

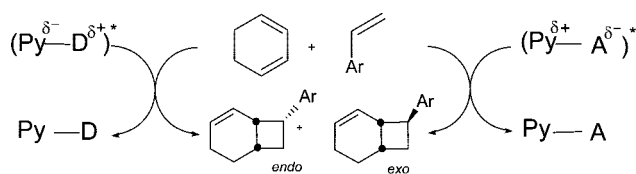
Pyrene–Indole Exciplexes as Positive Photocatalysts

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Photoinduced charge separation in pyrene-based bichromophoric systems provides an effective strategy in organic synthesis, as shown for the [2 + 2] cycloaddition between 1,3-cyclohexadiene and styrenes as a model reaction.

Bichromophoric compounds have attracted considerable interest during the last decades. They have been used as models for the study of a variety of processes, including (i) drug photo-binding to proteins, lipids, and nucleic acids,¹ (ii) photoinduced electron and energy transfer as well as its implications in photosynthesis, development of molecular devices, etc.,² and (iii) chiral recognition in the intramolecular interactions in the excited state.³ They have also found application as ultraviolet stabilizers, to avoid UV degradation of organic compositions (such as polymers), and as effective systems for photodynamic therapy.^{4,5}

Light is an innocuous reagent, which can be used to induce the selective transformation of substrates under very mild

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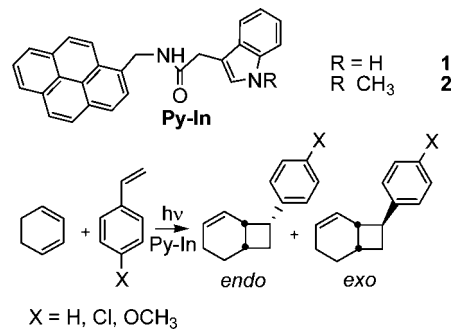
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SCHEME 1. Photocatalyzed [2 + 2] Cross-Cycloaddition between 1,3-Cyclohexadiene and Styrenes



conditions. In the framework of sustainable chemistry, special interest has been focused on photocatalyzed reactions.⁶ In many cases, the role of the photocatalyst (PC*) is to induce charge separation when interacting with substrates, generating intermediate species which finally give rise to the products.

The use of bichromophoric compounds as photocatalysts remains almost unexplored. It has recently been demonstrated that a donor–acceptor (D–A) bichromophoric system, such as pyrene–benzoylthiophene (Py–BT), behaves as a selective photocatalyst for the [2 + 2] cycloaddition between cyclohexadiene (CHD) and styrene (Sty).⁷

We are currently involved in a program aimed at knowledge-oriented production of effective positive photocatalysts. Unlike most photocatalytic processes, focused on photodegradation of pollutants to manage environmental problems, the term “positive photocatalysis” has been coined for applications of the concept with synthetic purposes.⁸ In this context, we wish now to report on the studies dealing with pyrene–indole (Py–In, **1** and **2**, Scheme 1) bichromophores, in which Py would act as the acceptor moiety. In fact, excitation of pyrene/indole intermolecular systems (Py/In) gives rise to charge-separated Py^{•-}/In^{•+} radical ion pairs, which lead to the neutral radical pairs after proton transfer.⁹ The goal of the present study is to investigate if (Py^{δ-}···In^{δ+})* intramolecular exciplexes, as already reported for analogous systems such as (Py^{δ+}···BT^{δ-})*, can induce [2 + 2] cycloaddition using CHD and Sty as model reaction partners. It will be shown that both bichromophoric compounds **1** and **2** actually photocatalyze formation of the [2 + 2] cross-cycloadducts in yields which strongly depend on the nature of the solvent. Steady-state and time-resolved studies have provided information on the involved mechanism.

The shape of the UV–visible absorption spectra of **1** and **2** at λ > 320 nm (Figure S1 in Supporting Information) was similar to that of 1-methylpyrene¹⁰ and *N*-(pyren-1-ylmethyl)acetamide (Py–Ac), which agrees with little, if any, electronic interchromophoric interaction in the ground state. In addition, more than

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TABLE 1. Photocatalytic Studies with Bichromophoric Compounds 1 and 2

run	PC	time h	X	[PC] 10 ⁻⁴ M	[CHD] 10 ⁻² M	[Sty] 10 ⁻¹ M	cycloadduct yield ^a		
							dioxane	THF	MBOH
1	Py	12	H	5	4	1	8 (2.0)	4 (2.0)	9 (2.1)
2	1	6	H	5	4	1	5 (2.3)	14(2.3)	21(2.4)
3	1	12	H	5	4	1	11(2.0)	33(2.2)	49 (2.2)
4	1	6	H	5	25	1			10 (2.1)
5	1	6	H	5	4	3			31 (2.5)
6	1	6	Cl	5	4	1			21 (2.3)
7	1	12	Cl	5	4	1			41 (2.3)
8	1	6	CH ₃ O	5	4	1			20 (2.5)
9	2	6	H	5	4	1			25 (2.5)
10	2	12	H	5	4	1			60 (2.5)
11	2	6	H	5	25	1			16 (2.0)
12	2	12	Cl	5	4	1			46 (2.3)

^a Given as percentages: *exo/endo* ratio in parentheses.

