Supporting Information

Preparation of sensitizers

3-(1-Pyrenyl)propionic acid (1b).[1,2] To a solution of 1-formylpyrene (461 mg, 2.0 mmol) in pyridine (1 mL, 12 mmol) was added malonic acid (1.04 g 10 mmol), and the solution was stirred for 9 h at 100 ºC. After HCl (1.0 M, 3 mL) was added to cease the reaction, the reaction mixture was filtered to afford 3-(1-pyrenyl)acrylic acid (500 mg, 92%) as yellow granules. Hydrogenation of 3-(1-pyrenyl)acrylic acid (140 mg, 0.50 mmol) was performed by stirring under a H_2 atmosphere (1 atm) in acetic acid (50 mL) in the presence of PtO_2 (14 mg, 0.060 mmol) for 15 h at room temperature. After the removal of catalyst and solvent, the residue was dissolved in ether. The ethereal solution was washed with water, and dried over Na_2SO_4. The solvent was removed to give the crude product (120 mg, 87%), which was purified by recrystallization from hexane-CH_2Cl_2 to give **1b** as light yellow granules: mp 183-185 ºC (lit.[1] mp 180-181 ºC); ^{1}H NMR ($CDCl_3$) δ 2.93 (2H, t, *J* = 8.0 Hz), 3.72 (2H, t, *J* = 8.0 Hz), 7.92 (1H, d, *J* = 7.6 Hz), 8.00-8.04 (3H, m), 8.11-9.19 (4H, m), 8.28 (1H, d, *J* = 9.2 Hz); MS m/z (rel intensity) 274 (M^+, 63), 215 ($M^+ - C_2H_4CO_2H$, 100); UV-vis (CH_3CN) λ_{max} (log ε) 342 (4.45), 326 (4.41), 313 (4.04), 276 (4.58), 265 (4.36), 255 (4.04), 242 (4.69), 234 (4.58) nm.

2-(1-Pyrenyl)ethylamine (2b).[3] To a solution of (1-pyrenyl)ethanol (**3b**) (350 mg, 1.4 mmol) and Et_3N (0.30 mL, 2.2 mmol) in CH_2Cl_2 (3.3 mL) was added a CH_2Cl_2 solution of methanesulfonyl chloride (1.0 M, 1.9 moL, 1.9 mmol) under a N_2 atmosphere at 0 ºC. After stirring for 2 h at 0 ºC, the reaction mixture was poured into ice-water, and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, and the solvent was removed to give the crude mesylate (434 mg, 94%) as yellow granules, which was purified by an alumina column chromatography with CH_2Cl_2 eluent to give 2-(1-pyrenyl)ethyl mesylate as yellow granules: mp 102-104 ºC. To convert the mesylate into the azide, a solution of the mesylate (130 mg,

0.40 mmol) and NaN_3 (182 mg, 2.8 mmol) in DMF (5 mL) was stirred for 43 h at room temperature. After the solvent was evaporated, the residue was extracted with CH_2Cl_2, and the organic layer was washed with an aqueous solution of $NaHCO_3$ and water, and dried over Na_2SO_4. The removal of the solvent afforded the crude 1-azido-2-(1-pyrenyl)ethane (65 mg, 60%), which was purified by recrystallization from hexane: mp 62-63 ºC. The hydrogenation of the resulting azide was perfomed by stirring the azide (50 mg, 0.18 mmol) under a H_2 atmosphere in THF (5 mL) in the presence of PtO_2 (5.0 mg, 22 μmol) for 22 h at room temperature. After removal of the catalyst by filtration, the removal of the solvent afforded the crude product, which was purified by recrystallization to give **3b** as light yellow granules (8.3 mg, 18%): mp 77-79 ºC; ^{1}H NMR ($CDCl_3$) δ 3.22 (2H, t, *J* = 7.3 Hz), 3.51 (2H, t, *J* = 7.3 Hz), 7.09 (1H, d, *J* = 7.5 Hz), 8.00 (1H, t, *J* = 7.5 Hz), 8.02-8.06 (2H, m), 8.12 (1H, d, *J* = 9.0 Hz), 8.13 (1H, d, *J* = 7.5 Hz), 8.17 (1H, d, *J* = 8.0 Hz), 8.17 (1H, d, *J* = 7.5 Hz), 8.31 (1H, d, *J* = 9.0 Hz); UV-vis (CH_3CN) λ_{max} (log ε) 343 (4.52), 327 (4.36), 313 (3.99), 276 (4.53), 266(4.30), 256 (3.97), 243 (4.63), 234 (4.63) nm.

2-(1-Pyrenyl)ethanol (3b).[4,5] To a suspension of $LiAlH_4$ (227 mg, 6.0 mmol) in THF (5 mL) was added a solution of (1-pyrenyl)acetic acid (**1a**) (390 mg, 1.5 mmol) in THF (5 mL) under a N_2 atmosphere. After stirring for 3 h at room temperature, the reaction mixture was quenched by the addition of methanol and 10% sulfuric acid. The organic material was extracted with ether, and the ethereal solution was washed with water, and dried over Na_2SO_4. The solvent was removed to give the crude product (350 mg, 95%), which was purified by a silica gel column chromatography with CH_2Cl_2 eluent to give **2b** as yellow granules: mp 105-106 ºC; ^{1}H NMR ($CDCl_3$) δ 1.49 (1H, brs), 3.63 (2H, t, *J* = 6.5 Hz), 4.12 (2H, q, *J* = 5.4 Hz), 7.91 (1H, d, *J* = 7.8 Hz), 7.97-8.19 (m, 7H); UV-vis (CH_3CN) λ_{max} (log ε) 342 (4.57), 326 (4.41), 313 (4.04), 276 (4.56), 265 (4.36), 255 (4.00), 242 (4.64), 234 (4.58) nm.

