Supporting Information

Novel Fluorescence Probes Based on 2,6-Donor-Acceptor-Substituted Anthracene Derivatives

Heiko Ihmels,* Andreas Meiswinkel, Christian J. Mohrschladt

Experimental Section

(*N*,*N*)-Diethyl-6-methoxyanthracene-2-carboxylic acid amide (1c): A solution of 53 mg (0.21 mmol) of 6-methoxy-2-anthracenecarboxylic acid in 5.3 mL of oxalyl chloride was kept at reflux for 18 h under argon-gas atmosphere. After evaporation of excess oxalyl chloride in vacuum the solid was dissolved in 10 mL of dichloromethane. 2 mL (19 mmol) of diethyl amine were added and the solution was stirred at 20 °C for 2 h. After evaporation of the solvent in vacuum water and diluted aqueous NaOH were added to the remaining solid until a pH of 8–9 was indicated. The aqueous phase was extracted three times with dichloromethane and the combined organic phases were washed with 2% aqueous $NaHCO_3$ and brine, dried with $MgSO_4$ and the solvent was evaporated in vacuum. Crystallization from *n*-hexane/dichloromethane gave 40 mg (0.13 mmol, 62%) of the amide **1c** as green-brown solid. mp 150–155 °C; UV (MeOH): λ (log ε) 320 (3.43), 334 (3.59), 353 (3.65), 372 (3.65), 392 (3.60); (C_6H_6): 321 (3.63), 336 (3.81), 355 (3.90), 375 (3.92), 395 (3.88); (MeCN): 319 (3.60), 333 (3.73), 351 (3.78), 372 (3.77), 392 (3.73); ^{1}H NMR ($CDCl_3$, 200 MHz) 1.24 (t, ^3J = 6.6 Hz, 6 H), 3.30-3.70 (m, 4 H), 3.97 (s, 3 H), 7.15-7.21 (m, 2 H), 7.44 (dd, ^3J = 9.1 Hz, ^4J = 1.5 Hz, 1 H), 7.86-7.99 (m, 3 H), 8.27 (s, 1 H), 8.36 (s, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) 13.7, 55.3, 103.6, 121.0, 123.8, 124.2, 126.3, 127.0, 128.0, 128.7, 129.3, 129.8, 131.6, 132.9, 133.4, 157.6, 171.5; IR (KBr): $\tilde{\nu}$ 1652 (C=O); MS (70 eV) *m/z* 307 (M^+, 86), 279 (2), 235 (100), 192 (4), 164 (35), 117.5 (7); HRMS calcd for $C_{20}H_{21}NO_2$ 307.1572, found 307.1564.

6-Methoxyanthracene-2-methyl carboxylate (1d): A solution of 41 mg (0.16 mmol) of 6-methoxy-2-anthracenecarboxylic acid, 5 mL (123 mmol) of methanol and 110 mg (3.5 mmol) of concd sulfuric acid in 10 mL of dichloromethane was kept at reflux for 18 h under argon-gas atmosphere. After evaporation of the solvent in vacuum the remaining solid was washed with water, 2% aqueous $NaHCO_3$ and brine. The solution was dried with $MgSO_4$ and the solvent was evaporated in vacuum. The remaining solid was crystallized from *n*-hexane/dichloromethane to give 24 mg (0.09 mmol, 56%) of the methyl ester **1d** as yellow solid. mp 228–229 °C; UV (MeOH): λ (log ε) 244 (4.43), 268 (4.51), 364 (3.67), 379 (3.75), 397 (3.63); (C_6H_6): 287 (4.51), 365 (3.69), 381 (3.79), 402 (3.66); (MeCN): 244 (4.31), 269 (4.52), 361 (3.52), 378 (3.59), 397 (3.48); ^{1}H NMR ($CDCl_3$, 200 MHz) 3.98 (s, 3 H), 4.00 (s,

3 H), 7.16-7.25 (m, 2 H), 8.03-7.90 (m, 3 H), 8.28 (s, 1 H), 8.46 (s, 1 H), 8.77 (s, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) 52.2, 55.3, 121.1, 124.1, 124.3, 125.9, 127.8, 128.5, 128.6, 128.9, 130.1, 132.4, 133.2, 134.4, 158.1, 167.4; IR (KBr): $\tilde{\nu}$ 1748 (C=O); MS (70 eV) *m/z* 266 (M^+, 100), 235 (27), 207 (33), 164 (50), 117.5 (7), 103.5 (8); HRMS calcd for $C_{17}H_{14}O_3$ 266.0943, found 266.0940.