99% of the excitation at wavelength longer than 320 nm will be absorbed by the pyrene moiety.

Deaerated solutions containing CHD (0.04 M), styrenes (0.1 M), and a catalytic amount of **1** (5×10^{-4} M) were irradiated (320 nm > λ > 360 nm) for 6 and 12 h in solvents of different polarity, such as dioxane, THF, and 2-methyl-2-butanol (MBOH); see runs 1–8 in Table 1. The [2 + 2] cycloadducts were the only detected products; their yields were strongly dependent on the solvent. The best results were obtained in MBOH, and the yields increased with irradiation time (compare runs 2 and 3 in Table 1). Comparatively, Py led to very low yield of cycloadducts after 12 h of irradiation (see run 1 in Table 1). Bichromophore **2** showed higher efficiency than **1** in formation of the cycloadducts (compare runs 3 and 10 in Table 1), indicating that the N–H bond is not responsible for the photocatalytic behavior of **1**. Under the irradiation conditions used for the photocatalysis studies, both **1** and **2** were photostable.¹¹ Interestingly, photocycloaddition occurred with less than 5% yield when using acetonitrile as solvent, where electron transfer from indole to pyrene, rather than exciplex formation, would be favored.

At this point, it must be taken into account that singlet photocatalysts (¹PC*), such as cyanoarenes,¹² lead to the [4 + 2] cross-cycloaddition (postulated to occur via ¹PC*/Sty/CHD ternary excited-state complexes, singlet triplexes). By contrast, [2 + 2] cross-cycloadducts (only one example reported involving styrene and CHD as reagents) are obtained when using triarylpyrylium salts as electron transfer photocatalysts, albeit with low yield (18%) and accompanied by a considerable amount of CHD dimers (24%).¹³ Interestingly, the Py(A)–In(D) bichromophores, like Py–BT systems, lead to selective formation of the [2 + 2] cycloadducts; that is, no CHD dimer formation is observed. Moreover, the *exo*-isomer is the predominating isomer using either triarylpyrylium salts or the Py-based bichromophores. The highest stereoselectivity has been found for the triarylpyrylium salt and for Py–In (*exo/endo* ratio ca. 2.5). Although the reasons for the [2 + 2] selectivity associated with bichromophore-derived exciplexes is not yet clear, it has to be

(11) By contrast, when pyrene in isooctane is irradiated in the presence of indole, bleaching of the Py absorption and the appearance of a new broad red-shifted absorption are observed at short time irradiation (less than 60 min). It has been proposed that this occurs by combination of pyrene and indole radicals (ref 8).

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TABLE 2. Photophysical Properties of Compounds 1 and 2 Compared with Pyrene^{a,b}

		dioxane	THF	MBOH
		1	Φ_f^c	0.46
	τ_f	210	91	39
	ΔG_{exc}	0.075 (7.2) ^b	–0.063 (–6.1) ^b	–0.043 (–4.2) ^b
2	Φ_f^c	0.33	0.043	0.115 (41% exciplex)
	τ_f			40
	ΔG_{exc}	0.125 (12.1) ^b	–0.013 (–1.3) ^b	0.007 (0.7) ^b
Py	Φ_f^c	0.65	0.65	0.73
	τ_f	295	211	284

^a Units: τ_f (ns), ΔG (eV). ^b Values in parentheses are given in kJ/mol. ^c Determined by a comparative method, using recrystallized quinine sulfate in 0.5 M H₂SO₄.

related to the spatial constraints imposed by intramolecular exciplex formation.

To gain insight into the photocatalytic behavior of the pyrene–indole systems, steady-state fluorescence as well as time-resolved fluorescence and transient absorption measurements were performed in the different solvents. The emission spectra of **1** (Figure S2 in Supporting Information) obtained after excitation at 313 nm (samples adjusted to 0.1 absorbance at this wavelength) showed a dramatic decrease of the fluorescence quantum yield in MBOH and THF, as compared with the emission in dioxane (which was close to that of pyrene in this solvent); see Table 2.