1-Ethylpyrene (4a).[6,7] A mixture of 1-acetylpyrene (500 mg, 2.0 mmol), hydrazine monohydrate (5 mL), and sodium hydroxide (4.0 g) in ethylene glycol (70 mL) was refluxed with stirring for 5 h. To the reaction mixture was added water, and the organic material was extracted with CH_2Cl_2. The orgainc layer was washed with water, and dried over Na_2SO_4. The solvent was removed to give the crude product, which was purified by recrystallization from ethanol to give **4a** (330 mg, 70%) as light yellow granules: mp 95-96 ºC (lit.[6] mp 94-95 ºC); ^{1}H NMR ($CDCl_3$) δ 1.49 (3H, t, *J* = 7.5 Hz), 3.39 (2H, q, *J* = 7.5 Hz), 7.90 (1H, d, *J* = 7.5 Hz), 7.97-8.05, (3H, m), 8.10-8.17 (4H, m), 8.30 (1H, d, *J* = 9.0 Hz); MS *m*/*z* (rel. intensity) 230 (M^+, 80), 215 ($M^+ - CH_3$, 100).

1-Octylpyrene (4b).[8] To a mixture of pyrene (650 mg, 3.2 mmol) and $AlCl_3$ (900 mg, 6.7 mmol) in CS_2 (15 mL) was added a solution of octanoyl chloride, which was prepared by the reaction of octanoic acid (0.50 mL, 3.2 mmol) with thionyl chloride (20 mL), in CS_2 (15 mL) with stirring at 0 ºC, and the mixture was stirred overnight at room temperature. To the reaction mixture was added ice and chilled 5% HCl, and the organic material was extracted with CH_2Cl_2. The orgainc layer was dried over Na_2SO_4, and the solvent was removed to give the crude 1-octanoylpyrene, which was separated from the unreacted starting material by silica gel column chromatography with hexane-CH_2Cl_2 (3 : 1) eluent to give the pure 1-octanoylpyrene (700 mg, 64%). The Wolff-Kishner reduction of the ketone (110 mg, 0.32 mmol) was achieved in the same manner as that described for **4a** using hydrazine monohydrate (1 mL), sodium hydroxide (0.9 g), and ethylene glycol (20 mL). The crude product was purified by silica gel column chromatography with hexane-CH_2Cl_2 (20 : 1) eluent to give **4b** (80 mg, 78%) as colorless granules: mp 60-61 ºC; ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, *J* = 7.0 Hz), 1.25-1.32 (8H, m), 1.46-1.52 (2H, m), 1.82-1.88 (2H, m), 3.34 (2H, t, *J* = 8.0 Hz), 7.87 (1H, d, *J* = 8.0 Hz), 7.97-8.04, (3H, m), 8.09-8.17 (4H, m), 8.29 (1H, d, *J* = 9.0 Hz); MS

m/*z* (rel. intensity) 314 (M^+, 55), 215 ($M^+ - C_7H_{15}$, 100).

3-[6-(1-propyl)-1-pyrenyl]propionic acid (5a). A solution of 1,6-dibromopyrene[9] (900 mg, 2.5 mmol), $Pd(Ph_3P)_2Cl_2$ (23 mg, 32 μmol), and CuI (3.1 mg, 16 μmol) in morpholine (15 mL) was stirred for 10 min at 0 ºC, and to the solution was added a solution of 1-[3-(tetrahydropyran-2-yloxy)]propyne (880 mg, 6.3 mmol) in morpholine (3 mL), and the reaction mixture was stirred overnight at 100 ºC. After removal of the solvent under reduced pressure, the residue was extracted with CH_2Cl_2, and the organic layer was washed with water and dried over Na_2SO_4. The solvent was evaporated and the residue was developed on a silica gel column chromatography as CH_2Cl_2 eluent to afford the crude product, which was purified by recrystalization from ethanol to give 1,6-bis[3-(tetrahydropyran-2-yloxy)propyn-1-yl]pyrene (**6**) (59 mg, 19%) as yellow granules: mp 131-134 ºC; ^{1}H NMR ($CDCl_3$) δ 1.53-1.91 (12H, m), 3.60-3.68 (2H, m), 3.99-4.03 (2H, m), 4.70 (2H, d, *J* = 16.0 Hz), 4.77 (2H, d, *J* = 16.0 Hz), 5.06 (2H, t, *J* = 3.1 Hz), 8.10-8.13 (6H, m), 8.58 (2H, d, *J* = 16.0 Hz); MS *m*/*z* (rel. intensity) 478 (M^+, 57), 394 ($M^+ - C_5H_9O$, 22), 377 ($M^+ - C_5H_9O_2$, 30), 292 ($M^+ - C_5H_9O - C_5H_9O_2$, 40), 276 ($M^+ - C_5H_9O_2 - C_5H_9O_2$, 100). The pyrene **6** was dissolved in CH_2Cl_2 (0.8 mL) and ethanol (0.8 mL). To the solution was added pyridinium *p*-toluenesulfonate (5.0 mg, 20 μmol), and the reaction mixture was stirred for 6 h at 60 ºC. The precipitate was filtered, and washed with CH_2Cl_2 to afford 1,6-bis(3-hydroxypropyn-1-yl)pyrene (**7**) as yellow granules (37 mg, 91%). The hydrogenation of **7** (78 mg, 0.25 mmol) was performed by stirring under a H_2 atmosphere in THF (11.5 mL) in the presence of PtO_2 (8.6 mg, 38 μmol) for 20 h at room temperature. After removal of the catalyst by filtration, the solvent was evaporated to afford the crude produt, which was purified by recrystallization from hexane-CH_2Cl_2 to give 1,6-bis(3-hydroxy-1-propyl)pyrene (**8**) as light yellow granules (80 mg, 100%): mp 178-181 ºC. To a solution of **8** (21 mg, 66 μmol) in CH_2Cl_2 (10 mL) was added

