

Pyrene-benzoylthiophene bichromophores as selective triplet photosensitizers

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Chemical Communication

Supplementary Information

S2-S5: Experimental Section: *General. Fluorescence spectroscopy. Time-resolved absorption spectroscopy. Synthesis and characterization of compounds 1-3. General procedure for photoisomerization of (E)-stilbene.*

S6: Fluorescence emission spectra of **1-3** (10^{-3} M) in nitrogen-saturated dioxane.

Experimental Section

General. Dimethylformamide (DMF) was distilled from CaH_2 prior to use. Triethylamine (Et_3N), acetic acid and methanol were used as received. 2-(5-Benzoylthien-2-yl)propanoic acid (tiaprofenic acid, TPA) was extracted from commercially available samples in methanol. 1-pyrenemethylamine hydrochloride and 2-[4-(thien-2-ylcarbonyl)phenyl]propanoic (suprofen, SUP), [1-ethyl-3-(3-(diethylamino)propylcarbodiimide)] (EDC) and 1-hydroxybenzotriazole (HBT) were commercially available. All reactions were performed under dried nitrogen (N_2) atmosphere unless otherwise noted. Analytical TLC was performed on 0.25 mm silica gel 60-F aluminium plates and visualized under UV light. Flash chromatography was performed on silica gel 60 (0.040–0.063 mm). ^1H NMR spectra were obtained at either 300 or 400 MHz-Brucker as indicated. ^{13}C NMR spectra were obtained at 100 MHz. Chemical shift (δ) are given in ppm and coupling constant (J) are given in (Hz). Melting points were obtained on pre-cleaned microscope slides and are uncorrected. UV-Vis spectra were recorded on a UV-2101PC SHIMADZU spectrophotometer, using quartz-cuvettes. IR spectra were recorded on Satellite FTIR instrument using dried KBr.

Fluorescence spectroscopy. Steady-state fluorescence spectra were measured on a Photon Technology spectrofluorometer, equipped with a lamp power supply (LPS-220B), working at room temperature. The excitation wavelength for emission spectra and quantum yield measurements was 355 nm. Quantum yield measurements were measured and compared to quinine sulfate (dissolved in 0.5 M sulfuric acid). For relative emission quantum yield measurements, the excitation bandwidth was 1 nm, and the absorbance of the measured sample and the quinine sulfate were prepared at an

absorbance value of ca. 0.3 at 355 nm. Samples used for emission spectra and quantum yield determinations were placed into quartz cells of 1 cm path length and purged with argon for 20 min. Fluorescence decays were recorded on the same spectrofluorometer using a Time Master control modul lamp. Emission for all lifetime measurements was excited at 355 nm.

Time-resolved absorption spectroscopy. These experiments were carried out using a pulsed Nd-YAG Spectrum laser system instrument (mLFP-111). The single pulses were ca. 10 ns duration and the energy was ca. 10 mJ/pulse. A Xenon lamp was employed as detecting light source. The laser flash photolysis apparatus consisted of the pulsed laser, the Xe lamp, a monochromator, a photomultiplier (PMT) system made up of side-on PMT, PMT housing and a PMT power supply. The output signal from the oscilloscope was transferred to a personal computer for study. Samples were contained in 7x7 mm cells made of Suprasil quartz and were deaerated with dry nitrogen prior to the experiments.

Synthesis of *N*1-(1-pyrenylmethyl)acetamide (1). 1-pyrenemethylamine hydrochloride (0.20 g, 0.75 mmol) was dissolved in glacial acetic acid in (5 mL) and acetic anhydride (5mL). The mixture was heated at reflux for 10 min. After reflux, the solution was cooled and water was added affording a white precipitate, which was filtered washed with water and dried. The solid precipitate was further purified via column chromatography (SiO₂, ethyl acetate/hexane (2:1; v/v)) to provide *N*1-(1-pyrenylmethyl)acetamide as white crystals (0.18 g, 0.7 mmol) in 90% yield. $R_f = 0.2$ (ethyl acetate/hexane (2:1; v/v)). Mp: 210 °C. ¹H NMR (300 MHz, CDCl₃): δ 2.1 (s, 3H), 5.2 (d, $J = 5.2$ Hz, 2H), 5.9 (br, NH), 7.9-8.3 (m, 9H). ¹³C NMR (100, CDCl₃): δ 23.0 (q), 42.2 (t), 122.8 (d), 124.8 (d), 125.0 (d), 125.4 (d), 126.1 (d), 127.3 (d), 127.4

(d), 127.6 (d), 128.4 (d), 128.9 (s), 130.8 (s), 131.0 (s), 131.3 (s), 169.7 (s). MS m/z 73 (100), 215 (59), 230 (34), 273 (95). HRMS Calcd. for $C_{19}H_{15}NO$: 273.1153. Found: 273.1165.

General procedure for the synthesis of bichromophoric compounds 2 and 3. The corresponding aryl propanoic acid (SUP or TPA) (0.15 g, 0.6 mmol), the 1-pyrenemethylamine hydrochloride (0.15 g, 0.6 mmol), EDC (0.11 g, 0.6 mmol) and HBT (0.08 g, mmol) were combined in DMF (8 mL) at room temperature. The pH of the mixture was adjusted to 9.0-9.5 with Et_3N and kept with vigorous stirring overnight. Afterwards, the solvent was removed and the residue was treated with 10% HCl (15 mL) and extracted with ethyl acetate (3x10 mL). The combined organic fractions were washed with 10% HCl (10 mL), saturated aqueous sodium bicarbonate (2x 10 mL), water (10 mL) and dried over Na_2SO_4 , filtered, and evaporated. The residual oil was purified via column chromatography (SiO_2 , ethyl acetate/hexane (2:1; v/v)) to yield the corresponding bichromophore 2 or 3.

