

Experimental

General. 9-Phenylanthracene, **PA**, (Aldrich, 98%) was recrystallized from benzene, mp 153-154 °C; 2-ethyl-9,10-dimethoxyanthracene, **EDA**, (Aldrich, 97%) was recrystallized from diethyl ether; mp 117-119 °C. Perylene, **PE**, (Aldrich, 99.5+%) was used as received, mp 278-280 °C. Acetonitrile (Sigma-Aldrich) was distilled from CaH₂ and stored over 4A molecular sieves.

NMR Studies. ¹H NMR spectra were recorded on dilute solutions with a GE-300 spectrometer, using TMS as an internal chemical shift standard: Deuterated acetonitrile (Cambridge isotopes, 99.8%) was used as solvent. 1,2-Dichloroethane, **DCE**, was used as a reference for the quantitative analysis. A solution of **1-BF₄** (0.01M) and **PA** (0.01M) in CD₃CN containing **DCE** (0.01M) was irradiated under the same condition as quantum yield measurements and the NMR spectra were recorded every 20 min. The concentrations of phenylmethylsulfide and sulfonium salt were evaluated from peak areas at δ 2.5 and δ 3.2, respectively, by comparison to the peak area of **DCE** at δ 3.8.

GC/MS Analysis. GC/MS analysis used a Hewlett Packard 5970 mass spectrometer (70 eV) coupled with a Hewlett Packard 5890 gas chromatograph: HP 5 column (30 m x 0.25 mm x 0.25 μ m), temperature program 50-200 °C at 10 °C min⁻¹. Solutions for GC/MS analyses were passed through a silica gel column (eluent: methylene chloride) to remove unreactive sulfonium salt before analysis.

HPLC Analyses. The HPLC analyses used an Hewlett Packard 1050 Series System with a Water Nova-Pak Phenyl column (8 mm x 100 mm, Radial-Pak Cartridge), UV detection at 236 and 254 nm, eluent 1/1 CH₃CN/H₂O, flow rate 1 mL/min. Integrated peak areas were compared to standard curves of peak area vs concentration for authentic materials.

Redox Potentials. Redox potentials were determined with a BAS Model 100B electrochemical apparatus at a scan rate of 0.1 V/sec. The reference electrode was Ag/AgCl, the working electrode was a glassy carbon disk, and a platinum disk was used as the counter electrode. The reference electrode is +0.19 V with respect to SCE.¹ Samples were 1-2 mM in

MeCN, containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte and were purged with argon.

Spectroscopy. The steady state fluorescence spectra were recorded using a Spex Fluorolog 2 Spectrofluorometer at room temperature. Fluorescence lifetime experiments were performed using the time-correlated single-photon counting technique in both the deoxygenated and nondeoxygenated acetonitrile. The UV/VIS absorption spectra in acetonitrile were recorded with a Hewlett-Packard 8452 diode array spectrophotometer. Fluorescence quenching experiments were performed by measuring the emission peak areas at room temperature in the nondeoxygenated acetonitrile.

Syntheses of Sulfonium Salts. Phenylmethyl(4-cyanobenzyl)sulfonium tetrafluoroborate, **1-BF₄**, was synthesized by reaction of 4-cyanobenzyl bromide with phenyl methyl sulfide in the presence of silver tetrafluoroborate in acetonitrile and recrystallized from ethanol, mp 146-147 °C (lit. mp 129-131 °C)²; ¹H NMR (CD₃CN): 3.22 (s, 3H), 4.74 (d, 1H, J = 12 Hz), 4.94 (d, 1H, J = 12 Hz), 7.36 (d, 2H, J = 8 Hz), 7.5-7.9 (m, 7H). The corresponding hexafluorophosphate salt, **1-PF₆**, was prepared similarly, using AgPF₆, mp 135-6 °C; ¹H NMR(CD₃CN): 3.00 (s, 3H), 4.72 (d, 1H, J = 12 Hz), 4.92 (d, 1H, J = 12 Hz), 7.35 (d, 2H, J = 8 Hz), 7.6-7.9 (m, 7H). Anal. Calcd for C₁₅H₁₄PF₆NS: C, 46.75; H, 3.63; N, 3.63; S, 8.31. Found: C, 47.10; H, 3.60; N, 3.28; S, 9.29.

Phenylethyl(4-cyanobenzyl)sulfonium tetrafluoroborate, **2-BF₄**, was prepared by reaction of phenylethylsulfide with 4-cyanobenzyl bromide in the presence of silver tetrafluoroborate in acetonitrile. A colorless clear oil was obtained. ¹H NMR (CD₃CN): 1.32 (t, 3H, J = 6 Hz), 3.74 (q, 2H, J = 6 Hz), 4.84 (d, 1H, J = 12 Hz), 5.03 (d, 1H, J = 12 Hz), 7.42 (d, 2H, J = 8 Hz), 7.6-7.9 (m, 7H).

The corresponding hexafluorophosphate salt, **2-PF₆**, was prepared by anion exchange of **2-BF₄** with NH₄PF₆ in an aqueous acetonitrile solution, mp 137-8 °C; ¹H NMR (CD₃CN): 1.32 (t, 3H, J = 6 Hz), 3.74 (q, 2H, J = 6 Hz), 4.75 (d, 1H, J = 12 Hz), 4.95 (d, 1H, J = 12 Hz), 7.40 (d, 2H, J = 8 Hz), 7.5-8.1 (m, 7H). Anal. Calcd for C₁₆H₁₆PF₆NS: C, 48.12; H, 4.01; N, 3.51; S,

8.02. Found: C, 48.33; H, 4.07; N, 3.57; S, 9.01. The photosensitized reduction by ¹PA gave $k_q = 1.2 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ and $\Phi_{\text{LIM}} = 0.5$.