Since no ground-state complex was detected in the UV–visible spectrum, this effect should be due to the intramolecular quenching of the pyrene singlet excited state (¹Py*–In) by the indole moiety (dynamic intramolecular quenching). In agreement, the ¹Py* lifetime in ¹Py*–In was drastically diminished, from several hundreds of nanoseconds in dioxane to ca. 39 ns in MBOH.

The quenching rate constant (k_{intra}) was estimated using eq 1 where τ_f and τ_f^0 are the fluorescence lifetimes of ¹Py*–In and

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

¹Py* in MBOH, respectively. The value estimated in MBOH is of 2.2×10^7 s⁻¹; values close to 6.0×10^8 s⁻¹ have been reported for pyrene–indole bichromophores in which pyrene and indole are connected by a flexible chain.¹⁴

In addition, in MBOH (less evident in THF), the quenching process took place with a slight distortion of the emission spectrum of pyrene, showing a new red-shifted structureless emission (Figure 1), which could be assigned to emissive (Py^δ•••In^{δ+})^{*} exciplexes (exciplex lifetime: $\tau_e = 60$ ns). This broadening could be caused by sufficient intramolecular electronic interaction to give to an “exciplex-type” emission, which does not require direct overlap of the chromophores. Rotation around the amide N–CO bond in **1** from the expected energetically more favorable *s-trans* to the less stable *s-cis* conformation could be not necessary.¹⁵ In this respect, it should be taken into account that pyrene–indole bichromophores in which pyrene and indole are connected by a flexible propyl chain show strong emission in many solvents.¹⁴

Contribution of the exciplex fluorescence to the registered fluorescence was estimated as 25% by comparison between the normalized fluorescence spectra of Py–CH₂NHCOCH₃ and that

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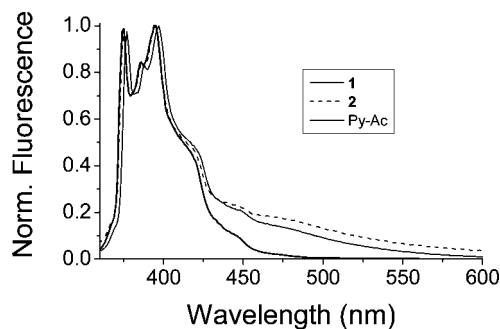


FIGURE 1. Normalized fluorescence spectra of **1**, **2**, and Py-Ac in MBOH.

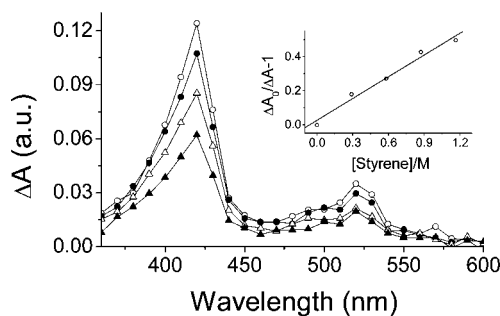


FIGURE 2. Transient absorption spectra of **1** in deaerated MBOH recorded 1.04 (○), 1.95 (●), 3.14 (△), and 4.80 (▲) μs after the laser pulse. Inset: Decrease of the absorbance at 420 nm in the presence of increasing amounts of Sty, measured immediately after the laser pulse.

of **1** in MBOH. Similar studies were performed on bichromophoric compound **2** (Table 2). In this case, the same kinetics was found for the locally excited $^1\text{Py}^*-\text{In}$ singlet excited state and for the exciplex ($\tau_f = 40$ ns, $\tau_e = 40$ ns). This result could reflect a fast reversible equilibrium between the locally excited state and the exciplex.¹⁶

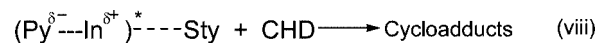
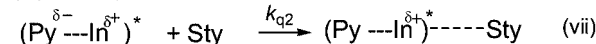
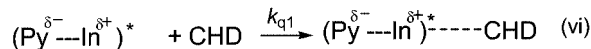
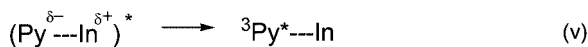
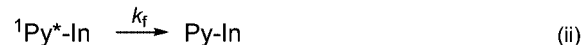
Exciplex formation was estimated using the known half-wave reduction potential of pyrene (-2.1 V vs SCE)¹⁷ and half-wave oxidation potential of 3-methylindole (1.1 V),¹⁸ as well as an average value of 0.75 eV for μ^2/ρ^3 ,¹⁹ in eq 2

