

Supporting Information

Realization of nitroaromatic chromophores with intense two-photon brightness

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1. Experimental part

General Remarks. All reagents and solvents were purchased from commercial sources and were used as received unless otherwise noted. Reagent grade solvents (CH₂Cl₂, hexanes) were distilled prior to use. Toluene was dried by distillation over sodium and stored under argon. Transformations with moisture- and oxygen-sensitive compounds were performed under a stream of argon. The reaction progress was monitored by means of thin-layer chromatography (TLC), which was performed on aluminum foil plates, covered with silica gel 60 F254. Product purifications were done by means of column chromatography with Kieselgel 60. The identity and purity of prepared compounds were proved by ¹H NMR and ¹³C NMR spectroscopies as well as by mass spectrometry (via EI-MS or ESI-MS/APCI). HRMS (ESI-TOF/APCI) and HRMS (EI): double-focusing magnetic sector instruments with EBE geometry were utilized. NMR spectra were measured on 400, 500 or 600 MHz instruments. Chemical shifts (δ, ppm) were determined with CDCl₃ as the internal reference; *J* values are given in Hz. All melting points for crystalline products were measured with an automated melting point apparatus and are given without correction. Compounds **1**¹, **2**², **3**,³ **11**³ and **12**³ were synthesized as described earlier.

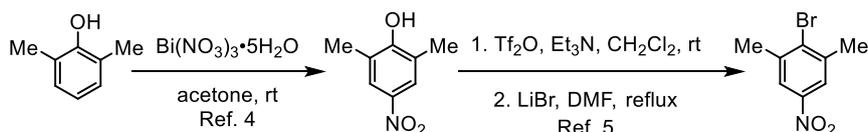
¹ M. Grzybowski, I. Deperasińska, M. Chotkowski, M. Banasiewicz, A. Makarewicz, B. Kozankiewicz, D. T. Gryko, *Chem. Commun.* **2016**, 52, 5108-5111.

² B. Sadowski, M. F. Rode, D. T. Gryko, *Chem. Eur. J.* **2018**, 24, 855-864.

³ B. Sadowski *et al.* *Chem. Sci.* **2021**, 12, 14039-14049.

Synthesis of commercially unavailable bromoarenes.

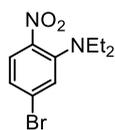
2-Bromo-1,3-dimethyl-5-nitrobenzene.



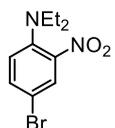
The title compound was prepared according to a depicted above, three step synthesis starting from 2,6-dimethylphenol.^{4,5} ^1H NMR (500 MHz, CDCl_3 , 25 °C) δ 7.92 (s, 2H), 2.51 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3 , 25 °C) δ 146.4, 140.2, 135.0, 122.6, 24.2. Anal. calcd for $\text{C}_{10}\text{H}_6\text{NO}_2\text{Br}$: C, 41.77; H, 3.51; N, 6.09; Br, 34.73; found: C, 41.97; H, 3.55; N, 5.95; Br, 34.69. HRMS (EI) calcd for $\text{C}_8\text{H}_8\text{BrNO}_2$ 228.9738 [M^+], found 228.9741.

To a solution of fluoronitrobenzene (1.0 g, 4.5 mmol, 1.0 eq) in DMSO (7 mL) was added diethylamine (0.494 g, 0.7 mL, 6.75 mmol). The reaction mixture was stirred at room temperature for 24 h. After that time, 20 mL of water was added and the aqueous layer was extracted with dichloromethane (3 x 30 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under reduced pressure to give a pure bromonitroarene.

5-Bromo-*N,N*-diethyl-2-nitroaniline and 4-bromo-*N,N*-diethyl-2-nitroaniline



5-Bromo-*N,N*-diethyl-2-nitroaniline. Yield: 1.17 g (95%). Yellow oil. ^1H NMR (500 MHz, CDCl_3 , 25 °C) δ 7.56 (d, 1H, $J = 8.5$ Hz), 7.24 (d, 1H, $J = 2.0$ Hz), 7.00 (dd, 1H, $J_1 = 8.5$ Hz, $J_2 = 2.0$ Hz), 3.17 (q, 4H, $J = 7.5$ Hz), 1.12 (t, 6H, $J = 7.0$ Hz). ^{13}C NMR (126 MHz, CDCl_3 , 25 °C) δ 145.6, 141.4, 127.4, 127.4, 124.7, 122.6, 46.4, 12.6. HRMS (APCI) calcd for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2\text{Br}$ 273.0239 [$\text{M}+\text{H}^+$], found 273.0235.



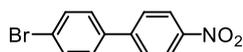
4-Bromo-*N,N*-diethyl-2-nitroaniline. Yield: 1.18 g (96%). Yellow oil. ^1H NMR (500

⁴ M. Wąsińska, A. Korczewska, M. Giurg, J. Skarżewski, *Synthetic Communications* **2015**, *45*, 143-150.

⁵ J.-H. Chun, C. L. Morse, F. T. Chin, V. W. Pike, *Chem. Commun.* **2013**, *49*, 2151-2153.

