

New quinacridone derivatives with π -extended conjugation in central core

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Synthesis

Characterization techniques

¹H and ¹³C NMR spectra were recorded on a Varian Mercury (500 and 125 MHz) spectrometer and referenced with respect to TMS and solvents. IR spectra were monitored on Bio-RAD FTS-165 spectrometer using KBr pellets. UV-Vis-NIR spectra were registered using a Cary 5000 (Varian) spectrometer. Mass spectra were measured by EI method on an AMD 604 mass spectrometer. All synthesized compounds studied were subject to C, H, N elemental combustion analysis.

Reagents

1-bromo-3-iodobenzene; 2,7-dibromocarbazole; 2,6-dibromonaphthalene; methyl anthranilate; *n*-octyl bromide; polyphosphoric acid; Cs₂CO₃; palladium acetate, Pd(OAc)₂; (dibenzylidene-

acetone)palladium(0), Pddba₂; tris-*tert*-butylphosphine, *t*-Bu₃P; potassium *tert*-butoxide, *t*-BuOK; anhydrous toluene; anhydrous THF; 1,3-dimethyltetrahydro-2(1H)-pyrimidinone, DMPU were purchased from Aldrich.

All glassware was oven dried, assembled hot, and cooled under a dry argon stream before use. All reactions were performed under dry argon.

Compound 3a

Pddba₂ (86.2 mg, 0.15 mmol) and *t*-Bu₃P (60.7 mg, 0.3 mmol) were mixed in 2 ml of dry toluene and stirred under an argon atmosphere for 0.5 h. Then 2,7-dibromo-9-octylcarbazole, 1.3 g (3 mmol), methyl anthranilate, 1.09 g (7.2 mmol), Cs₂CO₃, 2.93 g (9 mmol) and *ca.* 3 ml of dry toluene were added to the reaction flask. The mixture was stirred and heated at 110°C for 24 h. Then the mixture was cooled to room temperature, washed with 50 ml of NH₄Cl solution and extracted with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄. After evaporation of the solvent the crude product was purified by chromatography on silica gel eluting with CH₂Cl₂/hexanes (3:2) to give 0.92 g (1.59 mmol, 53% yield) of yellow powder.

¹H NMR (500 MHz, CDCl₃) δ, 9.65 (s, 2H), 8.01 (d, J=8 Hz, 2H), 7.97 (d, J=8 Hz, 2H), 7.32-7.31 (m, 4H), 7.24 (d, J=2 Hz, 2H), 7.14 (dd, J=2, 8 Hz, 2H), 6.73 (m, 2H), 4.17 (t, J=7.2 Hz, 2H), 3.94 (s, 6H), 1.86-1.80 (m, 2H), 1.43-1.24 (m, 10H), 0.87 (t, J=7.4 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ, 176.8, 169.0, 148.0, 138.1, 134.6, 134.4, 131.7, 130.0, 122.8, 119.6, 117.3, 115.9, 113.8, 111.9, 51.8, 31.8, 29.3, 27.0, 22.6, 14.1. IR (cm⁻¹): 3320, 3040, 2945, 2852, 1685, 1585, 1516, 1454, 1320, 1257, 1228, 1084, 748. Anal. Calcd. for C₃₆H₃₉N₃O₄: C, 74.84; H, 6.80; N, 7.28; O, 11.08. Found: C, 73.82; H, 6.28; N, 6.85.

Compound 3b

Diester (compound 3a), 2.07 g (1.73 mmol) was dissolved in *ca.* 5 ml of THF and added to the mixture of 3.9 g NaOH in 30 ml of ethanol. The mixture was stirred and heated at 70°C for 3 h. Then the mixture was cooled to room temperature, concentrated and added to 50 ml of water. The solution was acidified with concentrated HCl which resulted in the formation of orange precipitate. The precipitate was filtered, washed two times with water, then with acetone and vacuum dried to give 0.9 g (1.64 mmol) of green-yellow powder (95% yield).

¹H NMR (500 MHz, DMSO-d₆) δ, 9.80 (s, 2H), 8.04 (d, J=8.5 Hz, 2H), 7.92 (dd, J=1.5, 8 Hz, 2H), 7.43 (d, J=1.5 Hz, 2H), 7.39 (td, J=1.5, 7.5 Hz, 2H), 7.29 (d, J=8.5 Hz, 2H), 7.07 (dd, J=2, 8 Hz, 2H), 6.77 (t, J=7.5 Hz, 2H), 4.30 (t, J=6.8 Hz, 2H), 1.76-1.72 (m, 2H), 1.34-1.24 (m, 4H), 1.22-1.12 (m, 6H), 0.78 (t, J=7 Hz, 3H). ¹³C NMR (125 MHz, DMSO-d₆) δ, 170.1, 147.9, 141.5, 137.9, 134.2, 131.9, 120.5, 118.5, 117.0, 114.3, 113.5, 112.0, 102.6, 31.2, 28.7, 28.4,

26.5, 22.0, 13.9. **IR** (cm⁻¹): 3350, 3030, 2956, 2856, 1652, 1569, 1495, 1428, 1319, 1241, 1230, 1160, 1044, 896, 786, 745. **Anal.** Calcd. for C₃₄H₃₅N₃O₄: C, 74.30; H, 6.42; N, 7.64; O, 11.64. Found: C, 74.20; H, 6.36; N, 7.44.