$$\Delta G_{\text{exc}}^0 = E_{\text{ox}}(\text{D}/\text{D}^+) - E_{\text{red}}(\text{A}^-/\text{A}) - E_{0,0}^* - \mu^2/\rho^3 \{ [(\epsilon - 1)/(2\epsilon + 1)] - 0.19 \} + 0.38 \text{ eV} \quad (2)$$

where $E_{0,0}^*$ is the singlet energy of the pyrene chromophore (3.48 and 3.43 eV for **1** and **2**, respectively)²⁰ and ϵ is the dielectric constant of the solvent ($\epsilon = 2.21$ for dioxane, 7.58 for THF, and 5.78 for 2-methyl-2-butanol). The ΔG_{exc}^0 values are all near zero; this accounts for exciplex formation and against full electron transfer. Thus, exciplexes can be generated in THF and MBOH.

Laser flash photolysis (LFP) of Py-In compounds at 355 nm (Nd:YAG, 10 ns laser pulse) in deaerated MBOH led to transient absorption spectra (Figure 2) with two bands at λ_{max} 420 and 520 nm, ascribed to the pyrene triplet ($^3\text{Py}^*-\text{In}$, $\tau =$

SCHEME 2. Processes Involved in the Photoexcitation–Deactivation of **1** and **2** in the Presence of CHD and Sty



4.2 μs) by comparison with that of *N*-(pyren-1-ylmethyl)acetamide (see Figure S3 in Supporting Information).

From the ΔA_{420} measured immediately after the laser pulse, the quantum yield of $^3\text{Py}^*-\text{In}$ formation was 0.22 in MBOH (compared to quantum yield of ^3Py in MBOH, 0.16). Although, due to possible experimental errors, this difference should not be overemphasized; the value was consistently higher than that expected according to the precursor singlet excited state quenched (0.027, k_f/k_{isc} ratio of ca. 4.6); consequently, enhanced intersystem crossing to $^3\text{Py}^*-\text{In}$ could arise from $^1(\text{Py}^{\delta-} \cdots \text{In}^{\delta+})^*$ singlet exciplexes via fast intersystem crossing.¹⁵

Furthermore, quenching of **1** by styrene and 1,3-cyclohexadiene in MBOH was investigated to elucidate the mechanism responsible for the cross-cycloaddition process. The fluorescence experiments showed that neither the fluorescence of the locally excited pyrene singlet nor that of the emissive exciplex was significantly affected at the quencher concentrations used for the steady-state irradiation studies.

Interestingly, kinetic traces measured at 420 nm in the presence of increasing amounts of CHD and styrene showed a decrease of the end-of-pulse absorption of $^3\text{Py}^*-\text{In}$, while its decay kinetics remained essentially unchanged. Stern–Volmer analysis at 420 nm was done according to eq 3. A linear relationship was found when using small quencher concentrations (inset Figure 2 and Figure S4 in Supporting Information), and the estimated Stern–Volmer constant (K_{sv}) for the quenching of pyrenyl triplet precursor was much higher for CHD than for styrene (15 and 0.4 M⁻¹, respectively, i.e., 36 times faster for CHD), as expected from the relative oxidation potentials.^{21–24}

$$\Delta A_0/\Delta A - 1 = K_{\text{sv}}[Q] \quad (3)$$

To ascertain whether quenching by cyclohexadiene, $(\text{Py}^{\delta-} \cdots \text{In}^{\delta+})^* \cdots \text{CHD}$ (process vi, Scheme 2), or by styrene, $(\text{Py}^{\delta-} \cdots \text{In}^{\delta+})^* \cdots \text{Sty}$ (process vii), was responsible for the

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(20) Determined from the excitation and fluorescence spectra.

(21) Similarly, the K_{sv} value for the quenching of **2** by CHD was 17 M⁻¹.

(22) Half-wave oxidation potential of CHD is 1.15 V (see ref 23).

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(24) Half-wave oxidation potential of styrenes: styrene (2.05 V), *p*-chlorostyrene (2.13 V), *p*-methoxystyrene (1.54 V); see ref 13.

formation of the cycloadducts, several assays were done using different quencher concentrations. So, [CHD] was increased more than 6 times to further favor its efficiency in $(\text{Py}^{\delta-} \cdots \text{In}^{\delta+})^*$ quenching; the cycloaddition yield decreased significantly (run 4, Table 1). On the contrary, the yield increased when using a 3/4 Sty/CHD molar ratio (run 5, Table 1). These experiments agree with steps vii and viii as the predominating effective route. Here, the reactive intramolecular exciplexes would probably have a different geometry and charge distribution from those of the emissive exciplexes involved in step iv.