MHz, CDCl₃, 25 °C) δ 7.80 (d, 1H, J = 7.5 Hz), 7.48 (dd, 1H, J_1 = 8.5 Hz, J_2 = 2.0 Hz), 7.02 (d, 1H, J = 9.0 Hz), 3.14 (q, 4H, J = 7.0 Hz), 1.09 (t, 6H, J = 7.5 Hz). ¹³C NMR (126 MHz, CDCl₃, 25 °C) δ 143.8, 143.6, 135.5, 128.4, 123.9, 111.7, 46.7, 12.6. HRMS (APCI) calcd for C₁₀H₁₄N₂O₂Br 273.0239 [M+H⁺], found 273.0241.

4-bromo-4'-nitro-1,1'-biphenyl



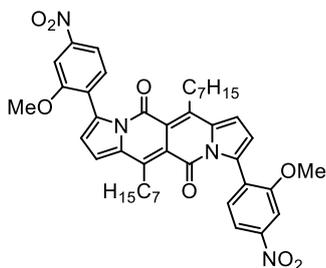
According to the literature procedure,⁶ 4-bromophenylboronic acid (1.29 g, 6.47 mmol), 4-iodo-1-nitrobenzene (1.00 g, 4.97 mmol), Pd(PPh₃)₄ (290 mg, 0.25 mmol) were added to 12 mL of anhydrous THF solution in round bottom flask under an argon atmosphere. Then, 6 mL of 2M solution of K₂CO₃ in water was added to the reaction mixture. The mixture was heated at 80 °C for 24 h under an argon atmosphere. After that time, 20 mL of water was added and the aqueous layer was extracted with dichloromethane (3 x 80 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified using column chromatography (SiO₂, hexanes : ethyl acetate = 100 : 2) to give the desired biphenyl.

Yield: 433 mg (31%). ¹H NMR (500 MHz, CDCl₃, 25 °C) δ 8.30 (m, 2H), 7.71 (m, 2H), 7.63 (m, 2H), 7.49 (m). ¹³C NMR (126 MHz, CDCl₃, 25 °C) δ 147.4, 146.5, 137.8, 132.5, 129.1, 127.8, 124.4, 123.6. HRMS (EI) calcd for C₁₂H₈NO₂Br 276.9738 [M⁺], found 276.9745.

⁶ S. Kang, H. Jung, H. Lee, S. Lee, M. Jung, J. Lee, Y. C. Kim, J. Park, *Dyes Pigm.* **2018**, *156*, 369-378.

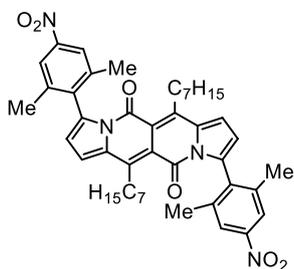
General procedure for a double direct arylation reaction and analytical data for all new compounds.

In a 25 mL Schlenk flask containing a magnetic stirring bar were placed: **1** (0.1 mmol, 43.3 mg, 1.0 eq), tris(dibenzylideneacetone)dipalladium(0) (9.2 mg, 0.01 mmol, 10 %_{mol}), PCy₃·HBF₄ (7.4 mg, 0.02 mmol, 20 %_{mol}), pivalic acid (6.2 mg, 0.06 mmol, 60 %_{mol}), K₂CO₃ (55.5 mg, 0.4 mmol, 4.0 eq) and the haloarene (0.3 mmol, 3.0 eq). The vessel was evacuated and backfilled with argon (3 times). Next, anhydrous, degassed toluene (2 mL) was added using a syringe. The vessel was tightly closed and again carefully evacuated and backfilled with argon (3 times). The content of the flask was stirred at 120 °C. After indicated time, all solvents were evaporated off and the residue was purified by column chromatography. All further manipulations are described below.



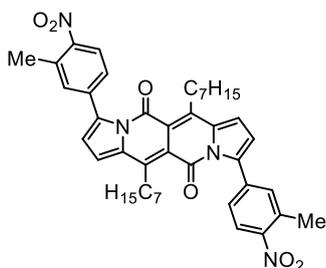
6,12-Diheptyl-3,9-bis(2-methoxy-4-nitrophenyl)-5H,11H-dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (4). Prepared using 1-bromo-2-methoxy-4-nitrobenzene (69.6 mg, 0.3 mmol). Time of heating: 72 h. Product was purified using column chromatography (SiO₂, hexanes : dichloromethane, 2:3). The residue after column was boiled in

