Supporting Information

Molecular Engineering of a Fluorene Donor for Dye-Sensitized Solar Cells

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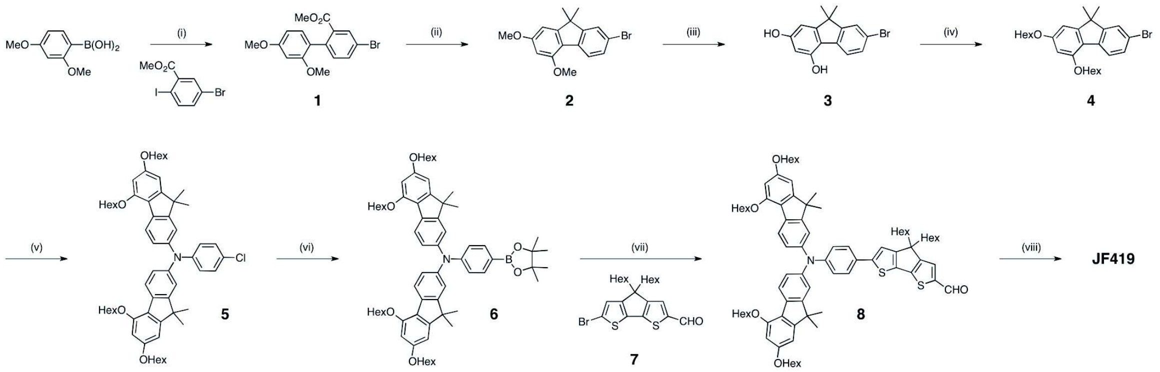
Experimental Section

Reagents. All reagents were purchased at the best grade available and used as received. Reagents were purchased from Aldrich unless otherwise stated. Anhydrous solvents (AcroSeal) were obtained from Acros and used as received. 2,4-Dimethoxyphenylboronic acid was purchased from Combi-Blocks, tetrakis(triphenylphosphine) palladium from TCI, methylmagnesium bromide and boron tribromide from Acros. 4*H*-Cyclopenta[2,1-*b*:3,4-*b′*]dithiophene was purchased from PSN Pharmaceutical Technology Co., Ltd. 6-bromo-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b′*]dithiophene-2-carbaldehyde (**7**) was prepared according to literature procedure.[1] Purification by column chromatography was carried out using silica (Merck: Kieselgel 230-400 mesh, 40-63 μm). Analytical thin-layer chromatography (TLC) was performed on aluminum-backed sheets pre-coated with silica 60 F254 adsorbent (0.25 mm thick; Merck, Germany) and visualized under UV light (254 and 365 nm) and potassium permanganate staining.

Analysis. 1D and 2D ^{1}H and ^{13}C{^{1}H} NMR were recorded at 400 MHz and 100 MHz, respectively, on a Bruker AV 400 instrument at ambient temperature unless otherwise stated. ^{1}H NMR chemical shifts (δ) are reported in parts per million (ppm) from low to high field and referenced to residual non-deuterated solvent. For ^{1}H NMR: $CDCl_3$, 7.24 ppm; acetone-d_6, 2.05 ppm; for ^{13}C{^{1}H} NMR: $CDCl_3$, 77.23 ppm; acetone-d_6, 29.84 ppm. Coupling constants are expressed in hertz (Hz). Standard abbreviations indicating multiplicity are used as follows: s = singlet; d = doublet; t = triplet; dd = doublet of doublet, m = multiplet. Elemental analysis (EA), electrospray ionization (ESI) and matrix assisted laser desorption ionization (MALDI) mass spectrometry data were collected at the EPFL.

Synthesis. The fluorene-based sensitizer was prepared in 9 steps starting from commercially available materials as depicted on Scheme S1. Biphenyl **1** is obtained using conventional Suzuki coupling. The subsequent cyclization reaction is key to this synthesis. First, the methyl-ester is reduced using methylmagnesium bromide. Then, the resulting tertiary alcohol is subjected to a Friedel-Crafts acid-promoted cyclization reaction. A mixture of concentrated sulfuric and acetic acid is the only combination that affords the desired 7-bromo-2,4-dimethoxy-9,9-dimethyl-9*H*-fluorene **2** in acceptable yield (46% over two steps). Methoxy-substituents can be easily cleaved using boron tribromide and the resulting resorcinol **3** can be further functionalized with linear or branched alkoxy chains. Here, hexyloxy pendant groups are used to allow for direct comparison with Y123 and C218. The triarylamine core **4** was assembled using selective chloro- *versus* bromo- palladium-catalyzed amination conditions,[2,3] and subsequently converted to boronic ester **6** following again a procedure developed by Buchwald *et al.*[4] After Suzuki coupling with compound **7**, a Knoevenagel condensation between intermediate aldehyde **8** and cyanoacrylic acid yields **JF419** as a purple crystalline solid. Details concerning the synthesis of this new sensitizer and characterization of the compounds are given in the Supporting Information (Figures S1–8).

Scheme S1. Synthetic scheme leading to JF419.



(i) $Pd(PPh_3)_4$, Na_2CO_3 in THF and water (44%); (ii) MeMgBr in THF, then H_2SO_4 in AcOH (46% over 2 steps); (iii) BBr_3 in CH_2Cl_2 (88%); (iv) 1-bromohexane, K_2CO_3, KI in DMF (95%); (v) 4-chloroaniline, NaO^tBu, $Pd_2(dba)_3$, XPhos in toluene (57%); (vi) bis(pinacolato)diboron, KOAc, $Pd_2(dba)_3$, XPhos in 1,4-dioxane (82%); (vii) **7**, K_3PO_4, $Pd(OAc)_2$, SPhos in 1,4-dioxane and water (86%); (viii) cyanoacetic acid, piperidine in $CHCl_3$ (72%).

Compound 1. An oven-dried two-necked flask was charged with methyl-5-bromo-2-iodobenzoate (97%, 7.57 g, 21.5 mmol), 2,4-dimethoxyphenylboronic acid (97%, 4.00 g, 21.5 mmol, 1.0 eq.) and tetrakis(triphenylphosphine) palladium. The solids were degassed with nitrogen and dissolved in a mixture of tetrahydrofuran (76 mL) and 2M aqueous sodium carbonate (33 mL). After further degassing with nitrogen, the solution was warmed to 80 °C and refluxed for 60 hours. Then the solution was cooled down to room temperature and partitioned between dichloromethane and water. The organic layer was decanted, dried over magnesium sulfate, filtered and evaporated to dryness. Purification by chromatography, (1) silica prepared in hexane / tetrahydrofuran 85:15, isocratic elution with hexane / tetrahydrofuran 85:15, and then (2) silica prepared in hexane / dichloromethane 40:60, isocratic elution with hexane / dichloromethane 40:60, afforded **1** as colorless oil (3.38 g, yield 44%). ^{1}H NMR ($CDCl_3$): δ 7.95 (d, 1H, ^4J = 2.2 Hz), 7.61 (dd, 1H, ^3J = 8.2 Hz, ^4J = 2.2 Hz), 7.16 (d, 1H, ^3J = 8.2 Hz), 7.12 (d, 1H, ^3J = 8.3 Hz), 6.55 (dd, 1H, ^3J = 8.3 Hz, ^4J = 2.4 Hz), 6.46 (d, 1H, ^4J = 2.4 Hz), 3.83 (s, 3H), 3.68 (s, 3H), 3.67 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.54, 160.93, 157.04, 137.56, 134.50, 134.41, 133.14, 132.32, 130.33, 122.19, 120.65, 104.58, 98.44, 55.49, 55.32, 52.09. HR-MS (ESI): *m/z* = 315.0225 $[M]^+$ (calcd. for $[C_{16}H_{15}BrO_4]^+$: *m/z* = 351.0232). Anal. calcd. for $C_{16}H_{15}BrO_4$: C, 54.72; H, 4.31. Found: C, 54.83; H, 4.47.