Compound 4a

The compound was prepared according to the procedure described for **3a**, however Pd(OAc)₂ (37.8 mg, 0.17 mmol) and *t*-Bu₃P (94 mg, 0.46 mmol) was used as the catalyst. 2,6-Dibromonaphthalene 1.0 g (3.5 mmol), methyl anthranilate 1.07 g (7.2 mmol), Cs₂CO₃, 3.6 g (11 mmol) and 5 ml of dry toluene were added to the reaction flask and heated at 110°C. The crude product was chromatographed on silica gel eluting with CH₂Cl₂ with 5%_v of THF. The crystallization from CH₂Cl₂/MeOH afforded yellow powder, 1.35 g (3.17 mmol, 90.5% yield).

¹H NMR (500 MHz, CDCl₃) δ, 9.62 (s, 2H), 8.01 (d, J=8 Hz, 2H), 7.71 (d, J=8.5 Hz, 2H), 7.64 (d, J=1.5 Hz, 2H), 7.36 (dd, J=2.5, 8 Hz, 2H), 7.35-7.33 (m, 4H), 6.77 (m, 2H), 3.93 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ, 169.0, 148.0, 137.4, 134.2, 131.7, 131.3, 128.3, 123.8, 118.4, 117.2, 114.2, 112.0, 51.8. **IR** (cm⁻¹): 3320, 3025, 2953, 2845, 1678, 1579, 1494, 1438, 1316, 1240, 1217, 1142, 1084, 882, 747. **Anal.** Calcd. for C₂₆H₂₂N₂O₄: C, 73.23; H, 5.20; N, 6.57; O, 15.00. Found: C, 73.16; H, 5.17; N, 6.52.

Compound 4b

The hydrolysis was performed in the same way as in the case of **3a**.

¹H NMR (500 MHz, DMSO-d₆) δ, 9.83 (s, 2H), 7.94 (dd, J=1.5, 8 Hz, 2H), 7.82 (d, J=8.5 Hz, 2H), 7.70 (d, J=2 Hz, 2H), 7.44-7.38 (m, 4H), 7.34 (d, J=8.5 Hz, 2H), 6.81 (td, J=1.5, 8 Hz, 2H). ¹³C NMR (125 MHz, DMSO-d₆) δ, 170.0, 147.1, 137.0, 134.3, 131.9, 130.7, 128.3, 123.0, 117.5, 116.8, 113.9, 112.7. **IR** (cm⁻¹): 3332, 3020, 2956, 2856, 1650, 1517, 1494, 1446, 1323, 1247, 1162, 878, 750. **Anal.** Calcd. for C₂₄H₁₈N₂O₄: C, 72.35; H, 4.55; N, 7.04; O, 16.06. Found: C, 71.57; H, 4.34; N, 6.94.

Compound 1. (5,7,9-trioctyl-5H-pyrrolo[3,2-b;4,5-b']diacridine-14,17,9H,9H)-dione)

Under an argon atmosphere diacid **3b**, 1.7 g (3.1 mmol) was mixed with 36 g of polyphosphoric acid and 1.7 g of P₂O₅. The mixture was stirred and heated at 160°C for 20 h. Then the viscous mixture was cooled to room temperature and added to cold water (400 ml). The red precipitate was formed, filtered and dispersed in 200 ml of water. NH₃ aq. was slowly added to the dispersion until the pH became *ca.* 8. The product was filtered, washed with water and vacuum dried at 70°C to give 1.1 g (2.1 mmol, 68% yield) of brown powder.

The crude product was not purified before the alkylation with octyl bromide. Thus, 0.96 g (1.87 mmol) of the powder was dispersed in 10 ml of toluene and 10 ml of DMPU. Then *t*-BuOK, 2.2 g (19 mmol) was added and the mixture was heated at 80°C followed by the drop wise addition of 2 ml of *n*-octyl bromide. The mixture was heated for 24 h. After cooled, toluene was evaporated and the mixture was poured into 400 ml of brine. The precipitate was formed, filtered and washed with water. The precipitate was dissolved in CH₂Cl₂ and dried over Na₂SO₄. The crude product was purified by chromatography on silica gel eluting with CH₂Cl₂/THF (from 7.5% to 20%) to give a yellow powder, 0.68 g (0.92 mmol, 30% yield).