Photolysis Products. Photolysis solutions were analyzed by HPLC, NMR, or GC/MS. Products were identified by comparison with authentic samples. In addition, authentic samples of several potential products were prepared. **Methyl phenyl sulfide** (Aldrich): ¹H NMR (CD₃CN): 2.50 (s, 3H), 0-7.6 (m, 5H); GC/MS: $m/z = 124 (M^+)$; HPLC 7.0 min. **Ethyl phenyl sulfide** (Aldrich): ¹H NMR (CD₃CN): 1.30 (t, 3H, $J = 6 \text{ Hz}$), 2.97 (d, 2H, $J = 6 \text{ Hz}$), 7.1-7.6 (m, 5H); GC/MS: $m/z = 138 (M^+)$; HPLC: 9.0 min. **Methyl (4-cyanobenzyl) sulfide** and **phenyl (4-cyanobenzyl) sulfide**, which were prepared by reactions of 4-cyanobenzyl bromide with the salts of the corresponding mercaptans, could not be detected as a reaction product (<0.1%) by ¹H NMR, GC/MS or HPLC. **1,2-Bis(4-cyanophenyl)ethane**, which was prepared by coupling the 4-cyanobenzyl bromide with nickel in glyme,³ could not be detected as a reaction product (<0.1%) by ¹H NMR, GC/MS or HPLC.

Minor products were identified: **4-tolunitrile** (Aldrich), GC/MS: $M/Z 117(M^+)$, HPLC: 5.7 min; **4-(hydroxymethyl)benzonitrile** was prepared by reaction of 4-cyanobenzyl bromide with silver nitrate in water. GC/MS: $m/z 133(M^+)$, HPLC: 3.8 min. **4-Cyanobenzaldehyde** (Aldrich), GC/MS: $m/z 131(M^+)$, HPLC: 4.6 min. 4-Cyanobenzyl substituted sensitizers were identified by FDMS: **(4-cyanobenzyl)-9-phenylanthracenes**, $m/z 369 (M^+)$, 484 (M^+), 599 (M^+), 714 (M^+); **4-cyanobenzyl-2-ethyl-9,10-dimethoxy anthracenes**, $m/z 381 (M^+)$, 496 (M^+). **2-Ethyl-9,10-anthraquinone** was also observed, GC/MS: $m/z 236(M^+)$. **N-(p-Cyanobenzyl)acetamide** was prepared by acetylation of α -amino-4-tolunitrile,⁴ mp 142-144 °C; ¹H NMR(CDCl₃): 2.10 (s, 3H), 4.54 (s, 2H), 5.94 (s, 1H), 7.3-7.8 (m, 4H); GC/MS: $m/z = 174(M^+)$. The amide was formed in PA-sensitized reactions, but was not detected (<0.1%) by HPLC in EDA- or PE-sensitized reactions.

Quantum Yields. Quantum yields were measured at <20% conversion on solutions in acetonitrile, 0.01 M in the sensitizers and 0.01-0.10 M in sulfonium salt. The samples (2 mL) were placed in a 1 cm spectrophotometer cell, deoxygenated by three freeze-pump-thaw cycles

and sealed. The sample were irradiated at 365 nm (**PA** and **EDA**), or 436 nm (**PE**) on an optical bench with light from the high-pressure mercury short arc lamp (OSRAM HBO 200 W), passed through filters (365 nm, mercury line filter # 56531, from Oriel Corporation) or (436 nm, mercury line filter # 35-3334 from Ealing Electro-Optics). The light intensity at 365 nm was measured using Aberchrome 540 (Aberchromics Ltd.)⁵ and at 436 nm using phenanthrenequinone/trans-stilbene actinometers.⁶ The typical values were $3\text{--}4 \times 10^8$ Einstein s^{-1} at 365 nm and $5\text{--}6 \times 10^8$ Einstein s^{-1} at 436 nm. Experimental values of $[\mathbf{1}\text{-BF}_4]$ and Φ_{OBS} are given in Table 1 and plotted in Figure 3 in the manuscript.

Aberchrome 540: $\Phi = 0.20$; $\lambda = 494$ nm; $\epsilon = 8200 \text{ M}^{-1} \text{ cm}^{-1}$.

Phenanthrenequinone/trans-stilbene: $\Phi = 0.065$; $\lambda = 410$ nm; $\epsilon = 1800 \text{ M}^{-1} \text{ cm}^{-1}$

Table 1. Quantum yields for formation of PhSCH₃ as a function of [1-BF₄].

9-Phenylanthracene		2-Ethyl-9,10-dimethoxyanthracene		Perylene	
[1-BF ₄]	Φ_{obs}	[1-BF ₄]	Φ_{obs}	[1-BF ₄]	Φ_{obs}
0.0018	0.0445	0.0027	0.3166	0.0021	0.0934
0.0050	0.1121	0.0049	0.4429	0.0449	0.1836
0.010	0.1827	0.0099	0.5504	0.0098	0.2777
0.020	0.3053	0.010	0.5352	0.010	0.2816
0.020	0.3307	0.010	0.5453	0.010	0.2905
0.020	0.3335	0.020	0.5852	0.020	0.3993
0.030	0.3204	0.020	0.6262	0.020	0.4085
0.040	0.4154	0.040	0.6862	0.0205	0.4107
0.040	0.4190	0.040	0.7308	0.030	0.4779
0.060	0.4468	0.060	0.7592	0.030	0.4874
0.060	0.4483	0.080	0.8338	0.030	0.4887
0.080	0.4611			0.040	0.5136
0.080	0.4722			0.040	0.5439
				0.050	0.5314
				0.050	0.5693

References

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