbf{5a} & \text{(viii)}
\end{array}$$

Scheme 2 summarizes the major pathways that can in principle be involved in the reaction mechanism. The relative contributions of the different processes were determined by means of steady-state fluorescence and transient absorption measurements. For this purpose, the main deactivation pathways considered for the singlet excited state were fluorescence emission, intermolecular quenching, and intramolecular deactivation by the BT moiety (Scheme 2, ii−v). Competition among them should be governed by the respective rate constants and by the quencher concentration.

As previously observed in dioxane, the emission spectrum of **3** in dichloromethane after excitation at 355 nm (Figure 2) was remarkably weaker than that of the parent compound, although the absorption of the samples at the excitation

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(6) Pérez-Prieto, J.; Pastor-Pérez, L.; González-Béjar, M.; Miranda, M. A.; Stiriba, S. E. *Chem. Commun.* **2005**, 5569.

(7) Standard procedure: A deaerated dichloromethane solution of **4a** (0.10 M), CHD (0.04 M), and Py-BT (5×10^{-4} M) was irradiated under a nitrogen atmosphere. After solvent evaporation, the product was purified by column chromatography (using hexane as eluent).

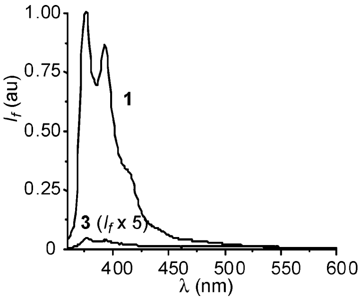

Figure 2. Fluorescence spectra of **1** (3.6×10^{-5} M) and **3** (×5) (2.5×10^{-5} M) ($\lambda_{exc} = 355$ nm) in deaerated dichloromethane.

wavelength was adjusted to the same value (0.3). In general, fluorescence quantum yields[8] were lower in dichloromethane than in dioxane (Table 2). The intramolecular quenching rate constant (k_{intra}) was estimated as 8.3×10^8 s^{-1} using eq 1

$$k_{intra} = (1/\tau_f - 1/\tau_f^{\,0}) \qquad (1)$$

where τ_f and $\tau_f^{\,0}$ are the pyrene singlet lifetimes in the bichromophoric compound **3** and in **1**, respectively.

Because the 2-benzoylthiophene chromophore has a singlet energy 0.43 eV higher than that of pyrene,[9] 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 dichloromethane was estimated using the known half-wave reduction potential of BT (around −1.6 eV vs SCE)[10] and the half-wave oxidation potential of pyrene (1.16 eV vs SCE) in the Rehm−Weller relationship[11] (eq 2).

$$\Delta G^0_{eT} = E_{ox}(D/D^+) - E_{red}(A^-/A) - E_{0,0}^* + 2.6\ \text{eV}/\epsilon - 0.13\ \text{eV} \qquad (2)$$

where $E_{0,0}$* is the singlet energy of the pyrene chromophore (3.3 eV).

Contrary to the case of dioxane, the ΔG^0_{eT} value (Table 2) indicates that photoelectron transfer between pyrene and BT in dichloromethane is now a thermodynamically feasible process.

Table 2. Values of ΔG^0_{eT}, ΔG^0_{exc}, Singlet and Triplet Quantum Yields, and Singlet Lifetimes for **1** and **3** in Dioxane and Dichloromethane[a]

	1 dioxane[b]	**1** CH_2Cl_2	**3** dioxane[b]	**3** CH_2Cl_2
ΔG^0_{eT}	na	na	0.47	−0.42
ΔG^0_{exc}	na	na	−0.22	–
Φ_f	0.67	0.30	0.02	0.01
τ_f	133.3	130.0	2.4	1.2
Φ_T	0.18	0.70	0.91	0.99

[a] Units: ns (τ_f), eV (ΔG^0). [b] From ref 6. [c] na: not applicable.

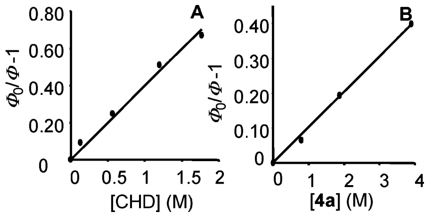

Figure 3. Stern−Volmer plots for fluorescence quenching of **3** (2.5×10^{-5} M) in dichloromethane by (A) CHD and (B) **4a**.

The fluorescence rate constant (k_f) and the intramolecular quenching rate constant (k_{intra}) are intrinsic properties of **3**. The value of the former was calculated with eq 3 and found to be $k_f = 8.3 \times 10^6$ s^{-1}.

$$\tau_f k_f = \Phi_f \qquad (3)$$

The fluorescence quenching of **3** by styrene and 1,3-cyclohexadiene was examined in dichloromethane. Indeed, the emission ($\lambda_{exc} = 350$ nm, $\lambda_{em} = 360{-}650$ nm) of **3** was efficiently quenched by CHD and **4a** with rate constants $k_{q1} = 4.0 \times 10^8$ M^{-1} s^{-1} and $k_{q2} = 0.9 \times 10^8$ M^{-1} s^{-1}, respectively. These values were obtained from the Stern−Volmer analysis (Figure 3A and B), according to eqs 4 and 5, using the singlet lifetime measured for **3** ($\tau_f^{\,0} = 1.2$ ns).