cyclohexane, then the flask was cooled down to room temperature and finally the crystals were filtered off to give 41.0 mg (56% yield) of product. $R_f = 0.36$ (SiO₂, hexanes : dichloromethane, 2:3). Mp. 205 - 206 °C. ¹H NMR (600 MHz, CDCl₃, 25 °C) δ 7.93 (dd, 2H, $J_1 = 8.4$ Hz, $J_2 = 1.8$ Hz), 7.78 (d, 2H, $J = 2.4$ Hz), 7.48 (d, 2H, $J = 8.4$ Hz), 6.89 (d, 2H, $J = 3.6$ Hz), 6.53 (d, 2H, $J = 4.2$ Hz), 3.87 (s, 6H), 3.14-3.12 (m, 4H), 1.67-1.62 (m, 4H), 1.46-1.43 (m, 4H + residual cyclohexane), 1.34-1.26 (m, 12H), 0.86 (t, 6H, $J = 7.2$ Hz). ¹³C NMR (151 MHz, CDCl₃, 25 °C) δ 159.3, 157.8, 148.8, 143.7, 135.5, 133.7, 130.2, 129.8, 118.6, 116.3, 116.0, 115.4, 105.5, 56.1, 32.0, 30.6, 30.5, 30.4, 29.2, 27.1 (residual cyclohexane), 22.9, 14.2. HRMS (EI) calcd for C₄₂H₄₆N₄O₈ 734.3316 [M⁺], found 734.3320.



3,9-Bis(2,6-dimethyl-4-nitrophenyl)-6,12-diheptyl-5H,11H-dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (5). Prepared

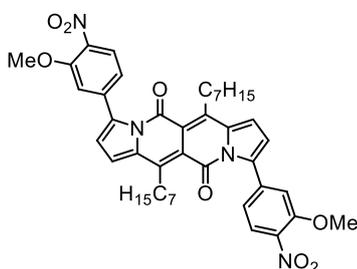
using 2-bromo-1,3-dimethyl-5-nitrobenzene (69.0 mg, 0.3 mmol). The reaction mixture was heated at 150 °C in a sealed tube for 72h. Product was purified using column chromatography (SiO₂, hexanes : dichloromethane, 1:1). Then, the obtained material was chromatographed again (SiO₂, hexanes : ethyl acetate, 100:5 → neat ethyl acetate) in order to get rid of traces of the mono-arylated derivative. The residue after column was reprecipitated from dichloromethane/methanol mixture to give 48.5 mg (66% yield) of product. *R_f* = 0.43 (SiO₂, hexanes : dichloromethane, 1:1). Mp. 256 - 257 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C) δ 7.98 (s, 4H), 6.94 (d, 2H, *J* = 3.5 Hz), 6.33 (d, 2H, *J* = 4.0 Hz), 3.15-3.12 (m, 4H), 2.18 (s, 12H), 1.61-1.55 (m, 4H), 1.43-1.37 (m, 4H), 1.31-1.23 (m, 12H), 0.86 (t, 6H, *J* = 7.0 Hz). ¹³C NMR (126 MHz, CDCl₃, 25 °C) δ 159.0, 147.4, 144.7, 141.1, 139.1, 134.8, 134.3, 121.9, 116.9, 115.9, 115.3, 31.8, 30.5, 30.1, 29.8, 29.1, 22.8, 20.8, 14.2. HRMS (EI) calcd for C₄₄H₅₀N₄O₆ 730.3730 [M⁺], found 730.3702.



6,12-Diheptyl-3,9-bis(3-methyl-4-nitrophenyl)-5H,11H-

dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (6). Prepared using 4-bromo-2-methyl-1-nitrobenzene (64.8 mg, 0.3 mmol). Time of heating: 48 h. Product was purified using column chromatography (SiO₂, hexanes : dichloromethane, 1:1). The residue after column was boiled in

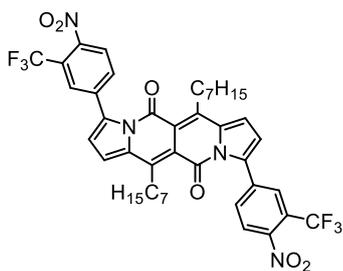
a minimal amount of cyclohexane, then the flask was cooled down to room temperature and finally the crystals were filtered off to give 26.6 mg (38% yield) of product. *R_f* = 0.46 (SiO₂, hexanes : dichloromethane, 1:1). Mp. 273 - 274 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C) δ 8.05 (d, 2H, *J* = 8.0 Hz), 7.44-7.42 (m, 4H), 6.92 (d, 2H, *J* = 4.0 Hz), 6.61 (d, 2H, *J* = 3.5 Hz), 3.22-3.19 (m, 4H), 2.68 (s, 6H), 1.69-1.63 (m, 4H), 1.50-1.44 (m, 4H), 1.37-1.27 (m, 12H), 0.87 (t, 6H, *J* = 7.0 Hz). ¹³C NMR (126 MHz, CDCl₃, 25 °C) δ 159.6, 148.1, 144.4, 137.8, 137.7, 136.3, 133.5, 132.8, 127.3, 124.5, 119.7, 116.2, 32.0, 30.7, 30.6, 30.3, 29.3, 22.8, 21.1, 14.2. HRMS (EI) calcd for C₄₂H₄₆N₄O₆ 702.3417 [M⁺], found 702.3404.