6-Methoxyanthracene-2-neopentyl carboxylate (1e): To a suspension of 220 mg (0.87 mmol) of 6-methoxy-2-anthracenecarboxylic acid in 70 mL of benzene were added 1.84 g (20.9 mmol) of 2,2-dimethyl-1-propanol and 126 mg (0.66 mmol) of *p*-toluenesulfonic acid. The mixture was kept at reflux for 3 days under argon-gas atmosphere. The solution was washed with water, three times with 2% aqueous $NaHCO_3$ and once with brine. The solution was dried with $MgSO_4$ and the solvent was evaporated in vacuum. The remaining solid was crystallized from *n*-hexane/dichloromethane to give 198 mg (0.61 mmol, 71%) of the neopentylester **1e** as yellow solid. mp 178–179 °C; UV (MeOH): λ (log ε) 238 (4.44), 244 (4.46), 271 (4.84), 362 (3.73), 379 (3.80), 398 (3.69); (C_6H_6): 289 (4.51), 363 (3.73), 381 (3.82), 402 (3.71); (MeCN): 237 (4.43), 244 (4.46), 270 (4.90), 363 (3.72), 379 (3.79), 398 (3.67); ^{1}H NMR ($CDCl_3$, 200 MHz) 1.10 (s, 9 H), 3.98 (s, 3 H), 4.10 (s, 2 H), 7.17−7.22 (m, 3 H), 7.90−8.05 (m, 3 H), 8.29 (s, 1 H), 8.49 (s, 1 H), 8.77 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) 26.7, 31.7, 55.4, 74.3, 103.6, 121.1, 124.1, 124.3, 126.3, 127.8, 128.6, 128.6, 129.0, 130.1, 132.2, 133.3, 134.4, 158.1, 166.9; IR (KBr): $\tilde{\nu}$ 1727 (C=O); MS (70 eV) *m/z* 322 (M^+, 100), 252 (83), 235 (37), 207 (30) 164 (32); HRMS calcd for $C_{21}H_{22}O_3$ 322.1568, found 322.1565.

2-[2-(6-Methoxyanthracenyl)]-4,4-dimethyl-2-oxazoline (1f): A solution of 38 mg (0.15 mmol) of 6-methoxy-2-anthracenecarboxylic acid in 3.8 mL of oxalyl chloride was kept at reflux for 18 h under argon-gas atmosphere. After evaporation of excess oxalyl chloride in vacuum the solid was dissolved in dichloromethane and added dropwise to a solution of 27 mg (0.30 mmol) of 2-amino-2-methylpropanol in 3.8 mL of dichloromethane at 0 °C. After stirring for 2 h at 20 °C the precipitated solid was filtered off. To the remaining solution was added 0.1 mL of thionyl chloride and the solution was kept at reflux for 2 h under argon-gas atmosphere and after that the solvent was evaporated in vacuum. The remaining brown solid was washed with diethyl ether. To the solid was added water, diethyl ether and diluted aqueous NaOH until a pH of 8–9 was indicated. The aqueous phase was extracted twice with diethyl ether and the combined organic phases were dried with $MgSO_4$ and the solvent was removed in vacuum. Crystallization from *n*-hexane/dichloromethane gave 25 mg (0.09 mmol, 60%) of oxazoline **1f** as yellow solid. mp 220–225 °C; UV (C_6H_6): λ (log ε) 278 (4.52), 359 (3.68), 375 (3.76), 396 (3.66); (MeCN): 276 (4.49), 357 (3.64), 372 (3.71), 392 (3.59); ^{1}H NMR ($CDCl_3$, 200 MHz) 1.44 (s, 6 H), 3.96 (s, 3 H), 4.18 (s, 2 H),

7.14-7.19 (m, 2 H), 7.87-8.01 (m, 3 H), 8.24 (s, 1 H), 8.38 (s, 1 H), 8.55 (s, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) 28.5, 55.3, 67.7, 79.2, 103.6, 120.9, 123.8, 124.1, 124.3, 127.7, 127.8, 128.5, 129.3, 129.5, 130.0, 132.6, 133.8, 157.8, 162.3; MS (70 eV) *m/z* 305 (M^+, 82), 290 (100), 233 (71), 219 (5), 207 (9), 176 (4), 164 (21)); HRMS calcd for $C_{20}H_{19}N_1O_2$ 305.1416, found 305.1416.