Et_3N (13 μL, 94 μmol) and methanesulfonyl chloride (4.9 μL, 63 μmol) at 0 ºC. The reaction mixture was stirred for 2 h at 0 ºC, and water was added to the reaction mixture. The organic material was extracted with CH_2Cl_2, and the organic layer was washed with water, and dried over Na_2SO_4. The solvent was evaporated to give a mixture of **8** and its mesylate (1 : 0.7). The mixture was dissolved in THF (1 mL), and to the solution was added a THF solution of $LiBHEt_3$ (1.0 M, 0.4 mL, 0.4 mmol). The reaction mixture was stirred for 20 min at 0 ºC, and water was added to cease the reaction. The organic material was extracted with ether, and the ethereal solution was washed with water and dried over Na_2SO_4. The solvent was evaporated, and the residue was developed on PTLC (CH_2Cl_2 : ether = 5 : 1) to give 3-[6-(1-propyl)-1-pyrenyl]propan-1-ol (**9**) as light yellow granules (11 mg, 67%), which was purified by recrystallization from hexane-CH_2Cl_2: mp 133-137 ºC; ^{1}H NMR ($CDCl_3$) δ 1.08 (3H, t, *J* = 7.3 Hz), 1.85-1.93 (2H, m), 2.13 (2H, quin, *J* = 7.0 Hz), 3.31 (2H, t, *J* = 8.0 Hz), 3.45 (2H, t, *J* = 7.5 Hz), 3.79 (2H, t, *J* = 6.3 Hz), 7.86 (1H, d, *J* = 7.5 Hz), 7.87 (1H, d, *J* = 7.5 Hz), 8.05 (1H, d, *J* = 9.5 Hz), 8.06 (1H, d, *J* = 9.0 Hz), 8.09 (2H, d, *J* = 8.0 Hz), 8.23 (1H, d, *J* = 9.5 Hz), 8.24 (1H, d, *J* = 9.0 Hz); MS *m*/*z* (rel. intensity) 302 (M^+, 100), 273 ($M^+ - C_2H_5$, 72), 257 ($M^+ - C_2H_4OH$, 49), 228 ($M^+ - C_2H_5 - C_2H_4OH$, 93). Finally, to a solution of pyridinium dichromate (135 mg, 0.36 mmol) in DMF (0.3 mL) was added to a solution of **9** (18 mg, 60 μmol) in DMF (1.2 mL). The reaction mixture was stirred for 10 h at room temperature. After addition of water to cease the reaction, the reaction mixture was extracted with ether. The aqueous layer was acidified with 5% sulfuric acid, and extracted with ether again. The combined ethereal solution was washed with water, and dried over Na_2SO_4. The solvent was evaporated to afford the crude product, which was purified by recrystallization from hexane-CH_2Cl_2 to give **5a** as brown granules (4.7 mg, 25%): mp 193-195 ºC; ^{1}H NMR ($CDCl_3$) δ 1.08 (3H, t, *J* = 7.3 Hz), 1.87-1.92 (2H, m), 2.92 (2H, t, *J* = 8.0 Hz), 3.32 (2H, t, *J* = 7.5 Hz), 3.71

(2H, t, J = 8.0 Hz), 7.87 (1H, d, J = 8.0 Hz), 7.90 (1H, d, J = 7.5 Hz), 8.06 (1H, d, J = 9.0 Hz), 8.08-8.12 (3H, m), 8.20 (1H, d, J = 9.5 Hz), 8.25 (1H, d, J = 9.0 Hz); MS *m*/*z* (rel. intensity) 316 (M^+, 100), 287 ($M^+ - C_2H_5$, 77), 257 ($M^+ - CH_2CO_2H$, 40), 228 ($M^+ - C_2H_5 - CH_2CO_2H$, 67); UV-vis (CH_2Cl_2) λ_{max} (log ε) 380 (3.43), 351 (4.61), 335 (4.43), 320 (4.04), 281 (4.66), 270 (4.38), 259 (4.04), 247 (4.76), 238 (4.58) 226 (4.49) nm; HRMS (FAB) *m/z* 339.1344 (MNa^+, $C_{22}H_{20}O_2Na$ requires 339.1361).