Compound 2. An oven-dried two-necked flask was charged with compound **1** (3.38 g, 9.62 mmol) and degassed with nitrogen, and the solid was dissolved in anhydrous tetrahydrofuran (48 mL, 5 mL/mmol). Methylmagnesium bromide (1M in tetrahydrofuran, 29.0 mL, 29.0 mmol, 3.0 eq.) was added drop wise over 3 hours and the solution was stirred overnight at room temperature. Then the solution was neutralized to pH • 7 with 1M aqueous hydrochloric acid and partitioned between dichloromethane and water. The organic layer was decanted, dried over magnesium sulfate, filtered and evaporated to dryness. The resulting tertiary alcohol was used without further purification and dissolved in a mixture of acetic acid and 98% sulfuric acid (80 and 20 mL, respectively). The solution was degassed with nitrogen, warmed to 110 °C and refluxed for 5 hours. Then it was cooled down to room temperature, partitioned between dichloromethane and water, and neutralized to pH • 7 with 25% aqueous ammonia. The organic layer was decanted, dried over magnesium sulfate, filtered and evaporated to dryness. Purification by chromatography, silica prepared in hexane / dichloromethane 80:20, isocratic elution with hexane / dichloromethane 80:20, afforded **2** as yellowish oil (1.48 g, yield 46%). ^{1}H NMR ($CDCl_3$): δ 7.82 (d, 1H, ^{3}J = 8.2 Hz), 7.48 (d, 1H, ^{4}J = 1.9 Hz), 7.41 (dd, 1H, ^{3}J = 8.2 Hz, ^{4}J = 1.9 Hz), 6.56 (d, 1H, ^{4}J = 1.9 Hz), 6.43 (d, 1H, ^{4}J = 1.9 Hz), 3.95 (s, 3H), 3.87 (s, 3H), 1.44 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 161.44, 156.69, 156.60, 154.84, 137.68, 130.08, 125.39, 124.10, 119.47, 119.03, 99.47, 97.27, 55.80, 55.54, 47.69, 27.31. HR-MS (MALDI): *m/z* = 331.9660 $[M]^+$ (calcd. for $[C_{17}H_{17}BrO_2]^+$: *m/z* = 332.0412). Anal. calcd. for $C_{17}H_{17}BrO_2$: C, 61.28; H, 5.14. Found: C, 61.38; H, 5.24.

Compound 3. An oven-dried two-necked flask was charged with compound **2** (1.00 g, 3.00 mmol) and degassed with nitrogen. The solid was dissolved in anhydrous dichloromethane (30 mL, 10 mL/mmol), and the mixture was cooled down to 0 °C. Boron tribromide (1M in dichloromethane, 9.0 mL, 9.00 mmol, 3.0 eq.) was added drop wise over 1 hour and the solution was left to warm up to room temperature overnight. Then the solution was neutralized by addition of methanol and partitioned between dichloromethane and water. The organic layer was decanted, dried over magnesium sulfate, filtered and evaporated to dryness. Purification by chromatography, silica prepared in dichloromethane / methanol 98:2, isocratic elution with dichloromethane / methanol 98:2, afforded **3** as white crystalline solid (0.81 g, yield 88%). ^{1}H NMR ($CDCl_3$): δ 7.76 (d, 1H, ^{3}J = 8.2 Hz), 7.45 (d, 1H, ^{4}J = 1.9 Hz), 7.40 (dd, 1H, ^{3}J = 8.2 Hz, ^{4}J = 1.9 Hz), 6.46 (d, 1H, ^{4}J = 2.0 Hz), 6.21 (d, 1H, ^{4}J = 2.0 Hz), 5.19 (s, 1H), 4.87 (s, 1H), 1.40 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.68, 156.62, 154.70, 152.37, 137.27, 130.26, 125.64, 123.94, 119.32, 118.57, 102.92, 102.11, 47.71, 27.39. HR-MS (ESI): *m/z* = 315.0162 $[M]^+$ (calcd. for $[C_{15}H_{13}BrO_2]^+$: *m/z* = 305.0177). Anal. calcd. for $C_{15}H_{13}BrO_2$: C, 59.04; H, 4.29. Found: C, 59.10; H, 4.37.

Compound 4. An oven-dried two-necked flask was charged with compound **3** (810 mg, 2.65 mmol), 1-bromohexane (98%, 1.34 g, 7.96 mmol, 3.0 eq.), anhydrous potassium carbonate (1.10 g, 7.96 mmol, 3.0 eq.) and a catalytic amount of potassium iodide (10.0 □g). The solids were degassed with nitrogen and dissolved in anhydrous dimethylformamide (25 mL). The mixture was warmed to 80 °C and refluxed for 18 hours under vigorous stirring. Then the solution was cooled down to room temperature and partitioned between hexane and water. The organic layer was decanted, dried over magnesium sulfate, filtered and evaporated to dryness. Purification by chromatography, silica prepared in hexane / dichloromethane 90:10, isocratic elution with hexane / dichloromethane 90:10, afforded **4** as colorless oil (1.19 g, yield 95%). ^{1}H NMR ($CDCl_3$): δ 7.79 (d, 1H, ^{3}J = 8.2 Hz), 7.43 (d, 1H, ^{4}J = 1.9 Hz), 7.38 (dd, 1H, ^{3}J = 8.2 Hz, ^{4}J = 1.9 Hz), 6.51 (d, 1H, ^{4}J = 2.0 Hz), 6.39 (d, 1H, ^{4}J = 2.0 Hz), 4.07 (t, 2H, ^{3}J = 6.6 Hz), 3.99 (t, 2H, ^{3}J = 6.6 Hz), 1.90 (m, 2H), 1.79 (m, 2H), 1.52 (m, 4H), 1.40 (s, 6H), 1.36 (m, 8H), 0.91 (2t, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.97, 156.53, 156.20, 154.89, 137.93, 130.09, 125.38, 124.01, 119.29, 118.88, 100.05, 98.22, 68.58, 68.27, 47.66, 31.85, 31.79, 29.58, 29.51, 27.37, 26.10, 26.02, 22.84, 22.82, 14.27 (2C). HR-MS

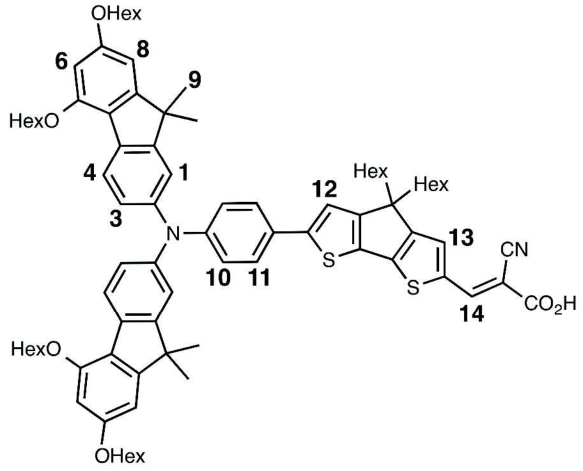
(MALDI): *m/z* = 472.1951 $[M]^+$ (calcd. for $[C_{27}H_{37}BrO_2]^+$: *m/z* = 472.1958). Anal. calcd. for $C_{27}H_{37}BrO_2$: C, 68.49; H, 7.88. Found: C, 68.58; H, 7.95.

Compound 5. An oven-dried two-necked flask was charged with 4-chloroaniline (73.0 mg, 5.72×10^{-4} mol), compound **4** (650 mg, 1.37 mmol, 2.0 eq.), anhydrous sodium *tert*-butoxide (165 □g, 1.72 mmol, 3.0 eq.), tris(dibenzylideneacetone) dipalladium (97%, 13.1 □g, 2.86×10^{-5} mol, 5% Pd) and XPhos (97%, 27.3 □g, 5.72×10^{-5} mol, 10%). The solids were degassed with nitrogen and dissolved in anhydrous toluene (5.7 mL, 10 mL/mmol). The mixture was warmed to 110 °C and refluxed for 24 hours in the dark. Then the solution was cooled down to room temperature, poured in diethylether, filtered over magnesium sulfate and rinsed with diethylether. After evaporation to dryness, the crude material was purified by chromatography, silica prepared in hexane / dichloromethane 90:10, gradient elution from hexane / dichloromethane 90:10 to 85:15, affording **5** as colorless oil (297 mg, yield 57%). ^{1}H NMR ($CDCl_3$): δ 7.89 (d, 2H, ^3J = 8.2 Hz), 7.20 (m-*AB*, 2H, ^3J = 8.8 Hz), 7.17 (d, 2H, ^4J = 2.0 Hz), 7.12 (m-*AB*, 2H, ^3J = 8.8 Hz), 7.07 (dd, 2H, ^3J = 8.2 Hz, ^4J = 2.0 Hz), 6.57 (d, 2H, ^4J = 1.8 Hz), 6.45 (d, 2H, ^4J = 1.8 Hz), 4.11 (t, 4H, ^3J = 6.3 Hz), 4.04 (t, 4H, ^3J = 6.5 Hz), 1.93 (m, 4H), 1.84 (m, 4H), 1.59 (m, 4H), 1.53 (m, 4H), 1.40 (m, 28H), 0.94 (2t, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.17, 156.70, 155.67, 154.26, 147.36, 145.44, 134.15, 129.17, 126.45, 124.40, 123.40, 123.11, 120.01, 118.54, 100.19, 98.05, 68.50, 68.14, 47.46, 31.86, 31.80, 29.60 (2C), 27.38, 26.16, 26.02, 22.83, 22.80, 14.26 (2C). HR-MS (ESI): *m/z* = 912.5714 $[M]^+$ (calcd. for $[C_{60}H_{78}ClNO_4]^+$: *m/z* = 912.5698). Anal. calcd. for $C_{60}H_{78}ClNO_4$: C, 78.86; H, 8.61; N, 1.53. Found: C, 78.69; H, 8.60; N, 1.62.