¹H NMR (500 MHz, CDCl₃) δ, 8.65 (s, 2H), 8.52 (dd, J=1.5, 8 Hz, 2H), 7.42 (td, J=1.5, 8 Hz, 2H), 7.17 (t, J=8 Hz, 2H), 6.98 (d, J=8 Hz, 2H), 6.70 (s, 2H), 4.34 (t, J=7 Hz, 2H), 3.87 (t, J=8 Hz, 4H), 1.94-1.91 (m, 2H), 1.70-1.67 (m, 4H), 1.48-1.23 (m, 30H), 0.93 (t, J=6.8 Hz, 6H), 0.83 (t, J=6.8 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ, 177.0, 146.3, 140.9, 140.5, 132.7, 127.4, 121.5, 120.3, 118.9, 118.4, 116.3, 114.2, 91.7, 31.8, 29.6, 29.4, 29.3, 27.9, 26.6, 14.1, 14.0. IR (cm⁻¹): 3025, 2926, 2852, 1589, 1500, 1457, 1334, 1226, 1193, 1132, 908, 825, 751, 695. Anal. Calcd. for C₅₀H₆₃N₃O₂: C, 81.37; H, 8.60; N, 5.69; O, 4.34. Found: C, 81.14; H, 6.53; N, 5.61. M/z=737.5.

Compound 2. (5,13-dioctylacridino[3,2-b]acridine-8,16(5H,13H)-dione)

Compound 2 was prepared in the same way as compound 1. Thus, compound 4b (0.82 g, 2.06 mmol) was reacted in the presence of P₂O₅/polyphosphoric acid mixture at 160°C for 24 h to give 0.7 g of yellow powder (1.9 mmol, 92% yield). The crude product was alkylated with *n*-octyl bromide which resulted in 0.62 g of yellow powder (1.06 mmol, 56% yield).

¹H NMR (500 MHz, CDCl₃) δ, 10.7 (d, J=9.5 Hz, 2H), 8.66 (dd, J=1.5, 8 Hz, 2H), 7.81 (d, J=9.5 Hz, 2H), 7.66 (td, J=1.5, 8 Hz, 2H), 7.45 (d, J=8 Hz, 2H), 7.33 (t, J=7.2 Hz, 2H), 4.40 (t, J=8.2 Hz, 4H), 2.02-1.96 (m, 4H), 1.62-1.56 (m, 4H), 1.51-1.46 (m, 4H), 1.41-1.34 (m, 12H), 0.93 (t, J=7 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ, 170.1, 141.4, 140.0, 134.1, 132.9, 127.9, 127.8, 124.8, 121.7, 117.0, 114.6, 47.2, 31.8, 29.3, 27.7, 26.9, 22.7, 14.1. IR (cm⁻¹): 3020, 2920, 2848, 1597, 1571, 1515, 1472, 1402, 1271, 1178, 1144, 1088, 829, 747, 640. Anal. Calcd. for C₄₀H₄₆N₂O₂: C, 81.87; H, 7.90; N, 4.77; O, 5.46. Found: C, 81.82; H, 7.87; N, 4.74. M/z=586.2.

NMR data of the compound 2

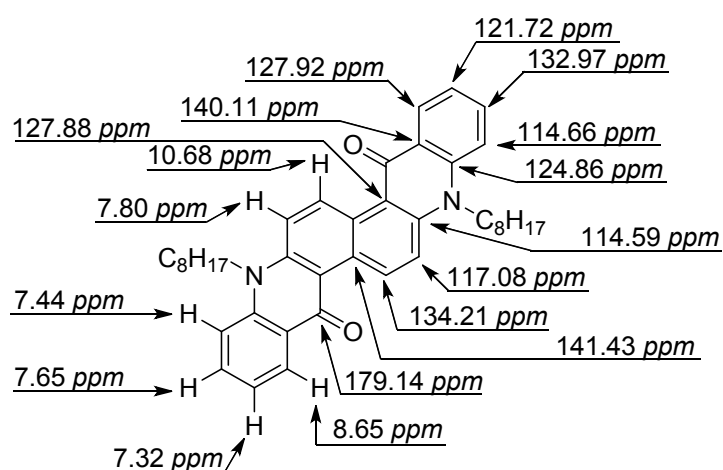


Figure S1. Chemical shifts of the hydrogen and carbon atoms in the compound 2 molecule.