6,12-Diheptyl-3,9-bis(3-methoxy-4-nitrophenyl)-5H,11H-

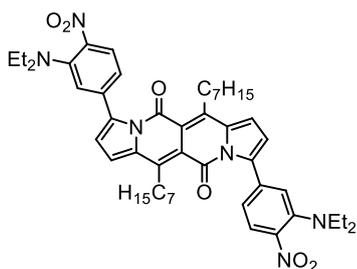
dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (7). Prepared using 4-bromo-2-methoxy-1-nitrobenzene (69.6 mg, 0.3 mmol). Time

of heating: 48 h. Product was purified using column chromatography (SiO₂, hexanes : dichloromethane, 1:2). The residue after column was boiled in a minimal amount of *n*-hexane, then the flask was cooled down to room temperature and finally the crystals were filtered off to give 19.5 mg (26% yield) of product. $R_f = 0.10$ (SiO₂, hexanes : dichloromethane, 1:2). Mp. 234 - 235 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C) δ 7.92 (d, 2H, $J = 8.5$ Hz), 7.19 (br s, 2H), 7.13 (dd, 2H, $J_1 = 8.5$ Hz, $J_2 = 1.5$ Hz), 6.93 (d, 2H, $J = 4.0$ Hz), 6.64 (d, 2H, $J = 4.0$ Hz), 4.00 (s, 6H), 3.21-3.17 (m, 4H), 1.69-1.63 (m, 4H), 1.51-1.45 (m, 4H), 1.36-1.25 (m, 12H), 0.87 (t, 6H, $J = 6.5$ Hz). ¹³C NMR (126 MHz, CDCl₃, 25 °C) δ 159.4, 152.7, 144.5, 139.1, 138.6, 137.8, 136.3, 125.5, 120.8, 119.8, 116.2, 114.2, 56.7, 31.9, 30.9, 30.6, 30.4, 29.3, 22.8, 14.2. HRMS (EI) calcd for C₄₂H₄₆N₄O₈ 734.3316 [M⁺], found 734.3298.



6,12-Diheptyl-3,9-bis(4-nitro-3-(trifluoromethyl)phenyl)-5H,11H-dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (8). Prepared using 4-bromo-1-nitro-2-(trifluoromethyl)benzene (81.0 mg, 0.3 mmol). Product was purified using column chromatography (SiO₂, hexanes : dichloromethane, 1:1). The residue after column was boiled

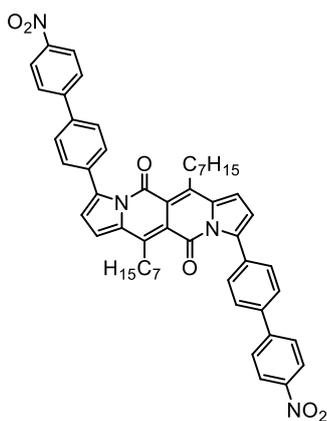
in a minimal amount of cyclohexane and the flask was cooled down to room temperature. Then the crystals were filtered off and washed with *n*-pentane to give 22.9 mg (28% yield) of product. $R_f = 0.34$ (SiO₂, hexanes : dichloromethane, 1:1). Mp. 263 - 264 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C) δ 7.96 (d, 2H, $J = 8.5$ Hz), 7.92 (d, 2H, $J = 1.0$ Hz), 7.79 (dd, 2H, $J_1 = 8.5$ Hz, $J_2 = 1.5$ Hz), 6.97 (d, 2H, $J = 4.0$ Hz), 6.69 (d, 2H, $J = 4.0$ Hz), 3.21-3.18 (m, 4H), 1.68-1.62 (m, 4H), 1.51-1.49 (m, 4H), 1.37-1.26 (m, 12H), 0.87 (t, 6H, $J = 6.5$ Hz). ¹³C NMR (126 MHz, CDCl₃, 25 °C) δ 159.4, 146.8, 145.1, 137.7, 136.6, 136.1, 132.5, 128.6, 128.5, 124.9, 123.4 (q, $J(C,F) = 34.0$ Hz), 122.1 (q, $J(C,F) = 274.4$ Hz), 120.4, 116.5, 116.1, 31.9, 30.9, 30.5, 30.3, 29.2, 22.8, 14.2. HRMS (EI) calcd for C₄₂H₄₀N₄O₆F₆ 810.2852 [M⁺], found 810.2850.



3,9-Bis(3-(diethylamino)-4-nitrophenyl)-6,12-diheptyl-5H,11H-dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (9). Prepared using 5-bromo-*N,N*-diethyl-2-nitroaniline (81.9 mg, 0.3 mmol). Product was purified using column chromatography (SiO₂, hexanes : dichloromethane, 1:1 → 2:3). The residue after column was

recrystallized from acetonitrile, then the flask was left overnight in the fridge and finally the crystals were filtered off to give 36.5 mg (45% yield) of product. $R_f = 0.14$ (SiO₂, hexanes :