Compound 6. An oven-dried two-necked flask was charged with compound **5** (295 mg, 3.23×10^{-4} mol), 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bi-1,3,2-dioxaborolane (98%, 251 mg, 9.70×10^{-4} mol, 3.0 eq.), anhydrous potassium acetate (95 □g, 9.70×10^{-4} mol, 3.0 eq.), tris(dibenzylideneacetone) dipalladium (97%, 7.7 □g, 1.62×10^{-5} mol, 5% Pd) and XPhos (97%, 15.9 □g, 3.23×10^{-5} mol, 10%). The solids were degassed with nitrogen and dissolved in anhydrous 1,4-dioxane (3.2 mL, 10 mL/mmol). The mixture was warmed to 110 °C and refluxed for 24 hours in the dark. Then the solution was cooled down to room temperature, filtered over magnesium sulfate and rinsed with ethylacetate. After evaporation to dryness, the crude material was purified by chromatography, silica prepared in hexane / ethylacetate 95:5, isocratic elution with hexane / ethylacetate 95:5, affording **6** as colorless oil (264 mg, yield 82%). ^{1}H NMR ($CDCl_3$): δ 7.90 (d, 2H, ^3J = 8.3 Hz), 7.62 (m-*AB*, 2H, ^3J = 8.7 Hz), 7.25 (d, 2H, ^4J = 2.1 Hz), 7.05 (m, 3H), 7.03 (d, 2H, ^4J = 2.0 Hz), 6.70 (d, 2H, ^4J = 1.9 Hz), 6.52 (d, 2H, ^4J = 1.9 Hz), 4.16 (t, 2H, ^3J = 6.3 Hz), 4.05 (t, 2H, ^3J = 6.5 Hz), 1.92 (m, 4H), 1.79 (m, 4H), 1.60 (m, 4H), 1.50 (m, 4H), 1.38 (m, 28H), 1.32 (s, 12H), 0.91-0.89 (2t, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 161.35, 157.42, 156.48, 155.06, 152.09, 145.83, 136.58, 135.52, 124.73, 123.90, 121.36, 120.26, 119.99, 101.21, 98.73, 84.15, 68.83, 68.66, 47.94, 32.38, 32.33, 30.28, 30.12, 27.40, 26.72, 26.56, 25.22, 22.31, 23.28, 14.32 (2C). HR-MS (MALDI): *m/z* = 1003.8815 $[M]^+$ (calcd. for $[C_{66}H_{90}BNO_6]^+$: *m/z* = 1003.6894). Anal. calcd. for $C_{66}H_{86}BNO_6$: C, 78.94; H, 9.03; N, 1.39. Found: C, 78.93; H, 9.19; N, 1.47.

Compound 8. An oven-dried two-necked flask was charged with compound **6** (130 mg, 1.30 x 10^{-4} mol), compound **7** (59.0 mg, 1.30 x 10^{-4} mol, 1.0 eq.), anhydrous potassium phosphate (140 μg, 6.50 x 10^{-4} mol, 5.0 eq.), palladium acetate (97%, 3.0 μg, 1.30 x 10^{-5} mol, 10% Pd) and SPhos (97%, 6.6 μg, 1.55 x 10^{-5} mol, 12%). The solids were degassed with nitrogen and dissolved in de-aerated mixture of 1,4-dioxane and water (12.7 and 1.3 mL, respectively). The mixture was warmed to 80 °C and refluxed for 24 hours in the dark. Then the solution was cooled down to room temperature and extracted with dichloromethane and water. The organic layer was decanted, dried over magnesium sulfate, filtered and evaporated to dryness. The crude material was purified by chromatography, silica prepared in hexane / ethylacetate 95:5, isocratic elution with hexane / ethylacetate 95:5, afforded **8** as thick red oil (140 mg, yield 86%). ^{1}H NMR ($CDCl_3$): δ 9.82 (s, 1H), 7.90 (d, 2H, ^{3}J = 8.2 Hz), 7.55 (s, 1H), 7.52 (m-*AB*, 2H, ^{3}J = 8.8 Hz), 7.22 (d, 2H, ^{4}J = 2.0 Hz), 7.19 (m-*AB*, 2H, ^{3}J = 8.8 Hz), 7.16 (s, 1H), 7.13 (dd, 2H, ^{3}J = 8.2 Hz, ^{4}J = 2.0 Hz), 6.56 (d, 2H, ^{4}J = 1.8 Hz), 6.45 (d, 2H, ^{4}J = 1.8 Hz), 4.11 (t, 4H, ^{3}J = 6.4 Hz), 4.03 (t, 4H, ^{3}J = 6.4 Hz), 1.92 (m, 8H), 1.83 (m, 4H), 1.59 (m, 4H), 1.51 (m, 4H), 1.40 (m, 28H), 1.17 (m, 16H), 0.99 (m, 4H), 0.94-0.92 (2t, 12H), 0.84 (t, 6H, ^{3}J = 7.6 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 182.24, 163.77, 160.22, 157.38, 156.72, 155.69, 154.27, 150.10, 148.67, 148.52, 145.10, 142.88, 134.43, 133.67, 127.42, 126.37, 123.82, 123.11, 122.82, 119.95, 118.89, 116.50, 100.19, 98.03, 66.48, 68.12, 54.24, 47.46, 38.02, 31.83, 31.78, 29.83 (2C), 29.58, 27.36, 27.09, 26.15, 25.99, 24.72, 22.79, 14.23 (2C). HR-MS (MALDI): *m/z* = 1249.6908 $[M]^+$ (calcd. for $[C_{82}H_{107}NO_5S_2]^+$: *m/z* = 1249.7575). Anal. calcd. for $C_{82}H_{107}N_5S_2$: C, 78.74; H, 8.62; N, 1.12. Found: C, 78.83; H, 8.65; N, 1.13.

Compound JF419. A two-necked flask was charged with compound **8** (140 mg, 1.12 x 10^{-4} mol), cyanoacetic acid (48.0 mg, 5.60 x 10^{-4} mol, 5.0 eq.) and piperidine (77.5 μL, 7.84 x 10^{-4} mol, 7.0 eq.). The solids were degassed with nitrogen and dissolved in anhydrous chloroform (10 mL). After further degassing, the mixture was warmed to 60 °C and refluxed for 18 hours in the dark. Then the solution was cooled down to room temperature and neutralized with 2M aqueous hydrochloric acid (30 mL). The aqueous layer was extracted with dichloromethane. The organic layer was decanted, dried over magnesium sulfate, filtered and evaporated to dryness. The crude material was purified by chromatography, silica prepared in dichloromethane / methanol 94:6, gradient elution from dichloromethane / methanol 94:6 to 93:7, then isocratic elution with dichloromethane / methanol / acetic acid 93:7:0.5. The fractions were merged and the volume was reduced under vacuum. The solution was extracted with dichloromethane and water to remove traces of acetic acid and afford **JF419** as purple crystalline solid (112 mg, yield 72%). ^{1}H NMR (acetone-d_6 + 10% pyridine-d_5): δ 8.43 (s, 1H, H-14), 7.95 (d, 2H, ^{3}J = 8.2 Hz, H-4), 7.82 (s, 1H, H-13), 7.65 (m-*AB*, 2H, ^{3}J = 8.6 Hz, H-11), 7.54 (s, 1H, H-12), 7.31 (d, 1H, ^{4}J = 1.9 Hz, H-1), 7.15 (m-*AB*, 2H, ^{3}J = 8.6 Hz, H-10), 7.10 (dd, 2H, ^{3}J = 8.2 Hz, ^{4}J = 1.9 Hz, H-3), 6.73 (d, 2H, ^{4}J = 1.7 Hz, H-8), 6.56 (d, 2H, ^{4}J = 1.7 Hz, H-6), 4.16 (t, 4H, ^{3}J = 6.3 Hz, H), 4.06 (t, 4H, ^{3}J = 6.4 Hz, H), 1.89 (m, 4H), 1.79 (m, 4H), 1.59 (m, 4H), 1.50 (m, 4H), 1.39 (s, 12H, H-9), 1.35-1.28 (m, 20H), 1.15 (m, 12H), 1.02 (m, 4H), 0.90-0.87 (2t, 12H), 0.78 (t, 6H, ^{3}J = 6.7 Hz). *The acetone / pyridine system is the only mixture that allows for recording a good quality proton NMR spectrum of the dye. Unfortunately, exploitable carbon NMR cannot* *be obtained in these conditions due to overlapping signals between the solvents and the substrate. Other polar solvents (DMF, DMSO, acetonitrile or methanol) or mixtures of the latters were attempted without success. Aromatic protons were fully assigned using COSY and ROESY NMR techniques.* HR-MS (MALDI): *m/z* = 1316.7641 $[M]^+$ (calcd. for $[C_{82}H_{107}NO_5S_2]^+$: *m/z* = 1316.7682). Anal. calcd. for $C_{82}H_{107}N_5S_2$: C, 78.74; H, 8.62; N, 1.12. Found: C, 78.73; H, 6.74; N, 1.20.