In summary, the fact that both pyrene–indole and pyrene–benzoylthiophene bichromophores act as selective photocatalysts opens the scope of the photoinduced charge separation in the exciplexes of bichromophoric systems as an effective strategy to accomplish organic reactions of synthetic interest.

Experimental Section

Fluorescence Spectroscopy. Steady-state fluorescence spectra were measured on a spectrofluorometer, equipped with a lamp power supply, working at room temperature. The excitation wavelength for emission spectra and quantum yield measurements was 313 nm. Quantum yields were measured using quinine sulfate in sulfuric acid as standard. For relative emission quantum yield measurements, the excitation bandwidth as 1 nm, and the absorbance of the samples and the quinine sulfate was fixed at an absorbance value of 0.1 at 313 nm. Samples used for emission spectra and quantum yield determinations were placed into quartz cells of 1 cm path length and purged with N_2 for 20 min.

Time-Resolved Absorption Spectroscopy. Laser flash photolysis system was based on a pulsed Nd:YAG laser, using 355 nm as exciting wavelength. The single pulses were ca. 10 ns duration, and the energy was ca. 15 mJ/pulse. A xenon lamp was employed as the detecting light source. The laser flash photolysis apparatus consisted of the pulsed laser, the Xe lamp, a monochromator, and a photomultiplier (PMT) system. The output signal from the oscilloscope was transferred to a personal computing machine.

Photochemical Reactor Description. Photochemical irradiations were carried out in a homemade photoreactor equipped with UVA lamps ($320 \text{ nm} < \lambda < 400 \text{ nm}$) centered at $\lambda = 350 \text{ nm}$. The samples were placed in a Pyrex tube, dissolved in the adequate solvent,

and purged with dry nitrogen over a period of 10–15 min prior to irradiation.

General Procedure for the Photocatalytic Studies. 1,3-Cyclohexadiene (CHD, 0.4 mmol), 1 mmol of the styrene, and 0.005 mmol of the photocatalyst (or the reference compound) were dissolved in 10 mL of the appropriate solvent in a Pyrex tube. The solution was purged with dry nitrogen for 20 min. Then the solutions were placed in a water bath (15°C) and irradiated. After solvent evaporation, NMR spectra were registered and used to quantify the photoreaction yield.²⁵

2-(1*H*-Indol-3-yl)-*N*-((pyren-1-yl)methyl)acetamide (1): ¹H NMR (300 MHz, CDCl_3) δ 3.77 (2H, s), 5.05 (2H, d, $J = 5.7 \text{ Hz}$), 6.01 (bb, NH), 6.97–7.03 (1H, m), 7.08–7.14 (1H, m), 7.24 (1H, d, $J = 8.1 \text{ Hz}$), 7.51 (1H, d, $J = 7.8 \text{ Hz}$), 7.73 (1H, d, $J = 7.8 \text{ Hz}$), 7.92–8.13 (9H, m); ¹³C NMR (75.4 MHz, DMSO) δ 33.1, 41.0, 109.3, 111.7, 118.6, 119.1, 121.3, 123.7, 124.2, 124.3, 124.4, 125.0, 125.5, 125.6, 126.6, 127.1, 127.4, 127.6, 127.7, 127.8, 128.5, 130.4, 130.7, 131.2, 133.4, 136.5, 171.1; HRMS EI (m/z) calcd for $\text{C}_{27}\text{H}_{20}\text{N}_2\text{O}$ 388.1576, found 388.1571.

2-(1-Methyl-1*H*-indol-3-yl)-*N*-((pyren-1-yl)methyl)acetamide (2): ¹H NMR (300 MHz, CDCl_3) δ 3.57 (3H, s), 3.74 (2H, s), 5.04 (d, 2H, $J = 5.7 \text{ Hz}$), 6.04 (bb, NH), 6.83 (1 H, s), 6.97 (1H, m), 7.12 (2H, m), 7.47 (1H, d, $J = 7.8 \text{ Hz}$), 7.72 (1H, d, $J = 7.8 \text{ Hz}$), 7.90–8.11 (9H, m); ¹³C NMR (75.4 MHz, CDCl_3) δ 30.2, 33.3, 34.0, 42.6, 107.4, 109.9, 110.0, 119.3, 120.0, 122.6, 123.2, 125.0, 125.2, 125.7, 126.4, 127.2, 127.7, 127.8, 128.4, 129.2, 131.1, 131.3, 131.4, 131.6, 137.5; HRMS EI (m/z) calcd for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}$ 402.1732, found 402.1730.

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Supporting Information Available: NMR spectra of compounds **1** and **2**, and complementary photophysical studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO900356C

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