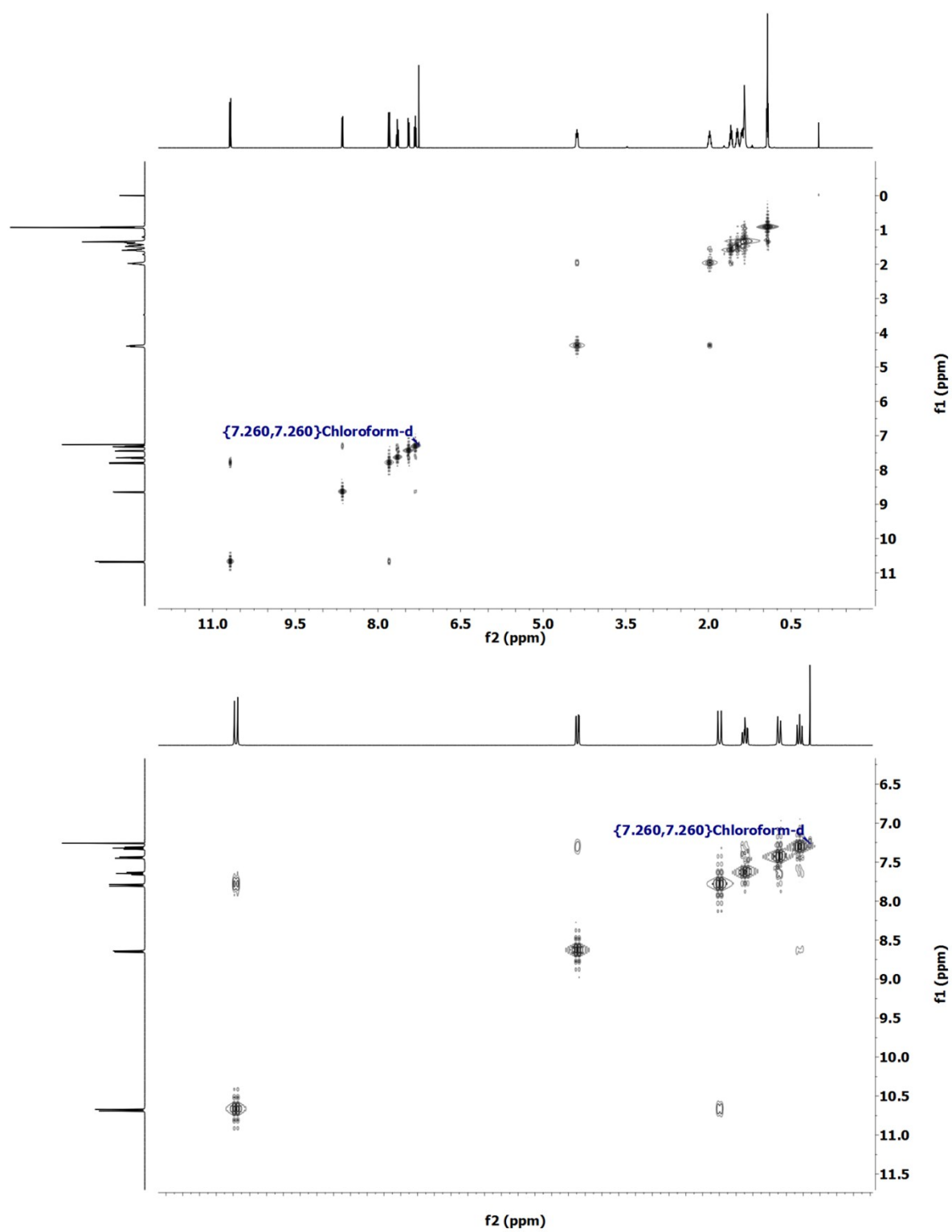


Figure S2. ^1H - ^1H COSY NMR spectrum of the compound 2.