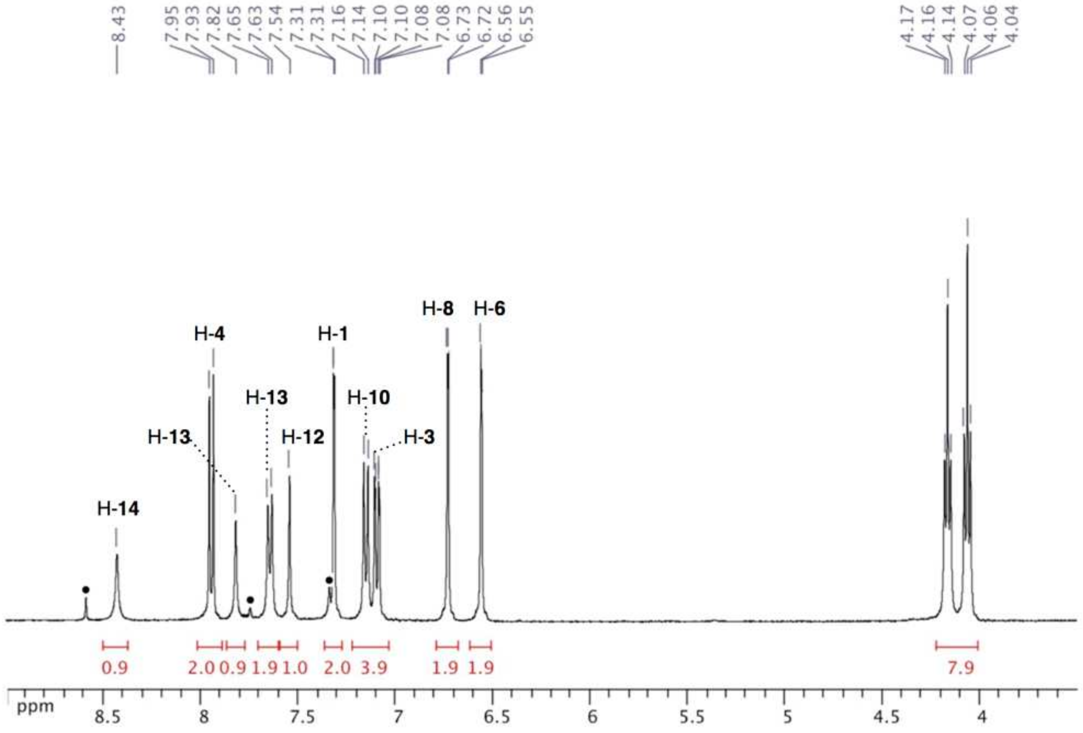


Figure S1. ^1H NMR (top – aromatic) and $^{13}C\{^1H\}$ NMR (bottom) spectra of compound **JF419** in $CDCl_3$.

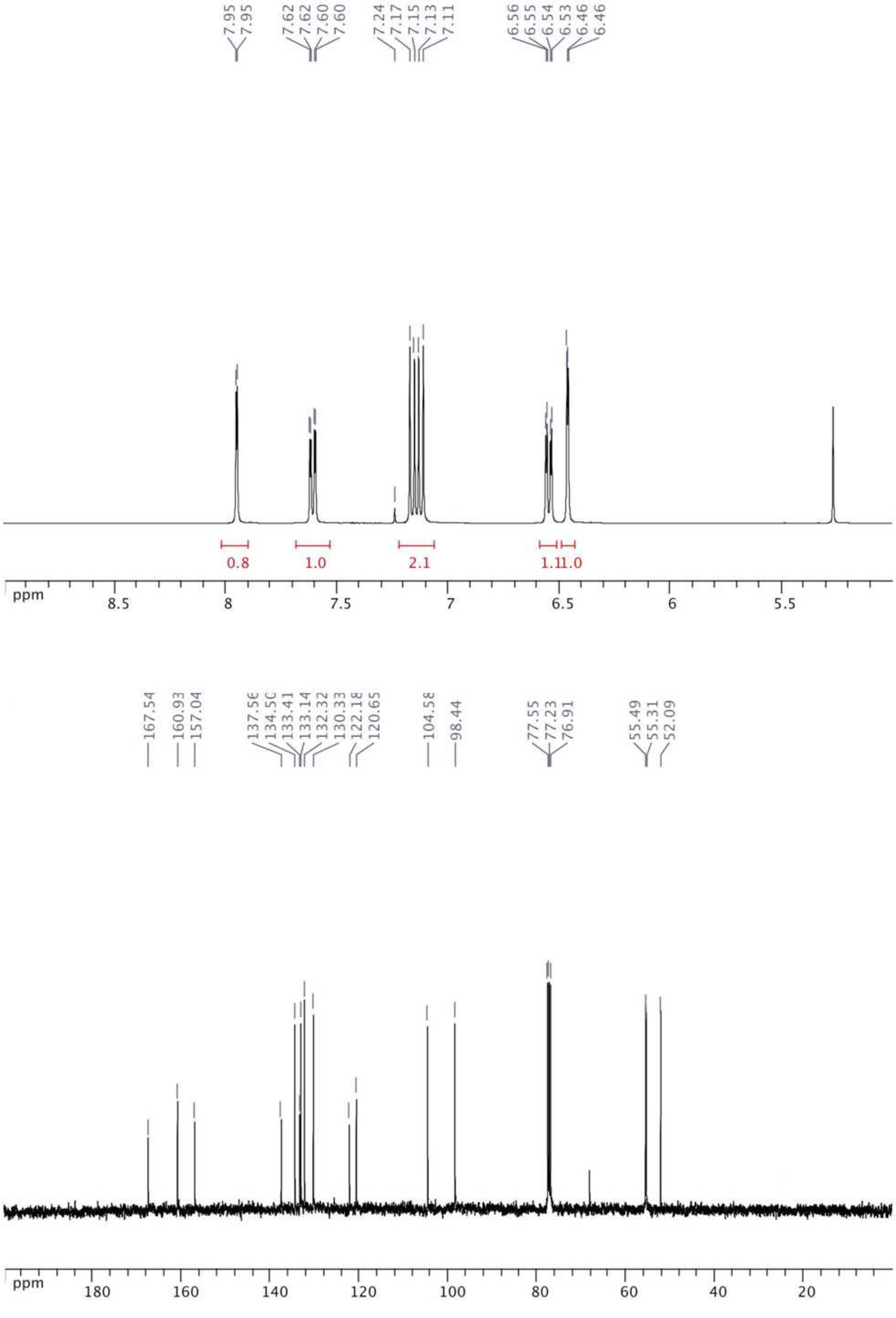


Figure S2. ^{1}H NMR (top – aromatic) and ^{13}C{^{1}H} NMR (bottom) spectra of compound **1** in $CDCl_3$.