2-[2-(6-Methoxyanthracenyl)]-benzoxazole (1g): A solution of 195 mg (0.77 mmol) of 6-methoxy-2-anthracenecarboxylic acid in 19.5 mL of oxalyl chloride was kept at reflux for 18 h under argon-gas atmosphere. After evaporation of excess oxalyl chloride in vacuum the solid was added to a solution of 88 mg (0.80 mmol) of 2-aminophenol in 2 mL of pyridine under argon-gas atmosphere. The solution was stirred for 1 h at 100 °C. The pyridine was evaporated and the remaining dark residue was heated for 0.5 h at 200 °C under argon-gas atmosphere. Purification by column chromatography (SiO_2, *n*-hexane/ethyl acetate 6:1, R_f = 0.31) and crystallisation from *n*-hexane/dichloromethane gave 84 mg (0.26 mmol, 34%) of the benzoxazoline **1g** as yellow solid. mp 148–149 °C; UV (MeOH): λ (log ε) 204 (4.16), 248 (4.43), 266 (4.41), 305 (4.95), 318 (4.85), 368 (4.02), 384 (4.10), 403 (4.01); (C_6H_6): 297 (4.58), 307 (4.60), 320 (4.60), 368 (3.98), 387 (4.09), 407 (3.99); (MeCN): 248 (4.39), 266 (4.40), 303 (4.69), 317 (4.68), 368 (3.97), 384 (4.05), 404 (3.95); ^{1}H NMR ($CDCl_3$, 200 MHz) 3.98 (s, 3 H), 7.17−7.22 (m, 2 H), 7.34−7.42 (m, 2 H), 7.59−7.66 (m, 1 H), 7.78−7.87 (m, 1 H), 7.94 (d, *J* = 9.8 Hz, 1 H), 8.05 (d, *J* = 9.0 Hz, 1 H), 8.23−8.29 (m, 2 H), 8.48 (s, 1 H), 8.91 (s, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) 55.4, 103.7, 110.6, 119.9, 121.2, 122.8, 123.2, 124.3, 124.6, 125.1, 128.0, 128.5, 128.8, 129.1, 129.4, 130.1, 132.7, 134.1, 142.2, 150.8, 158.0, 163.4; MS (70 eV) *m/z* 325 (M^+, 100), 282 (87), 190 (21), 164 (24). Anal. Calcd for $C_{22}H_{15}N_1O_2 \cdot 0.5H_2O$: C, 79.03; H, 4.82; N, 4.19. Found: C, 79.10; H, 4.85; N, 4.11.

Absorption and emission spectra. UV/VIS: Hitachi U3200; emission: Perkin Elmer LS50. Absorption and emission spectra were recorded in deoxygenated spectral grade solvents (Fluka). Distilled water was further deionized by employing Millipore MilliQ equipment. If not noted otherwise, the solution concentrations were 10^{-4} M for absorption spectroscopy and 10^{-5} M for fluorescence spectroscopy. Emission spectra were recorded with an excitation wavelength close to the absorption maximum (λ = 380 nm or 390 nm). The relative fluorescence quantum yields were determined by the standard method[i] with quinine sulfate in 1 N H_2SO_4 as reference (ϕ_{Fl} = 0.546[ii]).