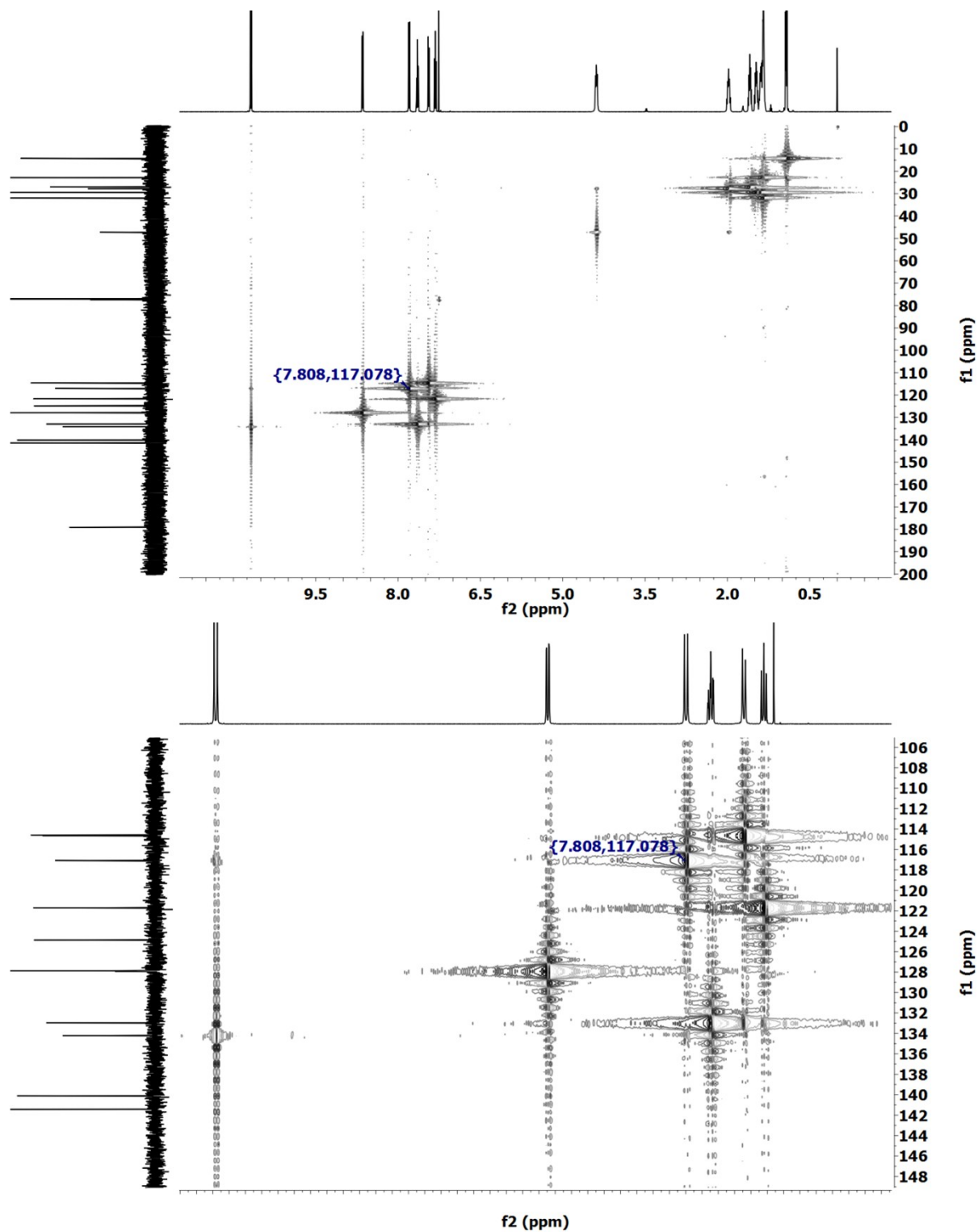


Figure S3. ^1H - ^{13}C HSQC NMR spectrum of the compound 2.