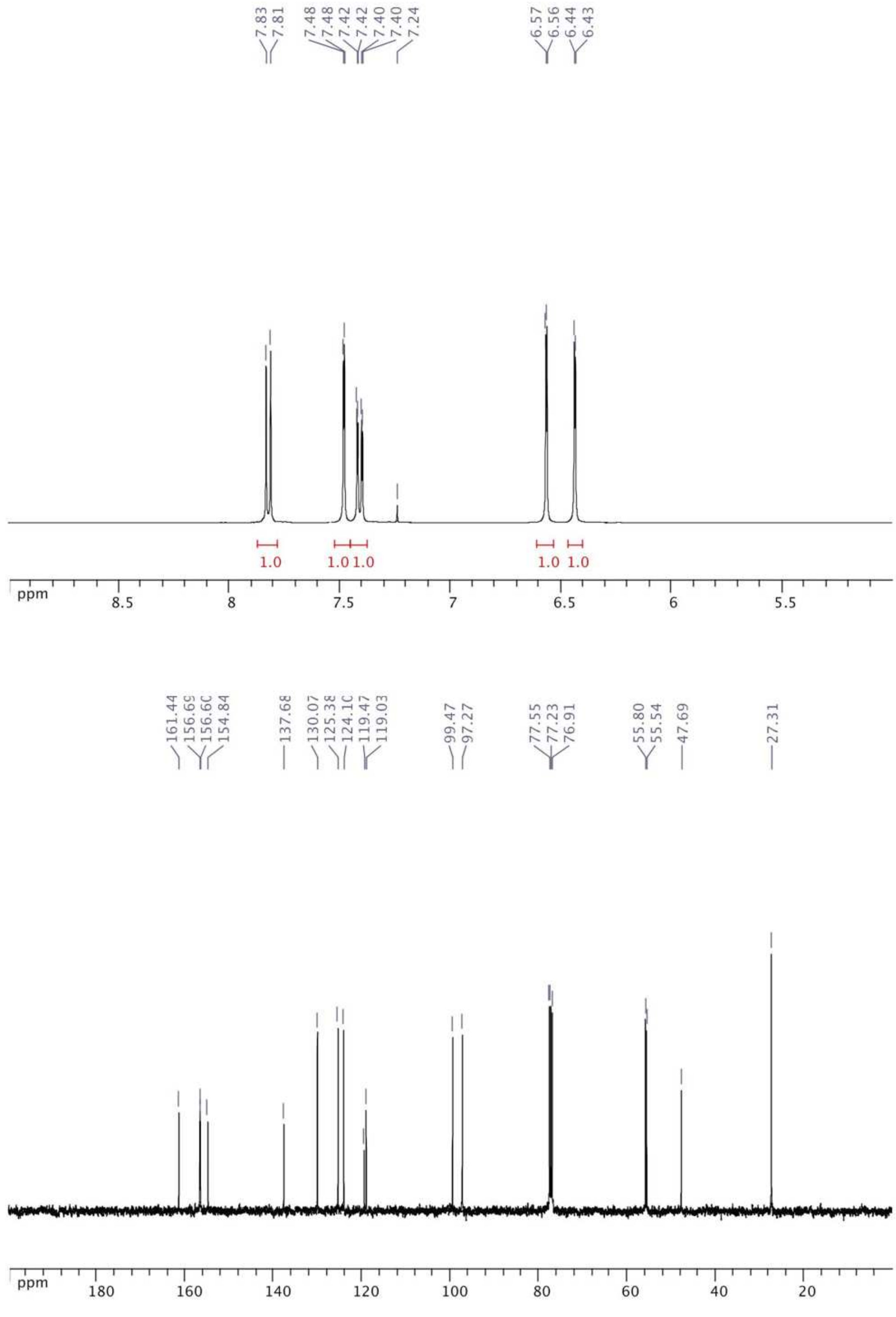


Figure S3. ^{1}H NMR (top – aromatic) and ^{13}C{^{1}H} NMR (bottom) spectra of compound **2** in CDCl$_3$.

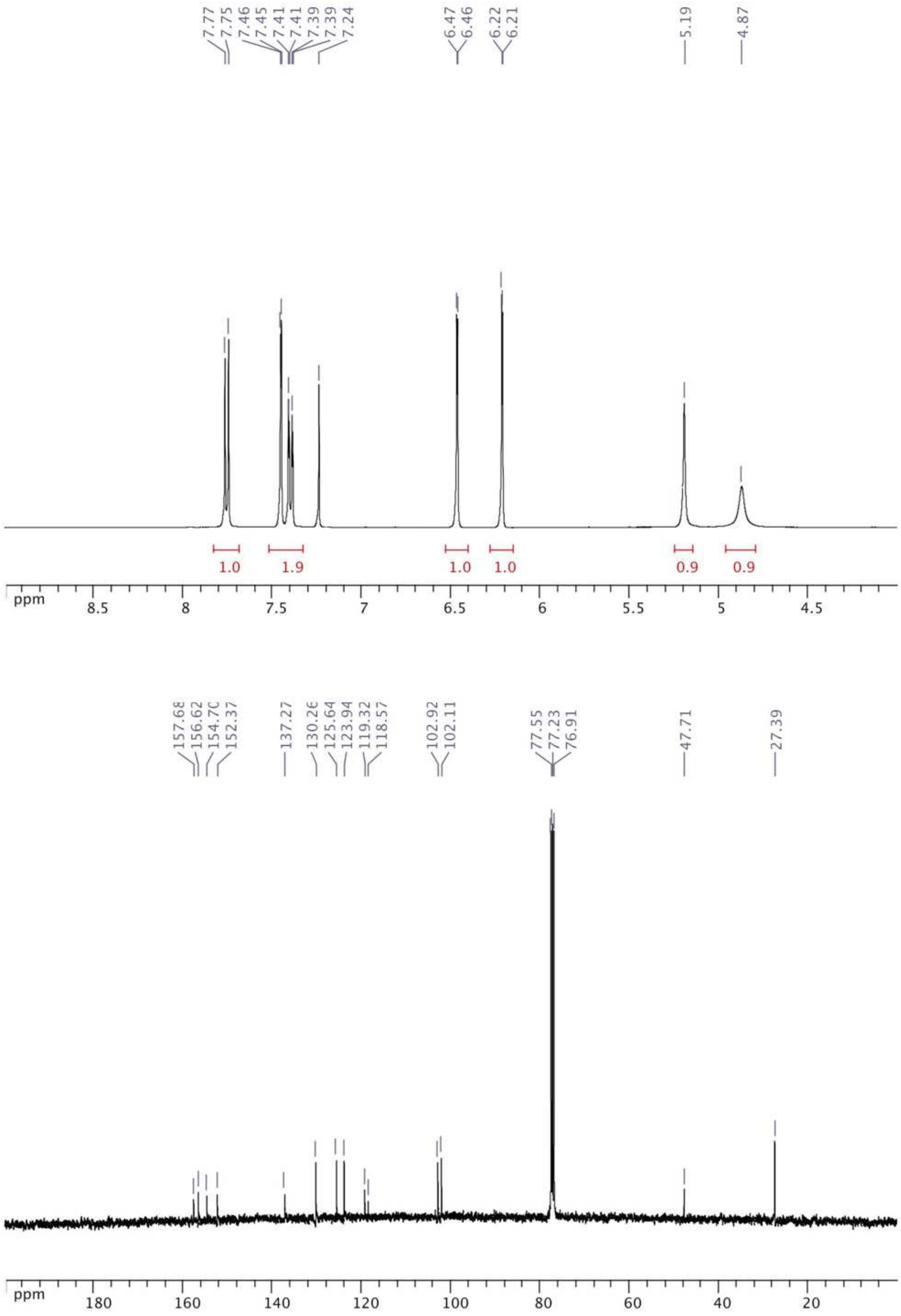


Figure S4. ^{1}H NMR (top – aromatic) and ^{13}C{^{1}H} NMR (bottom) spectra of compound **3** in $CDCl_3$.

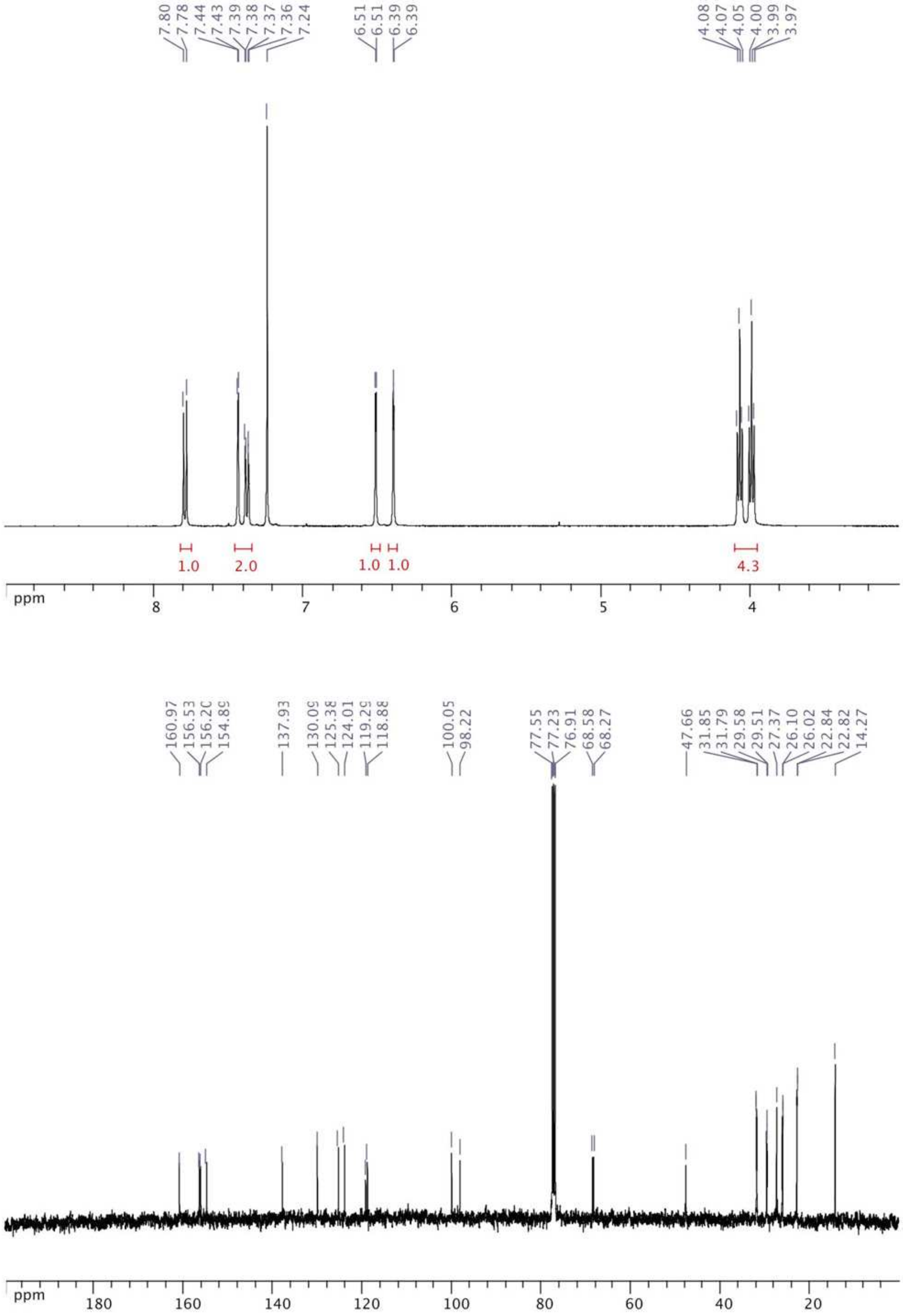


Figure S5. ^{1}H NMR (top – aromatic) and $^{13}C\{^{1}H\}$ NMR (bottom) spectra of compound **4** in $CDCl_3$.