dichloromethane, 1:1). Mp. 194 - 195 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C) δ 7.74 (d, 2H, *J* = 8.0 Hz), 7.26-7.25 (m, 2H + residue signal of CDCl₃), 7.06 (d, 2H, *J* = 8.0 Hz), 6.90 (d, 2H, *J* = 4.0 Hz), 6.60 (d, 2H, *J* = 3.5 Hz), 3.21-3.15 (m, 12H), 1.69-1.63 (m, 4H), 1.49-1.43 (m, 4H), 1.36-1.26 (m, 12H), 1.15 (t, 12H, *J* = 7.0 Hz), 0.87 (t, 6H, *J* = 6.5 Hz). ¹³C NMR (126 MHz, CDCl₃, 25 °C) δ 159.5, 144.2, 143.0, 138.4, 137.3, 136.1, 125.4, 123.5, 120.8, 119.4, 116.1, 116.0, 46.9, 32.0, 30.8, 30.6, 30.4, 29.3, 22.8, 14.3, 12.8. HRMS (EI) calcd for C₄₈H₆₀N₆O₆ 816.4574 [M⁺], found 816.4551.



6,12-Diheptyl-3,9-bis(4'-nitro-[1,1'-biphenyl]-4-yl)-5H,11H-dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (10). Prepared using 4-bromo-4'-nitro-1,1'-biphenyl (83.4 mg, 0.3 mmol). Time of heating: 24 h. Product was purified using column chromatography (SiO₂, hexanes : dichloromethane, 1:1). The residue after chromatography was reprecipitated from dichloromethane/methanol mixture to give 38.6 mg (47% yield) of product. *R_f* = 0.23 (SiO₂, hexanes : dichloromethane, 1:1). Mp. 295 - 296 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C) δ 8.33 (d,

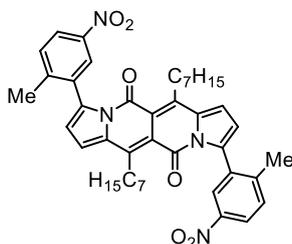
4H, *J* = 9.0 Hz), 7.81 (d, 4H, *J* = 9.0 Hz), 7.68 (d, 4H, *J* = 8.5 Hz), 7.63 (d, 4H, *J* = 8.5 Hz), 6.92 (d, 2H, *J* = 4.0 Hz), 6.61 (d, 2H, *J* = 3.5 Hz), 3.26-3.23 (m, 4H), 1.73-1.67 (m, 4H), 1.52-1.46 (m, 4H), 1.39-1.25 (m, 12H), 0.86 (t, 6H, *J* = 7.0 Hz). ¹³C NMR (126 MHz, CDCl₃, 25 °C) δ 159.9, 147.3, 143.8, 139.3, 138.1, 135.9, 133.7, 129.5, 127.8, 126.8, 124.3, 118.9, 116.1, 116.0, 32.0, 30.7, 30.6, 30.4, 29.3, 22.9, 14.3. HRMS (EI) calcd for C₅₂H₅₀N₄O₆ 826.3730 [M⁺], found 826.3693.



6,12-Diheptyl-3,9-bis(2-methyl-5-nitrophenyl)-5H,11H-dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (13). Prepared using 1-bromo-2-methoxy-3-nitrobenzene (69.6 mg, 0.3 mmol). Time of heating: 7 days. Product was purified using column chromatography

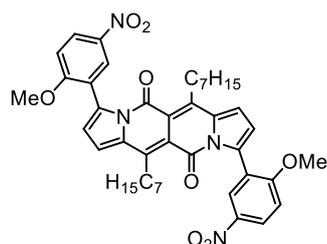
(SiO₂, hexanes : dichloromethane, 2:3). The residue after column was washed with a minimal amount of *n*-pentane and then the crystals were filtered off to give 15.8 mg (21% yield) of product. *R_f* = 0.28 (SiO₂, hexanes : dichloromethane, 2:3). Mp. 169 - 170 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C) δ 7.83 (dd, 2H, *J*₁ = 8.0 Hz, *J*₂ = 1.5 Hz), 7.56 (dd, 2H, *J*₁ = 7.5 Hz, *J*₂ = 1.5 Hz), 7.24 (m, 2H + residue signal from CDCl₃), 6.89 (d, 2H, *J* = 3.5 Hz), 6.58 (d, 2H, *J* = 4.0 Hz), 3.60 (s, 6H), 3.16-3.13 (m, 4H), 1.66-1.60 (m, 4H), 1.45-1.39 (m, 4H), 1.33-1.25 (m, 12H), 0.87 (t, 6H, *J* = 7.0 Hz). ¹³C NMR (126 MHz, CDCl₃, 25 °C) δ 159.4, 151.6, 144.1, 144.1, 135.3, 134.4, 132.8, 130.5, 125.0,

123.3, 118.5, 116.1, 115.4, 62.0, 31.9, 30.6, 30.5, 30.3, 29.2, 22.8, 14.3. HRMS (ESI) calcd for $C_{42}H_{46}N_4O_8Na$ 757.3213 $[M+Na^+]$, found 757.3229.