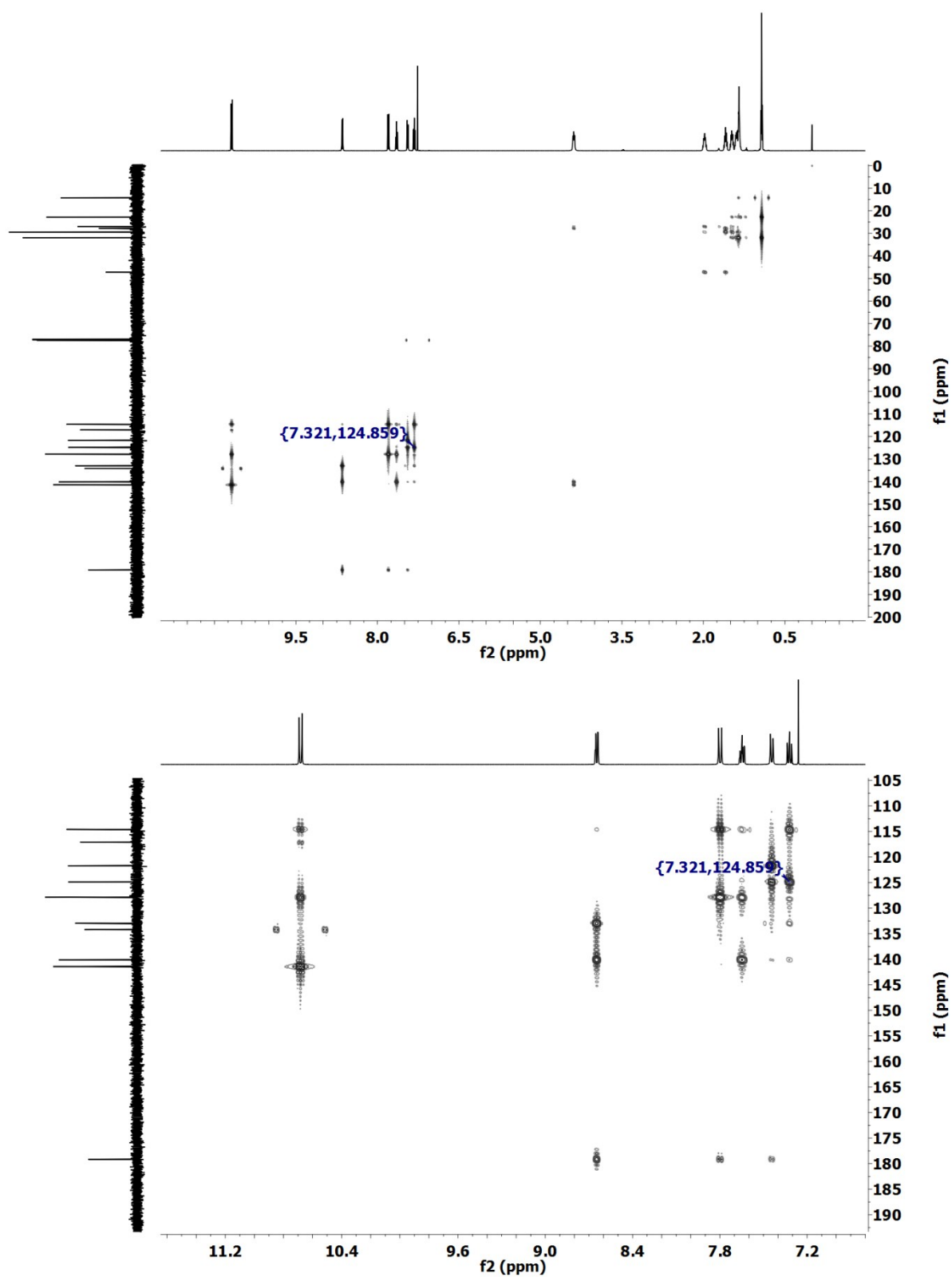


Figure S4. ^1H - ^{13}C HMBC NMR spectrum of the compound 2.

Electrochemical studies

Cyclic voltammograms (scan rate 50 mV/s or 100 mV/s) and differential pulse voltammograms (modulation time: 50 ms, modulation amplitude: 10 mV, step potential: 5 mV) of the synthesized compounds (concentration 10^{-3} M in 0.1 M Bu_4NBF_4 /dichloromethane electrolyte) were registered using an Autolab potentiostat (EcoChemie). The measurements were performed in an inert atmosphere, using a platinum working electrode of the surface area of 3 mm^2 , a platinum wire counter electrode and an $\text{Ag}/0.1 \text{ M Ag}^+$ /acetonitrile reference electrode, whose potential was verified using the ferrocene couple at the end of each set of experiment.

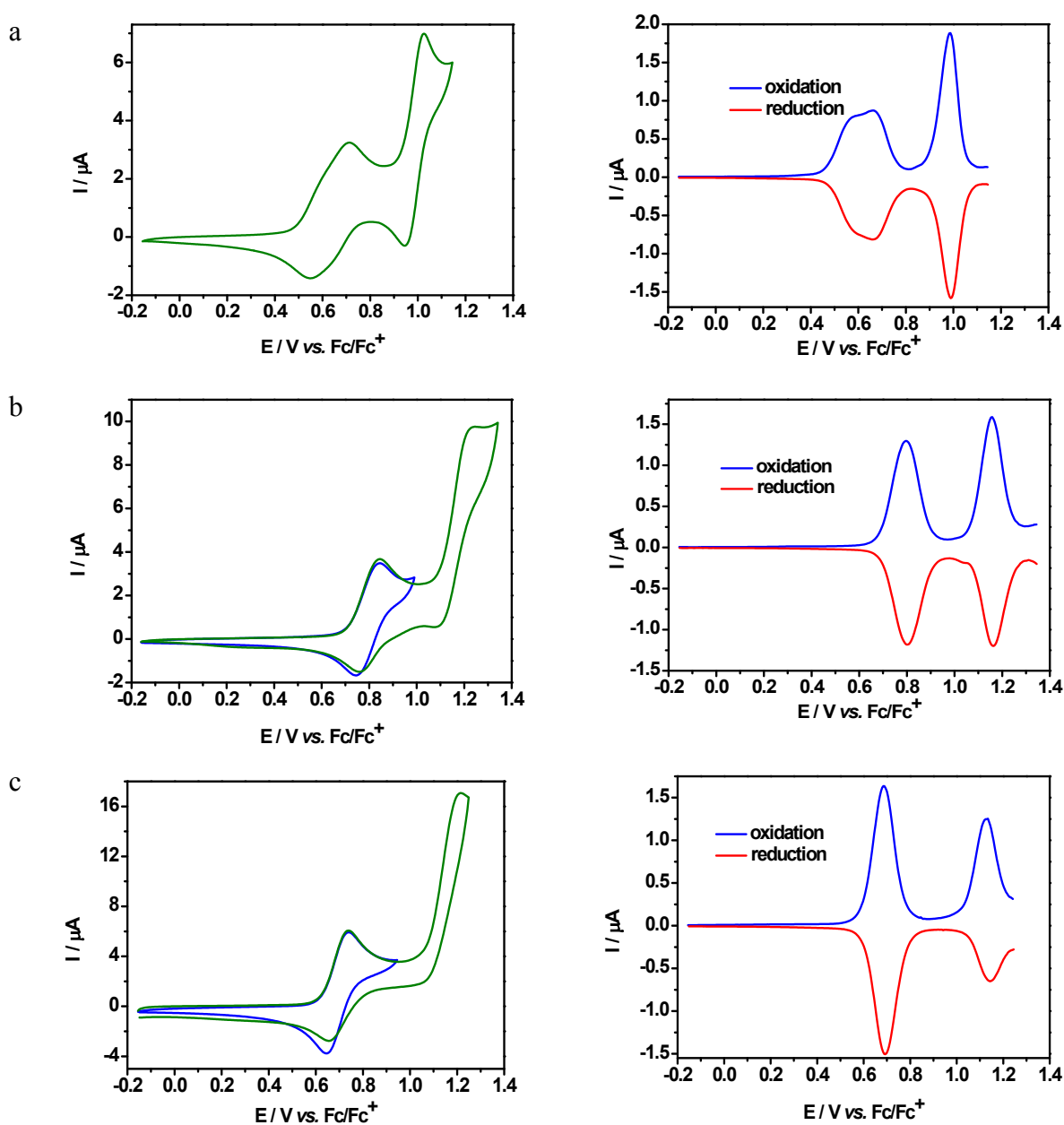


Figure S5. Electrochemical oxidation of studied compounds. Cyclic voltammograms (left column) and differential pulse voltammograms (right column) of **1** (a) **2** (b) and **QA-C8** (c).