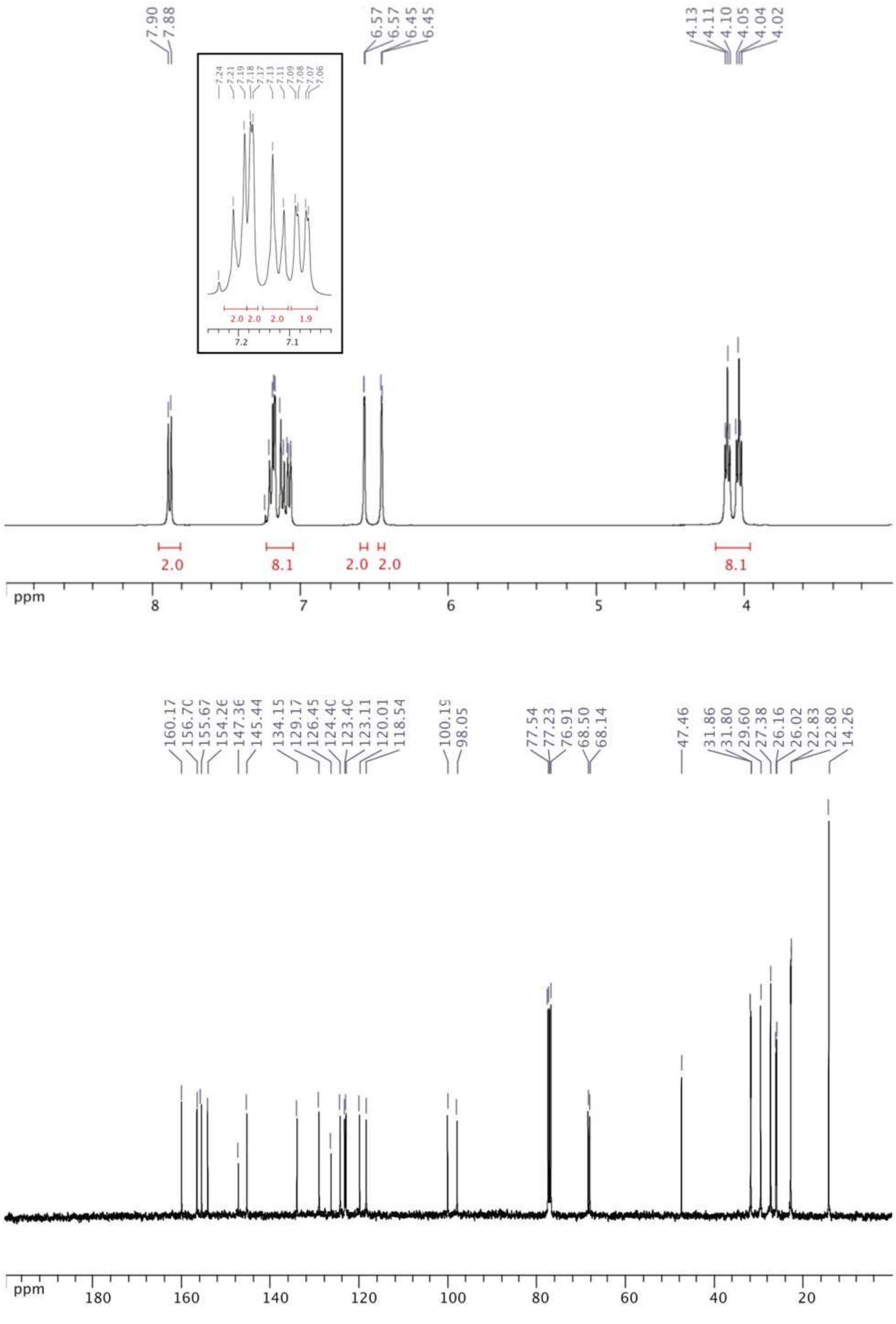


Figure S6. ^{1}H NMR (top – aromatic) and ^{13}C{^{1}H} NMR (bottom) spectra of compound **5** in $CDCl_3$.

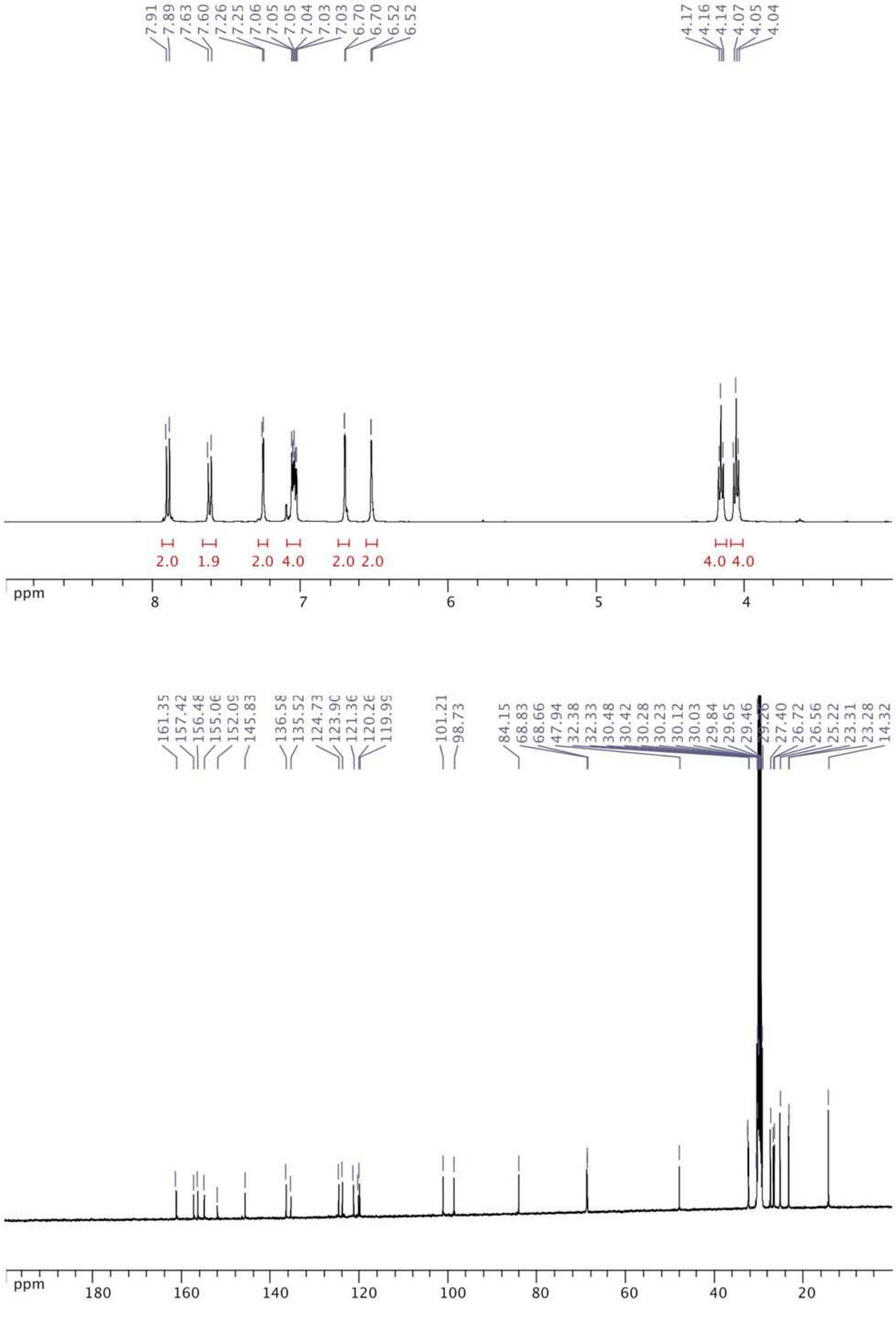


Figure S7. ^{1}H NMR (top – aromatic) and $^{13}C\{^{1}H\}$ NMR (bottom) spectra of compound **6** in $CDCl_3$.