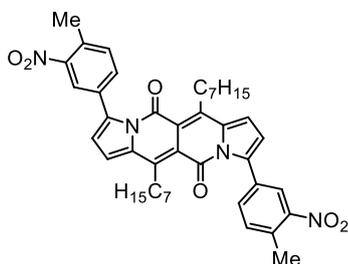
6,12-Diheptyl-3,9-bis(2-methyl-5-nitrophenyl)-5H,11H-dipyrrolo[1,2-b:1',2'-g][2,6]naphthyridine-5,11-dione (14). Prepared using 2-bromo-1-methyl-4-nitrobenzene (64.8 mg, 0.3 mmol). Time of heating: 48 h. Product was purified using column chromatography (SiO_2 , hexanes : dichloromethane, 1:1). The residue after column was boiled in

acetonitrile/cyclohexane = 1:1 (v/v), then the flask was cooled down to room temperature and finally the crystals were filtered off to give 31.0 mg (44% yield) of product. R_f = 0.28 (SiO_2 , hexanes : dichloromethane, 1:1). Mp. 238 - 240 °C. 1H NMR (500 MHz, $CDCl_3$, 25 °C) δ 8.19-8.15 (m, 4H), 7.41 (d, 2H, J = 8.5 Hz), 6.91 (d, 2H, J = 3.5 Hz), 6.46 (d, 2H, J = 3.5 Hz), 3.14 (br s, 4H), 2.29 (s, 6H), 1.63-1.54 (m, 4H+ residual cyclohexane), 1.44-1.38 (m, 4H), 1.33-1.26 (m, 12H), 0.87 (t, 6H, J = 7.0 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ 159.2, 146.0, 145.6, 144.8, 136.1, 135.4, 134.7, 130.4, 124.5, 123.3, 118.3, 115.7, 31.9, 30.6, 30.6, 30.2, 29.1, 22.8, 20.6, 14.2. HRMS (EI) calcd for $C_{42}H_{46}N_4O_6$ 702.3417 $[M^+]$, found 702.3416.



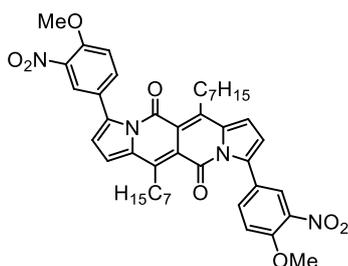
6,12-Diheptylo-3,9-bis(2-metoksy-5-nitrofenylo)-5H,11H-dipirolo[1,2-b:1',2'-g][2,6]naftyrydyno-5,11-dion (15). Prepared using 2-bromo-1-methoxy-4-nitrobenzene (69.6 mg, 0.3 mmol). Time of heating: 48 h. Product was purified using column chromatography (SiO_2 , hexanes : dichloromethane, 2:5). The residue after column was

recrystallized from toluene, the crystals were carefully filtered off and washed with *n*-pentane to give 40.7 mg (55% yield) of product. R_f = 0.46 (SiO_2 , hexanes : dichloromethane, 1:2). Mp. 270 - 271 °C. 1H NMR (500 MHz, $CDCl_3$, 50 °C) δ 8.32 (dd, 2H, J_1 = 9.0 Hz, J_2 = 3.0 Hz), 8.24 (d, 2H, J = 2.5 Hz), 6.98 (d, 2H, J = 9.0 Hz), 6.88 (d, 2H, J = 3.5 Hz), 6.53 (d, 2H, J = 4.0 Hz), 3.88 (s, 6H), 3.16-3.13 (m, 4H), 1.69-1.63 (m, 4H), 1.47-1.42 (m, 4H+residual water in $CDCl_3$), 1.36-1.26 (m, 12H), 0.88 (t, 6H, J = 7.0 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, 50 °C) δ 162.7, 159.3, 143.9, 141.4, 135.3, 133.5, 126.0, 125.6, 124.6, 118.4, 116.3, 115.3, 110.1, 56.4, 32.0, 30.6, 30.5, 30.4, 29.2, 22.8, 14.2. HRMS (ESI) calcd for $C_{42}H_{46}N_4O_8Na$ 757.3213 $[M+Na^+]$, found 730.3209.



6,12-Diheptyl-3,9-bis(4-methyl-3-nitrophenyl)-5H,11H-dipyrrolo[1,2-b:1',2'-g][2,6]naphthyridine-5,11-dione (16). Prepared