3-[6-(1-octyl)-1-pyrenyl]propionic acid (5b). A solution of 1,6-dibromopyrene[9] (860 mg, 2.4 mmol), $Pd(Ph_3P)_2Cl_2$ (22 mg, 32 μmol), and CuI (3.1 mg, 15 μmol) in morpholine (15 mL) was stirred for 10 min at 0 ºC, and to the solution added a solution of 1-octyne (0.42 mL, 2.8 mmol) in morpholine (5 mL). The reaction mixture was stirred for 21 h at 100 ºC. After removal of solvent under reduced pressure, water was added to the reaction mixture and the organic material was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, and the solvent was evaporated to afford the crude product. Purification by a silica gel column chromatography with hexane eluent gave 1-bromo-6-(1-octynyl)pyrene (**10b**) as yellow viscous oil (114 mg, 26%). The coupling of **10b** (102 mg, 0.26 mmol) with 1-(3-tetrahydropyran-2-yloxy)propyne (222 mg, 1.6 mmol) was performed in the presence of $Pd(Ph_3P)_2Cl_2$ (22 mg, 32 μmol) and CuI (3.1 mg, 15 μmol) in morpholine (8 mL) in the same procedure as described in the synthesis of **10b**. Purification by a silica gel column chromatography with hexane-CH_2Cl_2 (2 : 1) eluent gave 1-(1-octynyl)-6-[3-(tetrahydropyran-2-yloxy)-1-propynyl]pyrene (**11b**) as yellow granules (40 mg, 43%): mp 136-139 ºC; ^{1}H NMR ($CDCl_3$) δ 0.94 (3H, t, J = 6.5 Hz), 1.37-1.42 (4H, m), 1.57-1.67 (4H, m), 1.73-1.91 (6H, m), 2.64 (2H, t, J = 7.0 Hz), 3.61-3.65 (1H, m), 3.95-4.00 (1H, m), 4.71 (1H, d, J = 15.5 Hz), 5.06 (1H, t, J = 3.5 Hz), 8.05-8.11 (6H, m), 8.52 (1H, d, J = 9.0 Hz), 8.55 (1H, d, J = 9.0 Hz); MS *m*/*z* (rel. intensity) 448 (M^+, 7), 364 ($M^+ - C_5H_9O$, 5), 347 ($M^+ - C_5H_9O_2$, 5), 340 (M^+ –

C_8H_{13}, 21), 239 ($M^+ - C_5H_9O_2 - C_8H_{13}$, 100). The pyrene **11b** (66 mg, 0.15 mmol) was dissolved in CH_2Cl_2 (0.4 mL) and ethanol (0.8 mL), and pyridinium *p*-toluenesulfonate (1.3 mg, 5.3 μmol) was added to the solution. The reaction mixture was stirred for 18 h at 60 ºC. After removal of the solvent, the residue was developed on PTLC (hexane-CH_2Cl_2 = 1 : 3) and purified by recrystallization from hexane-CH_2Cl_2 to give 3-[6-(1-octynyl)-1-pyrenyl]prop-2-yn-1-ol (**12b**) as light yellow granules (42 mg, 78%): mp 137-141 ºC; ^{1}H NMR ($CDCl_3$) δ 0.95 (3H, t, *J* = 6.5 Hz), 1.39-1.43 (4H, m), 1.56-1.60 (2H, m), 1.78 (2H, quint, *J* = 7.5 Hz), 1.85 (1H, t, *J* = 6.0 Hz), 2.66 (2H, t, *J* = 7.0 Hz), 4.74 (2H, d, *J* = 6.0 Hz), 8.08-8.13 (6H, m), 8.53 (1H, d, *J* = 9.0 Hz), 8.59 (1H, d, *J* = 9.0 Hz). The hydrogenation of **12b** (37 mg, 0.10 mmol) was performed by stirring under a H_2 atmosphere in THF (5 mL) in the presence of PtO_2 (2.9 mg, 13 μmol) for 18 h at room temperature. After removal of the catalyst by filtration, the solvent was evaporated to give the crude product (39 mg, 100%). Purification by recrystallization from hexane-CH_2Cl_2 gave 3-[6-(1-octyl)-1-pyrenyl]propan-1-ol (**13b**) as light brown granules: mp 120-124 ºC; ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, *J* = 6.3 Hz), 1.25-1.32 (6H, m), 1.37 (2H, quin, *J* = 7.5 Hz), 1.48 (2H, quin, *J* = 7.7 Hz), 1.84 (2H, quin, *J* = 7.7 Hz), 2.13 (2H, m), 3.32 (2H, t, *J* = 8.0 Hz), 3.45 (2H, t, *J* = 7.8 Hz), 3.79 (2H, t, *J* = 6.0 Hz), 7.85-7.88 (2H, m), 8.04-8.10 (4H, m), 8.23 (1H, d, *J* = 9.5 Hz), 8.24 (1H, d, *J* = 8.5 Hz). To a solution of pyridinium dichromate (184 mg, 0.49 mmol) in DMF (0.3 mL) was added a solution of **13b** (30 mg, 81 μmol) in DMF (1.7 mL). The reaction mixture was stirred for 14 h at room temperature. After water was added to cease the reaction, the organic material was extracted with ether, and the ethereal solution was dried over Na_2SO_4. After evaporation of the solvent, the residue was stirred in a mixture of 5% sulfuric acid (3 mL) and ether (4 mL) for 15 min. The aqueous layer was extracted with ether, and the combined ethereal solution was washed with water, and dried over Na_2SO_4. After evaporation of the solvent, the residue