***N*1-(1-pyrenylmethyl)-2-[4-(2-thienylcarbonyl)phenyl]propanamide (2).** (0.23 g) 80% yield. R_f = 0.18 (ethyl acetate/hexane (2:1; v/v)). Mp: 105 °C. 1H NMR (400 MHz, $CDCl_3$): δ 1.6 (d, J = 7.1 Hz, 3H), 3.7 (q, J = 7.1 Hz, 1H), 5.1 (d, J = 5.3 Hz, 2H), 5.8 (br, NH), 7.1 (dd, J_1 = 3.6 Hz, J_2 = 4.8 Hz, 1H), 7.4 (d, J = 8.0 Hz, 2H), 7.5 (dd, J_1 = 1.2 Hz, J_2 = 4.0 Hz, 1H), 7.7 (dd, J_1 = 1.2 Hz, J_2 = 4.0 Hz, 1H), 7.8 (d, J = 8.0 Hz, 2H), 7.9 (d, J = 8.0 Hz, 1H), 8.0-8.2 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.6 (q), 42.4 (d), 47.3 (t), 122.7 (d), 122.8 (d), 124.6 (d), 124.7 (s), 124.8 (d), 125.4 (d), 125.5 (d), 126.0 (d), 126.1 (d), 127.2 (d), 127.3 (d), 127.6 (d), 127.9 (d), 128.2 (d), 129.0 (s), 129.7 (d), 130.5 (s), 130.7 (s), 131.2 (s), 131.3 (s), 134.2 (d), 134.7 (d), 137.1 (s), 145.7 (s), 172.8 (s), 187.6 (s). FTIR (KBr): 3300 (NH), 1638 (CONH), 1537, 1452, 1290 cm^{-1} . 1 . Anal. Calcd. For $C_{31}H_{23}NO_2S$ (473.1): C, 78.62; H, 4.90. Found C, 78.40; H, 5.32.

MS m/z 105 (5), 215 (100), 473 (55). HRMS Calcd. for $C_{31}H_{23}NO_2S$: 473.1449. Found: 473.1472.

N1-(1pyrenylmethyl)-2-(5-benzoyl-2-thienyl)propanamide (3). (0.24 g) 85% yield. $R_f = 0.22$ (ethyl acetate/hexane (2:1; v/v)). Mp: 200 °C. 1H NMR (400 MHz, $CDCl_3$): δ 1.7 (d, $J = 7.1$ Hz, 3H), 3.90 (q, $J = 7.0$ Hz, 1H), 5.2 (d, $J = 5.3$ Hz, 2H), 5.6 (br, NH), 7.0 (d, $J = 3.8$ Hz, 1H), 7.3-7.6 (m, 4H), 7.8 (d, $J = 7.1$ Hz, 2H), 7.9 (d, $J = 7.1$ Hz, 2H), 8.0-8.3 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.6 (q), 42.5 (d), 43.25 (t), 122.6 (d), 124.6 (d), 124.7 (s), 124.8 (d), 125.4 (d), 125.5 (d), 126.0 (d), 126.1 (d), 127.2 (d), 127.3 (d), 127.6 (d), 128.3 (d), 128.4 (d), 129.1 (d), 129.2 (d), 130.5 (s), 130.7 (s), 131.2 (s), 131.3 (s), 132.2 (d), 135.0 (d), 137.9 (s), 142.3 (s), 153.4 (s), 171.5 (s), 187.8 (s). FTIR (KBr): 3421 (NH), 1633 (CONH), 1551, 1441, 1290 cm^{-1} . MS m/z 110 (8), 215 (100), 473 (75). HRMS Calcd. for $C_{31}H_{23}NO_2S$: 473.1449. Found: 473.1533.

General procedure for the photoisomerization of (*E*)-stilbene.

Mixtures of (*E*)-stilbene (0.1 mmol) (crystallized from ethanol and sublimed prior to use) and the corresponding photosensitizer (**1-3**) (5 mol%) in dioxane (5 mL) were purged with dried nitrogen over 20 min and irradiated ($\lambda_{max} > 330$ nm) up to 24 h. The progress of the photoisomerization of (*E*)-stilbene into (*Z*)-stilbene was followed by gas chromatography (oven temperature 70 °C for 10 min, then 3 °C/min to 200°C, t_R : 39 min (*Z*)-stilbene; t_R : 47 min (*E*)-stilbene).

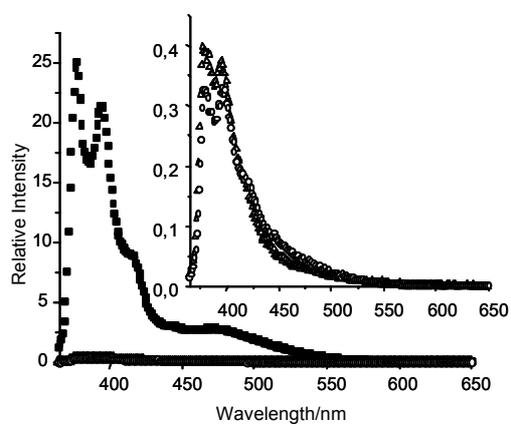


Figure S1. Fluorescence emission spectra of **1** (■, 1×10^{-3} M), **2** (○, 1×10^{-3} M) and **3** (△, 1×10^{-3} M) in nitrogen-saturated dioxane at $\lambda_{exc} = 355$ nm. Inset: magnification of the spectra for **2** and **3** above 380 nm.