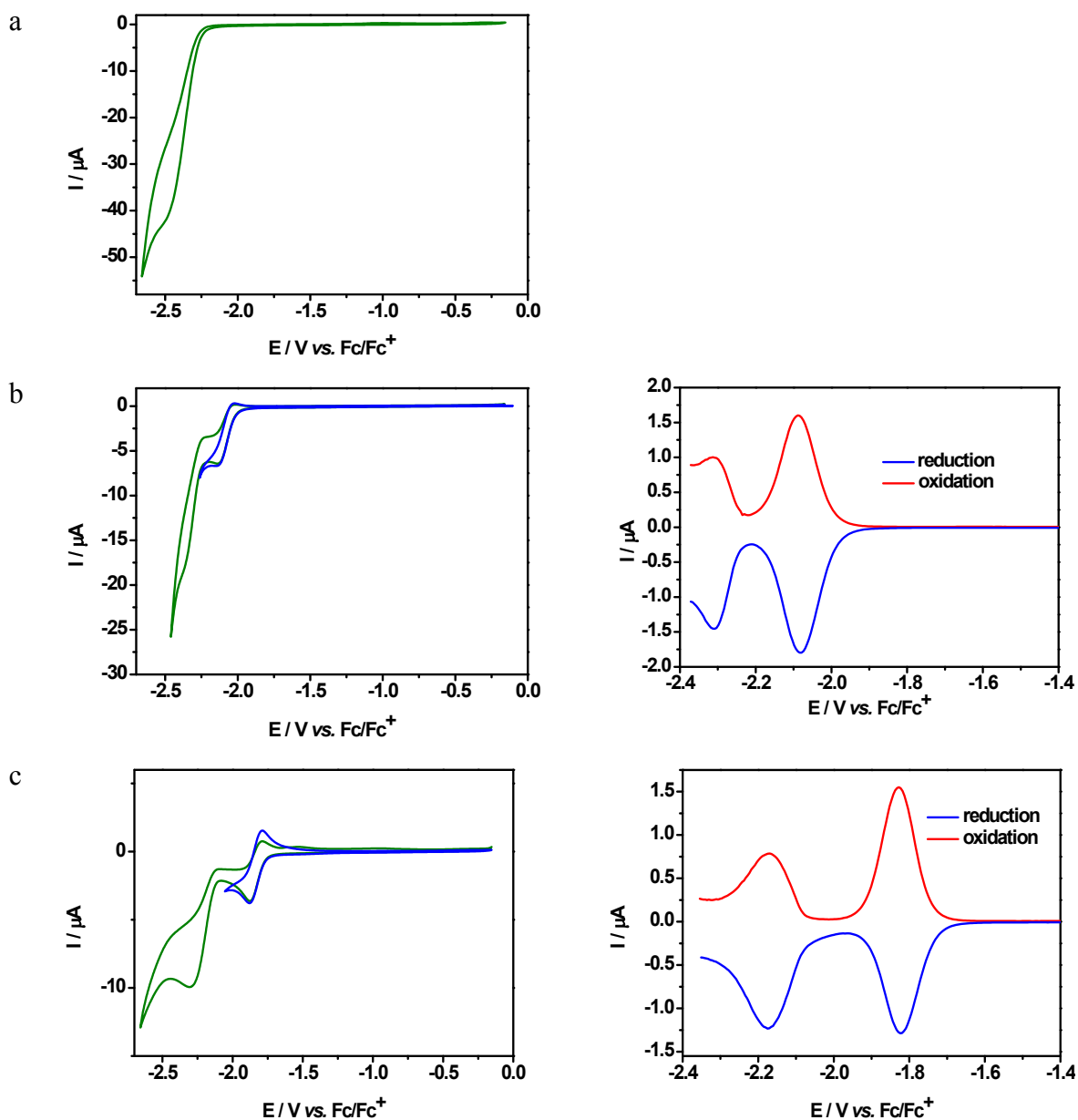


Figure S6. Electrochemical reduction of studied compounds. Cyclic voltammograms (left column) and differential pulse voltammograms (right column) of **1** (a) **2** (b) and **QA-C8** (c).