was purified by recrystallization from hexane-CH_2Cl_2 to give **5b** as light brown granules (7.7 mg, 25%): mp 169-172 ºC, ^{1}H NMR ($CDCl_3$) δ 0.87 (3H, t, *J* = 7.0 Hz), 1.27-1.31 (6H, m), 1.34-1.40 (2H, m), 1.45-1.51 (2H, m), 1.84 (2H, quin, *J* = 7.7 Hz), 2.92 (2H, t, *J* = 8.1 Hz), 3.33 (2H, t, *J* = 7.8 Hz), 3.70 (2H, t, *J* = 8.0 Hz), 7.86 (1H, d, *J* = 7.8 Hz), 7.89 (1H, d, *J* = 7.8 Hz), 8.05 (1H, d, *J* = 9.2 Hz), 8.08-8.11 (3H, m), 8.20 (1H, d, *J* = 9.4 Hz), 8.24 (1H, d, *J* = 9.4 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.5, 29.3, 29.6, 29.9, 31.9, 32.0, 33.8, 35.4, 121.8, 123.1, 124.6, 1245.8, 125.4, 125.5, 126.9, 127.1, 127.4, 127.9, 128.8, 128.9, 129.4, 130.1, 133.8, 137.5, 176.7; MS *m/z* (rel. intensity) 386 (M^+, 100), 287 ($M^+ - C_7H_{15}$, 70), 228 ($M^+ - C_7H_{15} - CH_2CO_2H$, 61); UV-vis ($CH_2Cl_2$) λ_{max} (log ε) 380 (3.34), 352 (4.59), 335 (4.46), 320 (4.08), 280 (4.54), 270 (4.40), 260 (4.08), 245 (4.60), 238 (4.60); HRMS (FAB) *m/z* 387.2300 (MH^+, $C_{27}H_{31}O_2$ requires 387.2324).

3-[6-(1-dodecyl)-1-pyrenyl]propionic acid (5c). This acid was synthesized in the same manner as that described for **5b** using 1-dodecyne as a staring material. The coupling of 1,6-dibromopyrene[9] (580 mg, 1.6 mmol) with 1-dodecyne (0.41 mL, 1.9 mmol) in the presence of $Pd(Ph_3P)_2Cl_2$ (27 mg, 39 μmol) and CuI (3.0 mg, 15 μmol) in morpholine (20 mL), followed by the subsequent coupling of the resulting 1-bromo-6-(1-dodecynyl)pyrene (**10c**) (187 mg, 0.42 mmol) with 1-[3-(tetrahydropyran-2-yloxy)]propyne (355 mg, 2.5 mmol) in the presence of $Pd(Ph_3P)_2Cl_2$ (22 mg, 32 μmol) and CuI (3.1 mg, 15 μmol) in morpholine (10 mL), gave 1-(1-dodecynyl)-6-[3-(tetrahydropyran-2-yloxy)-1-propynyl]pyrene (**11c**) as light brown viscous oil (71 mg, 9% in two steps): ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, *J* = 6.8 Hz), 1.28-1.80 (22H, m), 2.66 (2H, t, *J* = 6.8 Hz), 3.62-3.68 (1H, m), 3.95-4.03 (1H, m), 4.70 (1H, d, *J* = 15.8 Hz), 4.77 (1H, d, *J* = 15.8 Hz), 5.06-5.09 (1H, m), 8.08-8.12 (6H, m), 8.55 (1H, d, *J* = 8.9 Hz), 8.59 (1H, d, *J* = 8.9 Hz). The deprotection of **11c** (91 mg, 0.18 mmol) was achieved by stirring with pyridinium *p*-toluenesulfonate (1.6 mg, 6.4 μmol) in a binary solvent of

CH_2Cl_2 and ethanol to give 3-[6-(1-dodecynyl)-1-pyrenyl]prop-2-yn-1-ol (**12c**) as yellow granules (70 mg, 92%). The hydrogenation of **12c** (30 mg, 71 μmol) was performed by stirring under a H_2 atmosphere in THF (5 mL) in the presence of PtO_2 (3.0 mg, 13 μmol) for 19 h at room temperature to give 3-[6-(1-dodecyl)-1-pyrenyl]propan-1-ol (**13c**) as light yellow granules (24 mg, 78%). The alcohol **13c** (18 mg, 43 μmol) was oxidized with pyridinium dichromate (68 mg, 0.18 mmol) in DMF (1.2 mL) to afford **5c** as light brown granules (4.1 mg, 22%): mp 171-175 ºC; ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, *J* = 6.9 Hz), 0.99-1.34 (14H, m), 1.36-1.39 (2H, m), 1.48 (2H, quin, *J* = 7.6 Hz), 1.85 (2H, quin, *J* = 7.5 Hz), 2.93 (2H, t, *J* = 8.0 Hz), 3.34 (2H, t, *J* = 7.8 Hz), 3.71 (2H, t, *J* = 7.9 Hz), 7.87 (1H, d, *J* = 8.0 Hz), 7.90 (1H, d, *J* = 8.0 Hz), 8.06 (1H, d, *J* = 9.2 Hz), 8.09-8.12 (3H, m), 8.21 (1H, d, *J* = 8.9 Hz), 8.25 (1H, d, *J* = 9.2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.6, 29.4, 29.6, 29.7, 29.9, 31.9, 32.0, 33.8, 35.2, 121.8, 123.1, 124.6, 124.8, 125.4, 125.5, 126.9, 127.1, 127.4, 127.9, 128.8, 128.9, 129.4, 130.1, 133.8, 137.5, 175.8; MS *m*/*z* (rel. intensity) 442 (M^+, 100), 287 ($M^+ - C_{11}H_{23}$, 82), 227 ($M^+ - C_{11}H_{23} - CH_2CO_2H$, 71); UV-vis ($CH_2Cl_2$) λ_{max} (log ε) 380 (3.43), 352 (4.56), 335 (4.40), 321 (4.04), 281 (4.56), 270 (4.34), 259 (4.04), 246 (4.64), 238 (4.57) nm; HRMS (FAB) *m/z* 443.2923 (MH^+, $C_{31}H_{39}O_2$ requires 443.2950).