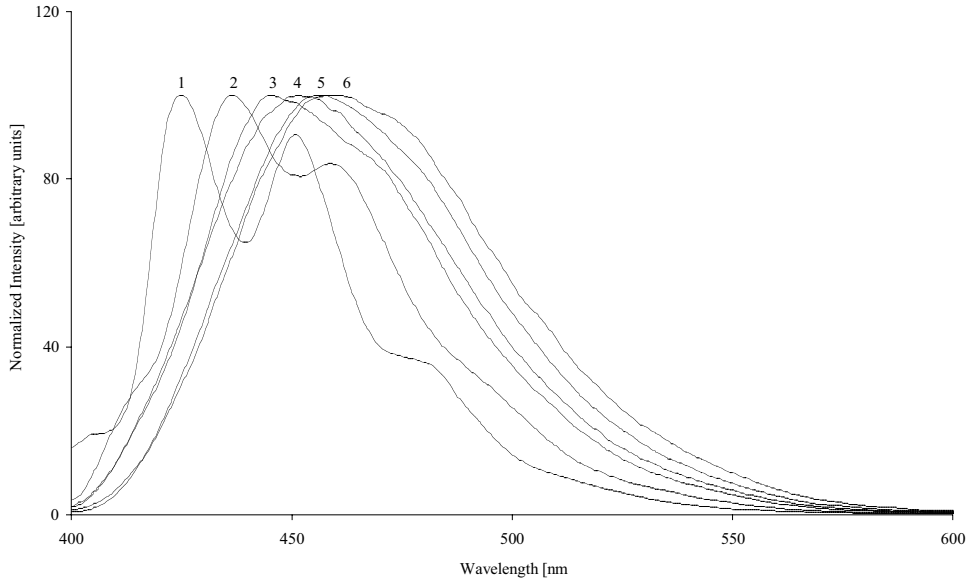

Figure A. Normalized fluorescence spectra of 6-Methoxyanthracene-2-neopentyl carboxylate (**1e**) in different solvents (λ_{ex} = 390 nm; T = 20 °C; c = 10^{-5} M); 1: Cyclohexane, 2: Benzene, 3: Butyronitrile, 4: Acetonitrile, 5: DMSO, 6: Methanol

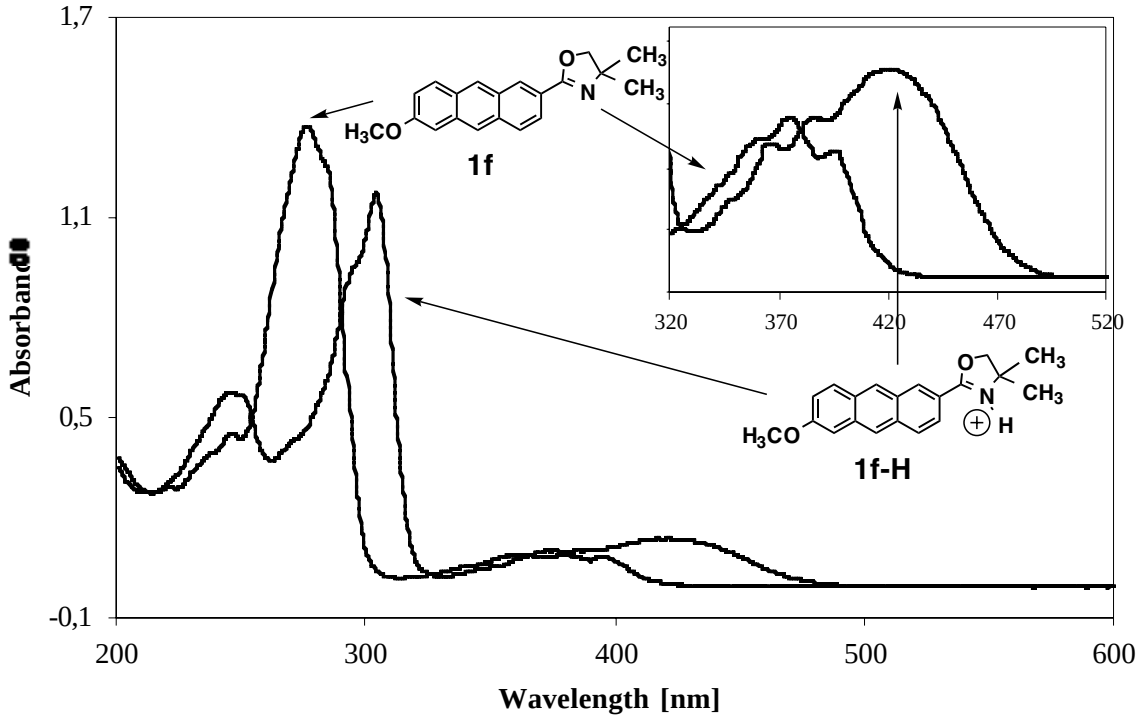

Figure B. Absorption spectra of neutral and protonated 2-[2-(6-Methoxyanthracenyl)]-4,4-dimethyl-2-oxazoline (**1f**) in methanol; T = 20 °C; c = 5 x 10^{-5} M; V = 2 mL.

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[i] J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991–1024

[ii] *Pure Appl. Chem.* **1988**, *60*, 1108–1114.