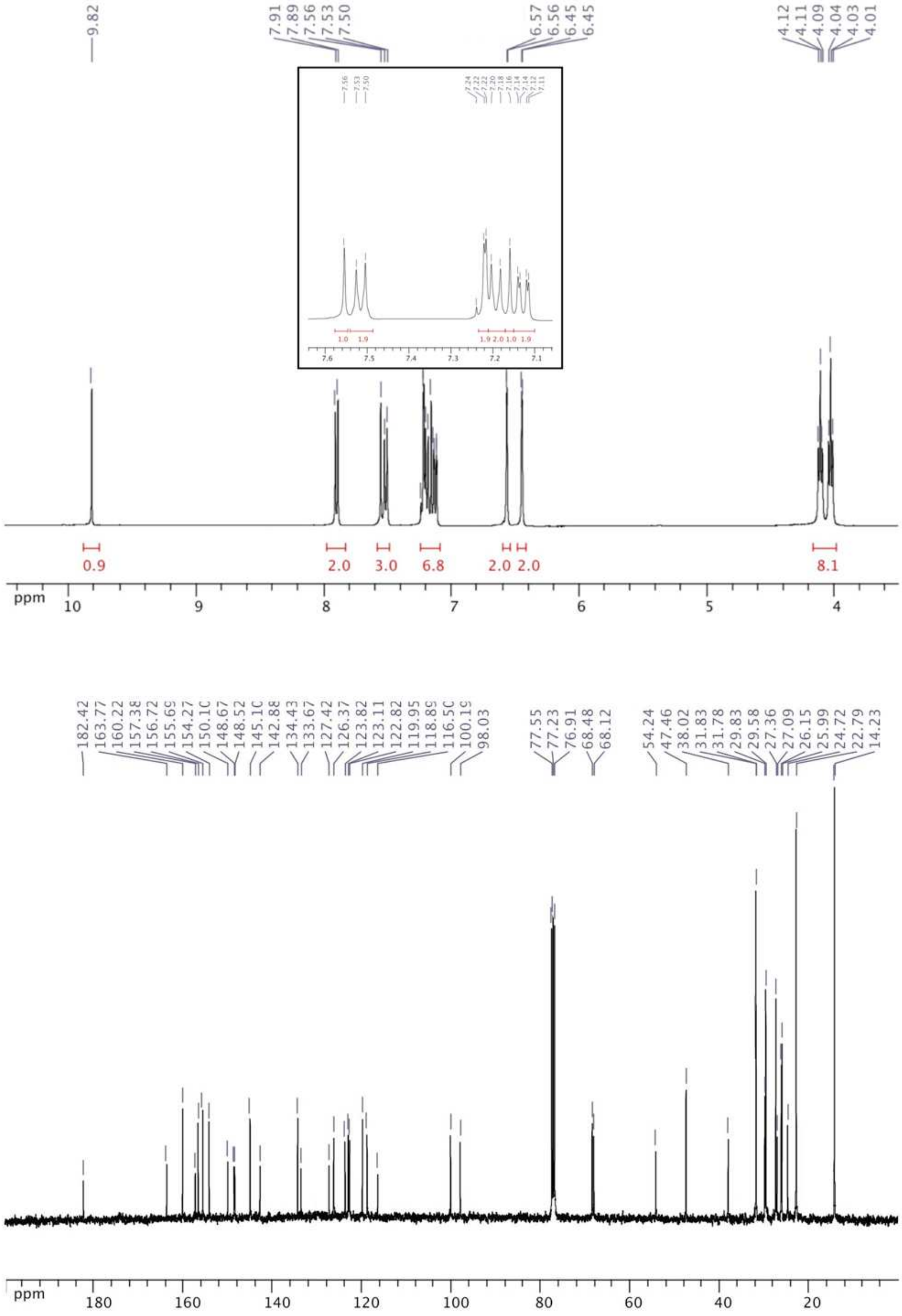


Figure S8. ^{1}H NMR (top – aromatic) and ^{13}C{^{1}H} NMR (bottom) spectra of compound **8** in CDCl$_3$.

Optical properties. Electronic spectroscopic data were collected in solution and on TiO_2 films using a Varian Cary 5 UV–vis–NIR spectrophotometer. Emission spectra were recorded with a Fluorolog Horiba Jobin Yvon Model FL-1065. Excited-state emission spectra and lifetimes were obtained at room temperature using FL-1061PC TCSPC and 406 nm Nanoled as excitation source.

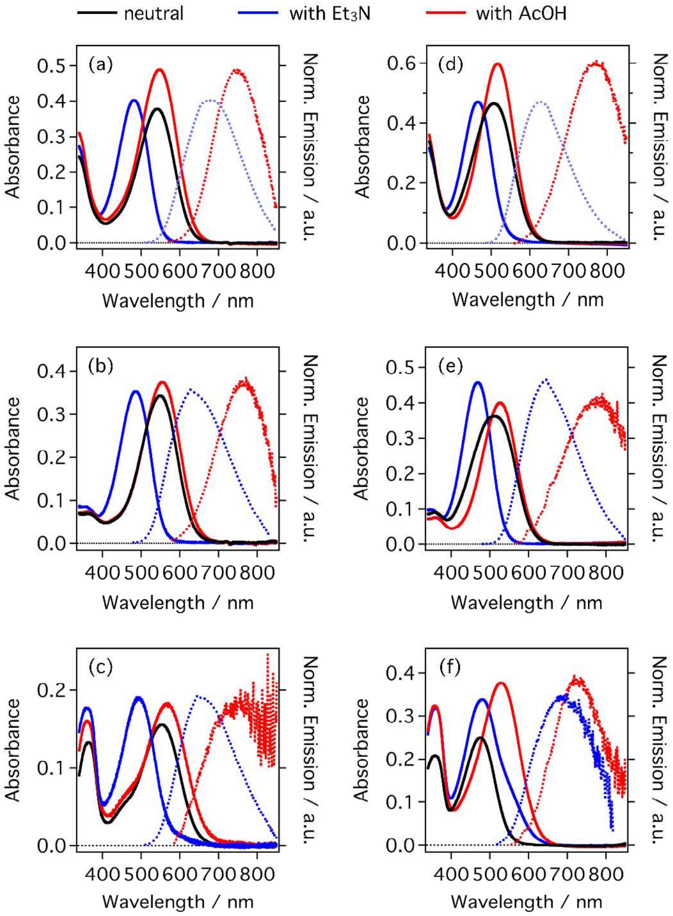


Figure S9. Steady-state absorption (plain) and normalized emission spectra of basic (dashed) and acid conjugate (—, ---) in dichloromethane (a, b, c) and acetonitrile (d, e, f) for Y123, C218 and JF419, respectively.

Table S1. Steady-state absorption and emission data of basic and acid conjugates of Y123, C218 and JF419 in dichloromethane and acetonitrile. E_{0-0} values are measured at the intersection of absorption and normalized emission.

	in CH_2Cl_2 with Et_3N		in CH_2Cl_2 with AcOH		in MeCN with Et_3N		in MeCN with AcOH	
	λ_{max} / nm	E_{0-0} / eV	λ_{max} / nm	E_{0-0} / eV	λ_{max} / nm	E_{0-0} / eV	λ_{max} / nm	E_{0-0} / eV
Y123	481	2.23	547	1.96	466	2.33	517	2.03
C218	486	2.28	556	1.95	469	2.30	526	2.02
JF419	494	2.20	568	1.94	480	2.15	529	2.02

Electrochemical properties. Voltammetric measurements employed a PC controlled AutoLab PSTAT 10 electrochemical workstation and were carried out under anaerobic conditions (Ar-filled glove, oxygen and water < 1 ppm). Experiments were realized at the same concentration of electrolyte (0.1M Bu_4NPF_6 in anhydrous acetonitrile or *N,N*-dimethylformamide). Measurements were carried using the TiO_2 films or a carbon glassy electrode as working electrode together with a set of Pt plate and Pt wire as counter and reference electrode, respectively. Ferrocene was used as internal standard. Scan rates are of 1000 mV s^{-1}.