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Derivation of Eq. 3 from Eq. 2

According to Scheme 1, the changes in the concentration of reactive intermediates involved in the $MV^{+\bullet}$ formation, that is, S_i^*, $S_i^{-\bullet}$, and $S_o^{-\bullet}$, are described by the following Equations (S1)-(S3).

$$d[S_i^*]/dt = \alpha I - \tau_s^{-1}[S_i^*] - k_q[S_i^*][Asc^-] \quad (S1)$$

$$d[S_i^{-\bullet}]/dt = k_q[S_i^*][Asc^-] - \tau_i^{-1}[S_i^{-\bullet}] - k_e[S_i^{-\bullet}][S_o] \quad (S2)$$

$$d[S_o^{-\bullet}]/dt = k_e[S_i^{-\bullet}][S_o] - \tau_o^{-1}[S_o^{-\bullet}] - k_t[S_o^{-\bullet}][MV^{2+}] \quad (S3)$$

The rate constants and lifetimes are defined in the text. Since these species are so reactive that their concentrations are considerably low, it can be assumed that their concentrations remain constant (a steady-state approximation). Thus, from Equations (S4)-(S6),

$$d[S_i^*]/dt = 0 \quad (S4)$$

$$d[S_i^{-\bullet}]/dt = 0 \quad (S5)$$

$$d[S_o^{-\bullet}]/dt = 0 \quad (S6)$$

the concentrations of these species are described by the following Equations (S7)-(S9).

$$[S_i^*] = \alpha I \ /(\tau_s^{-1} + k_q[Asc^-]) \quad (S7)$$

$$[S_i^{-\bullet}] = k_q[S_i^*][Asc^-] \ /(\tau_i^{-1} + k_e[S_o]) \quad (S8)$$

$$[S_o^{-\bullet}] = k_e[S_i^{-\bullet}][S_o] \ /(\tau_o^{-1} + k_t[MV^{2+}]) \quad (S9)$$

According to Scheme 1, the change in $[MV^{+\bullet}]$ is described by Eq. 2.

$$d[MV^{+\bullet}]/dt = k_t[S_o^{-\bullet}][MV^{2+}] - k_r[MV^{+\bullet}] \quad (2)$$

Applying Equations (S7)-(S9) to (2), Equation (S10) is obtained.

$$\frac{d[MV^{+\cdot}]}{dt} = \frac{k_t[MV^{2+}]}{\tau_o^{-1} + k_t[MV^{2+}]} \frac{k_e[S_o]}{\tau_i^{-1} + k_e[S_o]} \frac{\alpha I\, k_q[Asc^-]}{\tau_s^{-1} + k_q[Asc^-]} - k_r[MV^{+\cdot}] \quad (S10)$$

The term $k_q[Asc^-]/(\tau_s^{-1} + k_q[Asc^-])$ indicates that the proportion of the rate of the process effective for the electron transport, that is, quenching of the sensitizer excited state by Asc^-, to the total rate of the decay process of the sensitizer excited state. Therefore, this term can be described in terms of the quenching efficiency Φ_D. Similarly, the term $\Phi_E = k_e[S_o]/(\tau_i^{-1} + k_e[S_o])$ shows the efficiency for $S_i^{-\bullet}$ to transfer an electron to S_o, and the term $\Phi_A = k_t[MV^{2+}]/(\tau_o^{-1} + k_t[MV^{2+}])$ represents the efficiency for $S_o^{-\bullet}$ to transfer an electron to $MV^{+\bullet}$. Using these relations, Equation (S10) is rewritten as (S11).

$$d[MV^{+\bullet}]/dt = \alpha I\, \Phi_D\Phi_E\Phi_A - k_r[MV^{+\bullet}] \quad (S11)$$

Since Asc^- and MV^{2+} are used in large excess, their concentrations can be considered to be constant at the early stage of the reaction. Thus, Equation (S11) is solved to give Eq. 3.

$$[MV^{+\bullet}] = (\alpha I\, \Phi_D\Phi_E\Phi_A/\, k_r)[1 - \exp(-\, k_r\, t)] \quad (3)$$

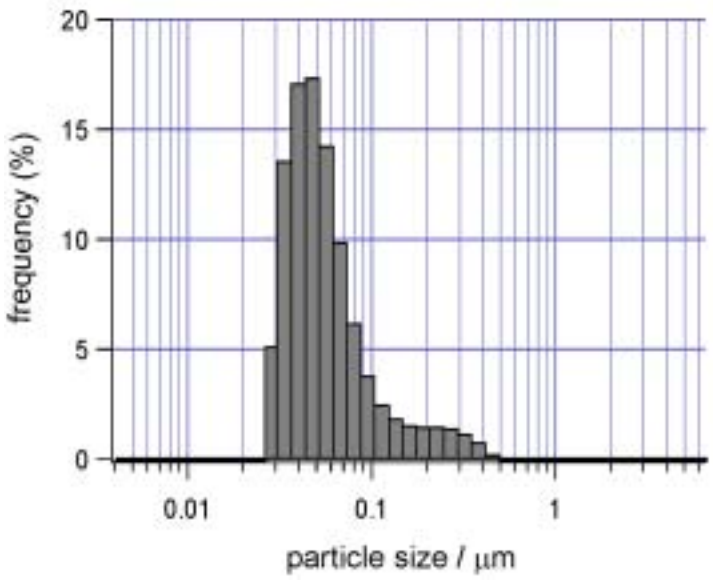

Fig. S1 Particle size distribution of PC vesicles containing **1a**.