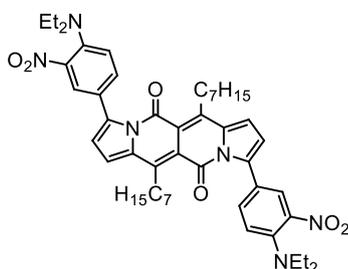
using 4-bromo-1-methyl-2-nitrobenzene (64.8 mg, 0.3 mmol). Time of heating: 48 h. Product was purified using column chromatography (SiO₂, hexanes : dichloromethane, 1:1) to give 33.2 mg (47% yield) of product. $R_f = 0.37$ (SiO₂, hexanes : dichloromethane, 1:1). Mp. 195 - 196 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C) δ 8.13 (d, 2H, $J = 1.5$ Hz), 7.61 (dd, 2H, $J_1 = 8.0$ Hz, $J_2 = 1.5$ Hz), 7.36 (d, 2H, $J = 8.0$ Hz), 6.91 (d, 2H, $J = 4.0$ Hz), 6.59 (d, 2H, $J = 4.0$ Hz), 3.21-3.18 (m, 4H), 2.68 (s, 6H), 1.69-1.63 (m, 4H), 1.49-1.43 (m, 4H), 1.37-1.27 (m, 12H), 0.87 (t, 6H, $J = 6.5$ Hz). ¹³C NMR (126 MHz, CDCl₃, 25 °C) δ 159.7, 148.6, 144.3, 137.4, 135.8, 133.3, 133.2, 132.1, 125.0, 119.0, 116.0, 115.9, 32.0, 30.7, 30.6, 30.3, 29.2, 22.8, 20.7, 14.3. HRMS (EI) calcd for C₄₂H₄₆N₄O₆ 702.3417 [M⁺], found 702.3424.



6,12-Diheptyl-3,9-bis(4-methoxy-3-nitrophenyl)-5H,11H-

dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (17). Prepared using 4-bromo-1-methoxy-2-nitrobenzene (69.6 mg, 0.3 mmol). Time of heating: 48 h. Product was purified using column chromatography (SiO₂, hexanes : dichloromethane, 1:2) to give 35.0 mg (48% yield) of

product. $R_f = 0.12$ (SiO₂, hexanes : dichloromethane, 1:2). Mp. 208 - 209 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C) δ 8.01 (d, 2H, $J = 2.5$ Hz), 7.66 (dd, 2H, $J_1 = 9.0$ Hz, $J_2 = 2.5$ Hz), 7.10 (d, 2H, $J = 8.5$ Hz), 6.88 (d, 2H, $J = 4.0$ Hz), 6.53 (d, 2H, $J = 4.0$ Hz), 4.03 (s, 6H), 3.20-3.17 (m, 4H), 1.68-1.62 (m, 4H), 1.50-1.44 (m, 4H), 1.37-1.28 (m, 12H), 0.88 (t, 6H, $J = 6.5$ Hz). ¹³C NMR (126 MHz, CDCl₃, 25 °C) δ 159.7, 152.8, 144.2, 138.8, 137.3, 135.6, 134.6, 126.3, 125.7, 118.6, 115.9, 115.7, 112.7, 56.8, 32.0, 30.7, 30.6, 30.3, 29.2, 22.8, 14.3. HRMS (EI) calcd for C₄₂H₄₆N₄O₈ 734.3316 [M⁺], found 734.3314.



3,9-Bis(4-(diethylamino)-3-nitrophenyl)-6,12-diheptyl-5H,11H-

dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione (18). Prepared using 4-bromo-*N,N*-diethyl-2-nitroaniline (81.9 mg, 0.3 mmol). Product was purified using column chromatography (SiO₂, hexanes : dichloromethane, 1:1). The residue after column was recrystallized

from acetonitrile, then the flask was left overnight in the fridge and finally the crystals were filtered off to give 49.3 mg (60% yield) of product. $R_f = 0.17$ (SiO₂, hexanes : dichloromethane, 1:1). Mp. 179 - 180 °C. ¹H NMR (500 MHz, CDCl₃, 25 °C) δ 7.86 (d, 2H, $J = 2.5$ Hz), 7.52 (dd, 2H, $J_1 = 8.5$ Hz, $J_2 = 2.0$ Hz), 7.11 (d, 2H, $J = 8.5$ Hz), 6.89 (d, 2H, $J = 4.0$ Hz), 6.53 (d, 2H, $J = 4.0$ Hz), 3.28-3.19 (m, 12H), 1.71-1.64 (m, 4H), 1.51-1.45 (m, 4H), 1.39-1.29 (m, 12H), 1.19 (t, 12H, $J = 7.0$ Hz),

0.88 (t, 6H, $J = 6.5$ Hz). ^{13}C NMR (126 MHz, CDCl_3 , 25 °C) δ 159.9, 144.2, 143.8, 141.2, 138.1, 135.6, 133.2, 126.5, 124.0, 120.3, 118.3, 116.0, 115.7, 46.3, 32.0, 30.7, 30.7, 30.4, 29.2, 22.8, 14.3, 12.8. HRMS (EI) calcd for $\text{C}_{48}\text{H}_{60}\text{N}_6\text{O}_6$ 816.4574 [M^+], found 816.4598.