$$\Phi_f^{\,0}/\Phi_f - 1 = \tau_f^{\,0} k_{q1}[\text{CHD}] \qquad (4)$$

$$\Phi_f^{\,0}/\Phi_f - 1 = \tau_f^{\,0} k_{q2}[\mathbf{4a}] \qquad (5)$$

From these data, using eqs 6−10, a very minor contribution of the pyrene singlet excited state to the cycloaddition should be expected under the employed reaction conditions.

$$k_s = k_f + k_{intra} + k_{q1}[\text{CHD}] + k_{q2}[\mathbf{4a}] \qquad (6)$$

Residual fluorescence:

$$k_f/k_s = 0.01 \qquad (7)$$

Intramolecular fluorescence quenching:

$$k_{intra}/k_s = 0.96 \qquad (8)$$

Fluorescence quenching by CHD:

$$k_{q1}[\text{CHD}]/k_s = 0.01 \qquad (9)$$

Fluorescence quenching by **4a**:

$$k_{q2}[\mathbf{4a}]/k_s = 0.02 \qquad (10)$$

Transient absorption studies were performed to check whether the pyrene triplet excited state may be involved in the catalytic process. Laser excitation of **3** at 355 nm (Nd:YAG, 10 ns laser pulse) of deaerated dichloromethane solutions showed for **3** (as in dioxane) the typical transient absorption spectrum of the pyrene triplet[12] with maxima at 420 and 520 nm (see Figure 4A).

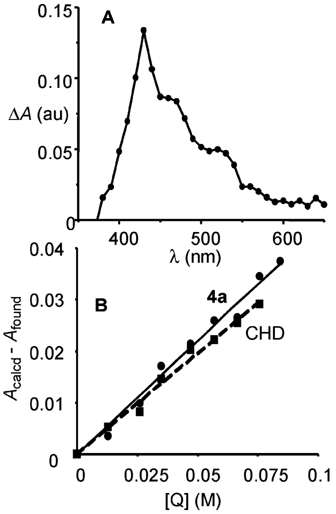

Figure 4. (A) Transient absorption spectrum of **3** in deaerated dichloromethane, recorded 200 ns after the 355 nm laser pulse. (B) Decrease of the triplet absorbance (measured at 420 nm inmediately after the laser pulse) in the presence of increasing amounts of **4a** and CHD.

The intersystem crossing quantum yield was even higher than in dioxane (Φ_T 0.99 vs 0.91[13]). Therefore, in both dioxane and dichloromethane a dramatic enhancement of intersystem crossing to the pyrene triplet (necessarily arising from the exciplex, route iii in Scheme 2) was observed in the bichromophore. Thus, no evidence for electron transfer within the Py−BT system was detected.

Interestingly, the triplet absorbance was markedly reduced in the presence of increasing amounts of CHD or **4a**. If the action of these quenchers was only limited to their interaction with the measured pyrene singlet excited state, the theoretical A_{calcd} value in the presence of the quencher could be calculated using eq 15, taking into account the expected pyrene singlet deactivation (eqs 11−14) for each quencher concentration.

$$k_s = k_f + k_{intra} + k_q[Q] \tag{11}$$

Residual fluorescence:

$$k_f/k_s \tag{12}$$

Intramolecular quenching of fluorescence:

$$k_{q1}/k_s \tag{13}$$

Quenching of fluorescence by Q:

$$k_q[Q]/k_s = y \tag{14}$$

$$A_{calcd} = A_o - yA_o \tag{15}$$

However, triplet formation could also be prevented via quenching of the exciplex by CHD or **4a**. In this case, the difference $A_{calcd} - A_{found}$ would be proportional to the quencher concentration (eq 16).

$$A_{calcd} - A_{found} = K[Q] \tag{16}$$

Indeed, a linear relationship was found for both quenchers (Figure 4B). This result confirms deactivation of the exciplex by the unsaturated compounds (Scheme 2, vi and vii).

These observations, together with the chemoselectivity toward [2+2] cross-cycloaddition, contrast with the results obtained with pyrylium salts and benzophenone and therefore constitute clear evidence against the involvement of either the cyclohexadiene radical cation or ^{3}CHD in the cycloaddition photocatalyzed by **3**. Accordingly, only polymerization products were obtained when using either **1** or **2** as the photocatalyst.

In summary, pyrene−benzoylthiophene systems act as selective photocatalysts in the cross-cycloaddition between CHD and styrenes. The concept is based on the efficient generation of intramolecular exciplexes, quenchable by unsaturated compounds to form reactive excited triplexes. The obtained [2+2] products are of synthetic interest, given the wide distribution of bicyclo[4.2.0]octanes in nature and the inherently difficult synthesis of these strained compounds.[14]

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Supporting Information Available: NMR spectra (crude after steady-state irradiation, compounds **5** and **4c**) and details of the characterization of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Weller, A. *Z. Isr. J. Chem.* **1970**, 259.

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(13) The triplet quantum yield was determined for **3** by a comparative method using a deaerated acetonitrile solution of pyrene ($\Phi_T = 0.38$) with the same absorbance at the excitation wavelength.

(14) Lee-Ruff, E.; Mladenova, G. *Chem. Rev.* **2003**, *103*, 1449.