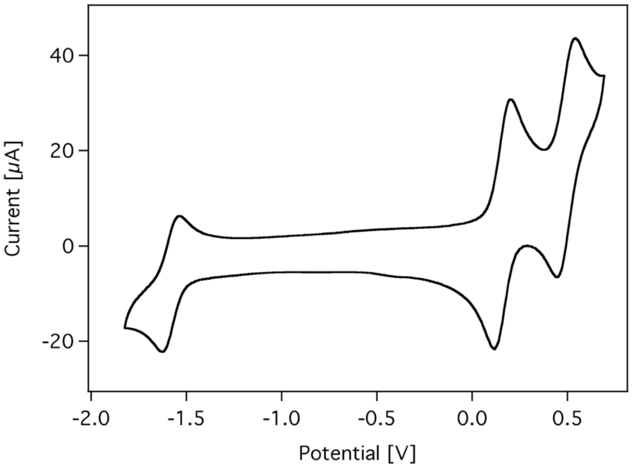


Figure S10. Cyclic voltammograms of JF419 in *N,N*-dimethylformamide (scan rate of 1000 mVs^{-1}). Potentials are reported versus Fc^+/Fc. $E_{RED} = -1.58$ V ($\Delta E = 100$ mV); $E_{OX1} = +0.17$ V ($\Delta E = 80$ mV); $E_{OX2} = +0.49$ V ($\Delta E = 100$ mV).

Computational details. Full geometry optimizations of the dyes in their electronic ground state were performed with DFT using the M06 functional[5] with the DGDZVP basis set[6] for all the atoms (double-□and polarizations), an ultrafine integration grid, and tight geometrical convergence criteria with the Gaussian 09 package.[7] The nature of all located stationary points was further checked by computations of the harmonic vibrational frequencies at the same theory level. For all compounds, methyl groups replaced the hexyl chains. All geometry optimizations were carried under implicit solvent effects. These condensed-phase effects were taken into account using a self-consistent reaction-field (SCRF) model in which the solvent is implicitly represented by a dielectric continuum characterized by its relative static dielectric permittivity. Within the different approaches that can be followed to calculate the electrostatic potential created by the polarized continuum in the cavity, we have employed the SMD variation[8] of the integral equation formalism of the polarizable continuum model (IEF-PCM)[9] relative permittivity of 8.93 or 37.22 was applied to simulate dichloromethane (DCM, LR-TDDFT calculations) or *N,N*-dimethylformamide (DMF, IE calculations), respectively, the two solvents used in the experimental work.

At each ground state (singlet) geometry, LR-TDDFT/BMK/SMD(DCM) calculations were performed for the first 30 singlet states, using the same basis set. The BMK exchange and correlation functional[10] was selected for the LR-TDDFT calculations following the protocol proposed in the following reference to simulate absorption spectra of organic dyes.[11]

Ionization energy (IE) of all compounds was computed in two different ways. The vertical IE of a given dye was obtained by computing the energy of the respective cationic species at the ground state optimized geometry of the dye, using an unrestricted UDFT/M06/SMD(DMF) calculations with the same parameters as described above, and subtracting it from the energy of the geometry optimized (neutral) dye. The adiabatic IE was obtained by first fully relaxing the molecular geometry of the oxidized dye (UDFT/M06/SMD(DMF)) and then by taking the difference between the energy of the geometry optimized cationic dye and the energy of the geometry optimized neutral dye. NTOs were computed with the software Nancy-EX (http://nancyex.sourceforge.net).[12] Graphical representation of the molecules and their orbitals were obtained with the software VMD v.1.9.0.[13]

Figure S13 summarizes the calculated absorption spectra for the three organic dyes, highlighting the good agreement not only for the charge transfer band, but also for the overall trends between the dyes. Interesting is the first vertical excitation computed for the deprotonated JF419, whose location matches well the observed experimental band.

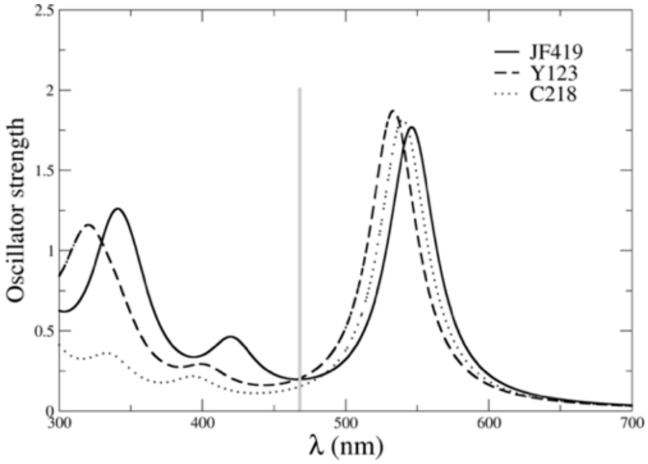


Figure S11. Theoretical electronic transitions of the three different organic dyes, as computed within LR-TDDFT/BMK/SMD(DCM). The vertical transition energies have been broadened with Lorentzian (halfwidth = 20 nm), using the Software Molden v5.0 (see G. Schaftenaar, J. H. Noordik, *J. Comput.-Aided Mol. Design* **2000**, *14*, 123). The grey bar highlight the first vertical transition energy of the deprotonated, geometry optimized JF419 (468 nm).

Photoinduced Absorption Spectroscopy (PIA). PIA spectra were recorded over 500–1100 nm under 9 Hz square-wave photo-modulation with a 470 nm LED. Phase-sensitive detection was made with a lock-in amplifier. White light from a halogen bulb was used as a probe. Spectra are recorded on transparent sealed devices loaded with dyes C218, Y123 or JF419 (samples identical to TAS).

Transient Absorption Spectroscopy (TA). Nanosecond laser flash photolysis was applied to samples loaded with Y123, C218 and JF419 dyes (identical to PIA samples). The samples were excited by 7 ns (fwmh) pulsed laser light produced at a repetition rate of 20 Hz by an optical parametric oscillator pumped by a frequency-tripled Q-switched Nd:YAG laser. The output excitation wavelength was tuned at 530 nm and the laser fluence on the sample was kept at a low level (< 40 μJ cm^{-2} per pulse) to ensure that, on average, less than one electron is injected per TiO$_2$ nanoparticle per pulse. The probe light consists of a xenon arc lamp passed through a 665 nm cutoff filter and a water filter, focused onto the sample and collected in a monochromator at 750 nm. The detector is a fast photomultiplier tube connected to a digital oscilloscope. Typical data are averaged over 1000 laser shots and smoothed using a Savitzky–Golay filter.

Solar Cells Preparation. Nanocrystalline TiO$_2$ pastes were prepared using a previously reported procedure.[14] The TiO$_2$ transparent electrodes were prepared by screen printing onto fluorine-doped tin oxide (FTO, Solar 4 mm thickness, 10 Ω sq^{-1}, Nippon Sheet Glass) conducting glass. The film thickness was adjusted to *ca.* 4.0 μm by the number of screen-printing cycles. The screen-printing paste was composed of ~20 nm diameter anatase particles that gave a mesoporous layer with ~32 nm pores. To render high PCE, a *ca.* 4 μm scattering layer (400 nm diameter, Catalysts & Chemicals Ind. Co. Ltd. (CCIC), HPW-400) was deposited on the transparent layer. The 8.0 μm thick TiO$_2$ electrodes were immersed into a tetrahydrofuran / ethanol solution of the corresponding dye (1:4 ratio, 0.2 mM) with 2 equivalents of 3α,7α-dihydroxy-5β-cholic acid (chenodeoxycholic acid, CDCA) and kept for 6 h at room temperature. The dye-adsorbed TiO$_2$ electrode and thermally platinized counter electrode were assembled into a sealed sandwich type cell with a gap of a hot-melt ionomer film, Surlyn (25 μm, Du Pont). Devices were completed by filling the electrolyte through pre-drilled hole in the counter electrode. A self-adhesive, anti-reflecting, ultraviolet cutoff film ($\lambda < 380$ nm, ARKTOP, ASAHI Glass) was attached to the top of active area to decrease light reflection loss. A black mask (0.159 mm^2) that is smaller than the active area of the cells was used in subsequent photovoltaic studies.

Solar Cells Characterization. For photovoltaic measurements of the DSCs, the irradiation source originated from a 450 W xenon light source (Osram XBO 450) with a filter (Schott 113), whose power was regulated to the AM 1.5 G solar standard by using a reference Si photodiode equipped with a color-matched filter (KG-3, Schott) to reduce the mismatch in the region of 350–750 nm between the simulated light and AM 1.5 G to less than 4%. The measurement-settling time between applying a voltage and measuring a current for the *J–V* characterization of DSCs was fixed to 80 ms. The incident photon to collected electron conversion efficiency (IPCE) measurement was plotted as function of wavelength by using the light from a 300-W xenon lamp (ILC Technology), which was focused through a Gemini-180 double monochromator (Jobin Yvon) onto the photovoltaic cell under test. A computer-controlled monochromator was incremented through the spectral range (300–900 nm) to generate a photocurrent action spectrum with a sampling interval of 10 nm and a current sampling time of 4s. To reduce scattered light from the edge of the glass electrodes of the dyed TiO_2 layer, a light-shading mask was used on the DSCs, so the active area of DSCs was fixed to 0.2 cm^2.

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