X-ray diffraction studies

Single crystals of **2** were grown from dichloromethane by slow solvent evaporation. Suitable single crystal was selected under a polarizing microscope and glued with a two-component epoxy resin to a cactus needle. Diffraction data were measured on the Rigaku Oxford Diffraction κ -CCD Gemini A Ultra diffractometer at room temperature with mirror-focused Cu- $K\alpha$ radiation. Cell refinement and data collection as well as data reduction and analysis were

performed with the CrysAlis^{PRO} software.¹ The structures were solved by intrinsic phasing with SHELXT and refined by full-matrix least-squares against F^2 with SHELXL-2014 within the Olex2 program suite.²⁻⁴ Three terminal carbon atoms of *n*-octyl group were disordered over two positions with occupations 0.504(10):0.496(10). All non-hydrogen atoms except for carbon atoms of the second disorder component were refined anisotropically. Hydrogen atoms were introduced at calculated positions and refined as riding atoms with isotropic displacement parameters equal to 1.2 times that of the parent atoms. Data were analyzed using Olex2, PLATON and Mogul programs.⁴⁻⁶ Crystal data and structure refinement parameters are given in Table S4.

Table S1. Crystal data and structure refinement for compound **2**.

identification code	2
chemical formula	C ₄₀ H ₄₆ N ₂ O ₂
formula weight	586.79
T / K	293.15
crystal system	monoclinic
space group	P21/c
a / Å	12.6799(5)
b / Å	8.8317(3)
c / Å	15.5666(6)
α / °	90
β / °	109.439(4)
γ / °	90
V / Å ³	1643.85(11)
Z	2
ρ_{calc} / cm ³	1.185
μ / mm ⁻¹	0.557
F(000)	632.0
crystal size/mm ³	0.89 × 0.20 × 0.10
radiation	CuK α (λ = 1.5418 Å)
2 Θ range / °	7.394 to 134.48
index ranges	-15 ≤ h ≤ 14, -10 ≤ k ≤ 10, -18 ≤ l ≤ 18
reflections collected	24321
independent reflections	2939 [Rint = 0.0980, Rsigma = 0.0342]
data/restraints/parameters	2939/0/215
goodness-of-fit on F ²	1.072

final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0559, wR2 = 0.1639
final R indexes [all data]	R1 = 0.0677, wR2 = 0.1781
largest diff. peak/hole / $e\text{\AA}^{-3}$	+0.26/-0.24

Optical studies

All optical studies were performed by using as a solvent dichloromethane, DCM (and *n*-hexane for **QA-C8**) provided by Merck (purity: for spectroscopy).

Absorption spectra were measured with the aid of a Perkin-Elmer Lambda 35 spectrophotometer. Fluorescence spectra and lifetimes were obtained by using facilities of a Horiba Fluorolog 3 Delta Diodes, 336 and 303 nm, were used as the excitation sources in kinetic studies.

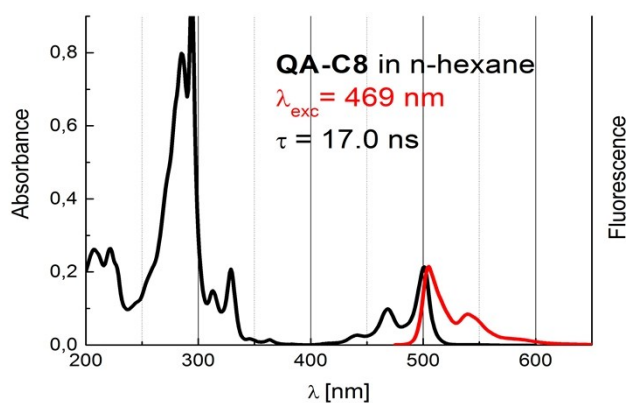


Figure S7. Absorption (black curve) and fluorescence (red) spectra of compound **QA-C8** in *n*-hexane at room temperature.

Table S2. Photophysical parameters derived from the spectroscopic measurements of the compounds **1**, **2** and **QA-C8**.

compound	λ_{abs} [nm]	λ_{em} [nm]	Stokes shift [cm^{-1}]	Φ_{F}	τ [ns]	k_{r} [10^7 s^{-1}]	k_{nr} [10^7 s^{-1}]
1	418	442 ^a	1299	0.41 ^a	3.92 ^d	10.5	15.0
2	449	454 ^b	245	0.83 ^b	0.92 ^e	90.2	18.5
QA-C8	520	533 ^c	469	0.76 ^c	19.1 ^d	4.0	1.2

λ_{exc} : (a) 402 nm, (b) 423 nm, (c) 487 nm, (d) 336 nm, (e) 303 nm.

Φ_{F} obtained using as a standard perylene in cyclohexane (compounds **1** and **2**) and Rh6G in EtOH (**QA-C8**).

The radiative (k_{r}) and nonradiative (k_{nr}) depopulation rate constants of the excited state were calculated according to the formulas: $k_{\text{r}} = \Phi_{\text{F}} / \tau$, $k_{\text{nr}} = (1 - \Phi_{\text{F}}) / \tau$.

Bibliography

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