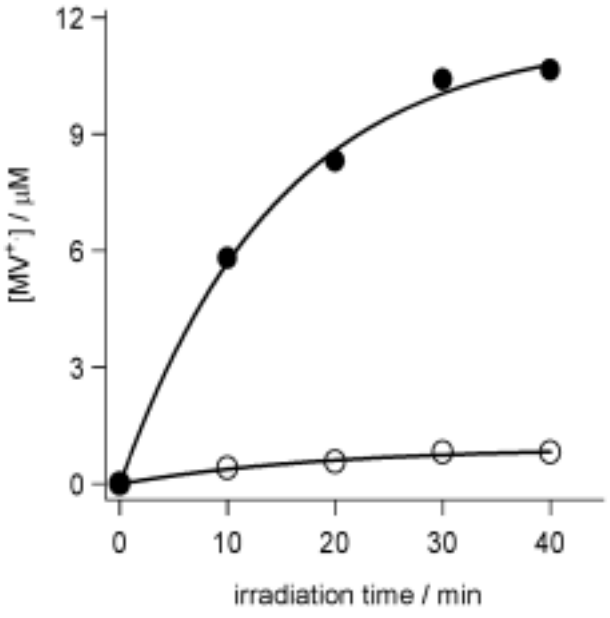

Fig. S2 Change in the concentration of $MV^{+\bullet}$ produced by the irradiation of a solution of vesicles containing **1a** and Asc^- in the presence (○) and the absence (●) of surfactant vs irradiation time.

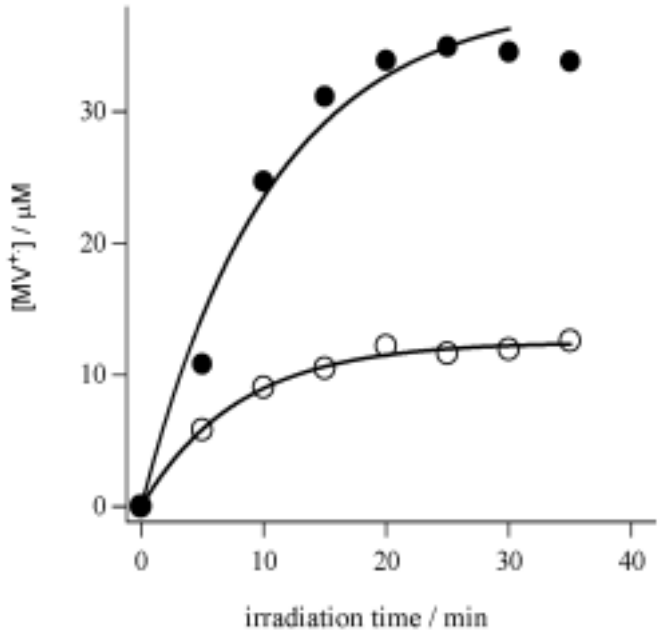

Fig. S3 Change in the concentration of $MV^{+\bullet}$ produced by the irradiation of a solution of vesicles containing **2a** in the presence (●) and the absence (○) of Acs^- in the inner waterpool vs irradiation time.

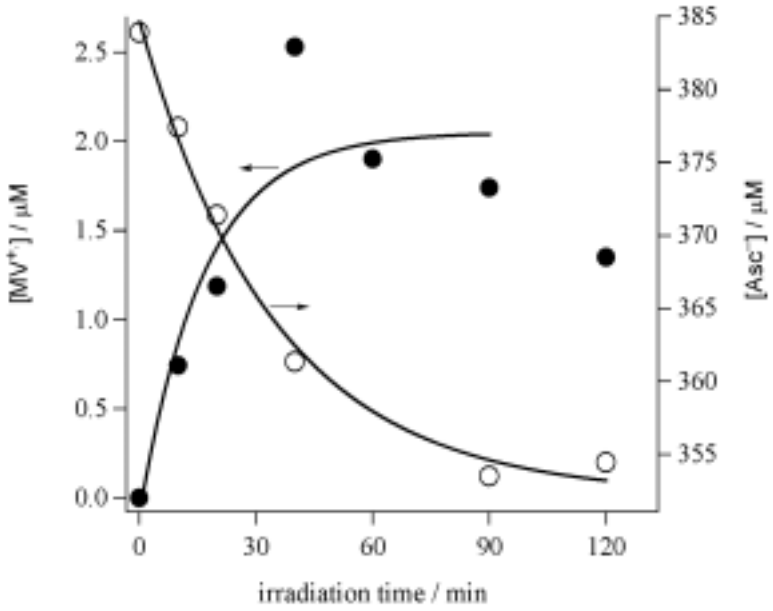

Fig. S4 Change in the concentration of $MV^{+\bullet}$ (●) produced and Asc^- (○) consumed by the irradiation of a solution of vesicles containing **1a** vs irradiation time.

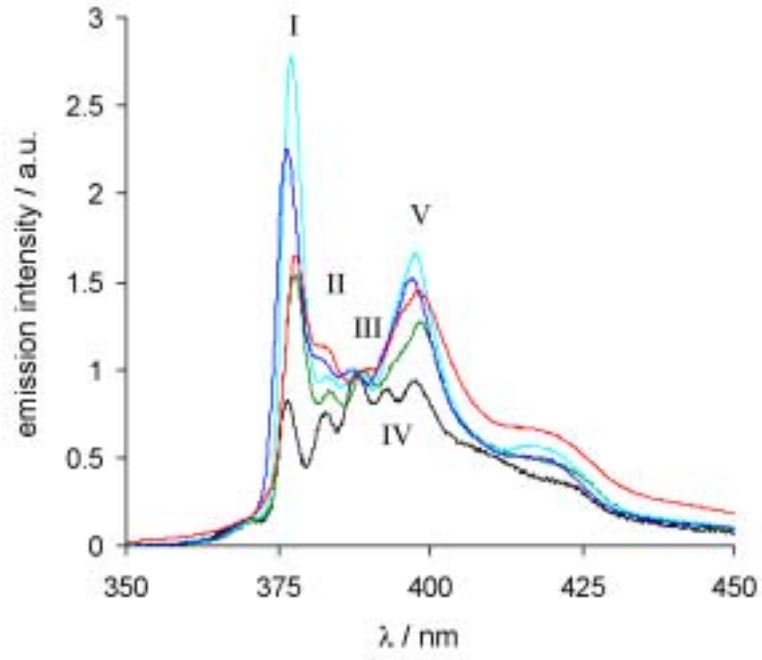

Fig. S5 Fluorescence spectra of **1a** in cyclohexane (black), chloroform (green), ethanol (light blue), water (blue), and vesicle solution (red). The emission intensities are normalized at the band III.

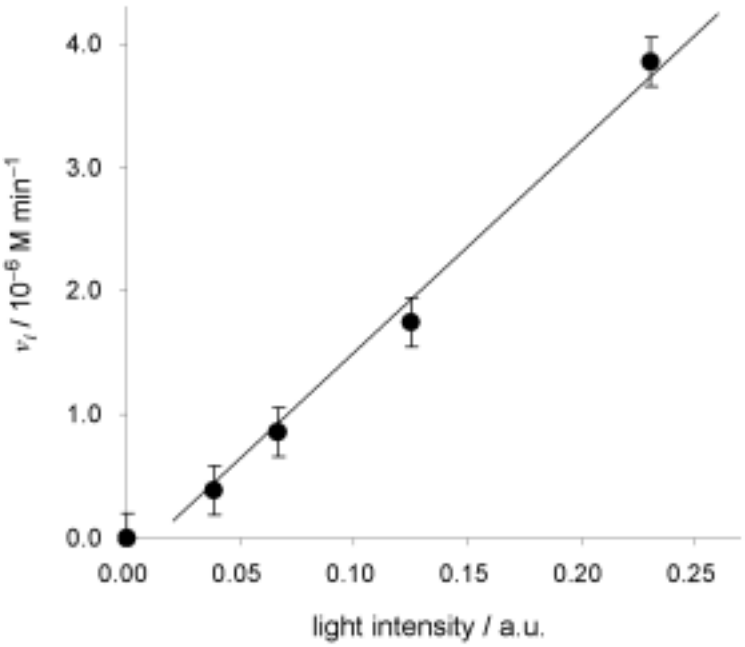

Fig. S6 Dependence of the initial rate of $MV^{+\bullet}$ formation on the incident light intensity for the irradiation (366 nm) of a solution of vesicles containing **1b** and Asc^{-}.

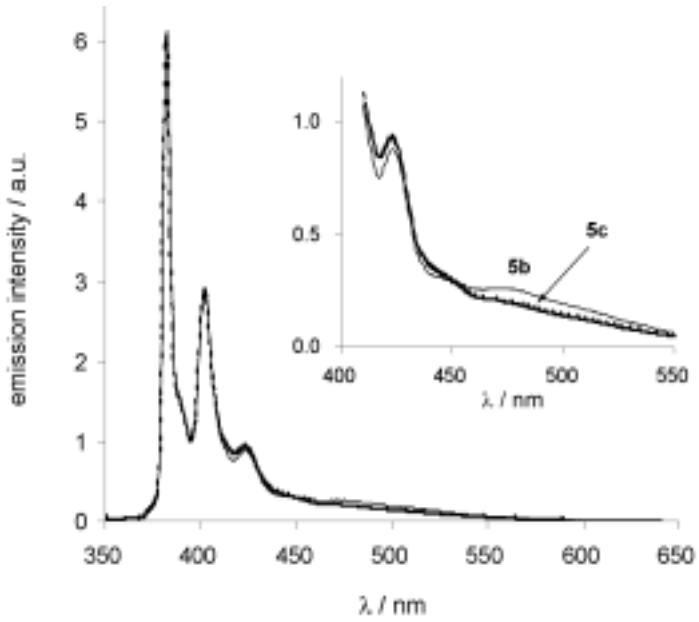

Fig. S7 Fluorescence spectra of **5b** (solid line) and **5c** (broken line) recorded in the vesicle solution on excitation at 330 nm. The inset figure shows an enlarged spectra of the range in wavelength from 400 to 550 nm.