2. Spectroscopic measurements

Table S1. Absorption and fluorescence properties of DPNDs **1-18**.

cmpd	solvent ^a	$\lambda_{\text{abs}}/\text{nm}^b$	$\lambda_{\text{fl}}/\text{nm}^b$	Stokes' shift/ cm^{-1c}	Φ_{fl}	τ/ns^d	$k_{\text{r}} \cdot 10^{-8}/\text{s}^{-1e}$	$k_{\text{nr}} \cdot 10^{-8}/\text{s}^{-1e}$
1^f	DCB	508	528	750	0.81	5.1	1.59	0.373
	DCM	504	523	720	0.73	5.7	1.28	0.474
	ACN	498	525	1030	0.65	5.7	1.14	0.614
2^f	DCB	569	605	1050	0.45	3.6	1.25	1.53
	DCM	562	601	1150	0.41	3.4	1.21	1.74
	ACN	559	599	1190	0.07	—	—	—
3^f	DCB	536	580	1410	0.61	4.3	1.42	0.91
	DCM	533	578	1460	0.49	3.3	1.48	1.55
	ACN	529	579	1630	0.013	0.049	2.65	201
4	DCB	547	612	1940	0.46	3.7	1.24	1.46
	DCM	543	610	2040	0.21	1.7	1.24	4.65
	ACN	542	604	1910	0.005	—	—	—
5	DCB	524	560	1230	0.96	4.7	2.04	0.085
	DCM	521	560	1340	0.34	1.9	1.79	3.47
	ACN	518	564	1570	0.005	—	—	—
6	DCB	557	607	1480	0.58	3.7	1.57	1.14
	DCM	549	605	1690	0.45	3.6	1.25	1.53
	ACN	545	608	1900	0.24	2.8	0.857	2.71
7	DCB	556	606	1480	0.58	3.6	1.61	1.17
	DCM	549	604	1660	0.44	3.5	1.26	1.60
	ACN	546	603	1890	0.31	3.2	0.969	2.16
8	DCB	558	606	1400	0.45	3.6	1.25	1.53
	DCM	548	602	1640	0.31	3.2	0.969	2.16
	ACN	543	606	1940	0.005	—	—	—
9	DCB	555	602	1390	0.006	—	—	—
	DCM	549	608	1760	0.003	—	—	—
	ACN	542	584	1330	0.003	—	—	—
10	DCB	563	618	1580	0.38	3.4	1.12	1.82
	DCM	555	615	1760	0.28	2.5	1.12	2.88
	ACN	550	608	1730	0.05	3.0	0.17	3.17

11 ^f	DCB	551	582	970	0.49	3.6	1.36	1.42
	DCM	544	577	1050	0.28	2.2	1.27	3.27
	ACN	541	575	1090	0.04	0.309	1.29	31.1
12 ^f	DCB	527	558	1050	0.95	4.7	2.02	0.106
	DCM	523	555	1100	0.92	4.8	1.92	0.167
	ACN	521	553	1110	0.43	2.7	1.59	2.11
13	DCB	532	583	1640	0.61	4.3	1.42	0.907
	DCM	525	584	1920	0.52	3.5	1.49	1.37
	ACN	524	582	1900	0.12	1.1	1.09	8.00
14	DCB	525	568	1440	0.76	4.9	1.55	0.490
	DCM	522	566	1490	0.58	3.2	1.81	1.31
	ACN	520	569	1660	0.075	—	—	—
15	DCB	535	586	1630	0.63	4.3	1.47	0.860
	DCM	531	582	1650	0.59	3.6	1.64	1.14
	ACN	528	590	1990	0.20	1.8	1.11	4.44
16	DCB	547	593	1420	0.69	3.8	1.82	0.816
	DCM	541	593	1620	0.46	3.6	1.28	1.50
	ACN	537	592	1730	0.17	2.0	0.850	4.15
17	DCB	553	604	1530	0.64	4.0	1.60	0.900
	DCM	546	604	1760	0.43	3.7	1.16	1.54
	ACN	543	609	2000	0.18	2.5	0.720	3.28
18	DCB	575	669	2440	0.12	2.6	0.462	3.38
	DCM	565	670	2770	0.02	—	—	—
	ACN	557	688	3420	0.04	2.8	0.143	3.43

^a DCB = 1,2-dichlorobenzene ($\epsilon = 9.93$, $n = 1.5514$, $f_0(\epsilon, n^2) = 0.37$, $\eta = 1.32$ cP)⁷; DCM = dichloromethane ($\epsilon = 9.08$, $n = 1.424$, $f_0(\epsilon, n^2) = 0.44$, $\eta = 0.45$ cP); ACN = acetonitrile ($\epsilon = 37.5$, $n = 1.3393$, $f_0(\epsilon, n^2) = 0.61$, $\eta = 0.37$ cP). ^b Absorption and fluorescence maxima. ^c Stokes' shifts. ^d Lifetimes of the emissive excited states obtained from time-correlated single photon counting (for $\tau \geq 1.5$ ns). ^e Radiative and non-radiative decay rate constants: $k_r = \Phi_f \tau^{-1}$ and $k_{nr} = (1 - \Phi_f) \tau^{-1}$. ^f The data were taken from: B. Sadowski *et al.* *Chem. Sci.*, 2021, **12**, 14039-14049.

⁷ a) M. Terazima, *J. Chem. Phys.* **1996**, *104*, 4988. b) A. I. Abramovich, L. V. Lanshina, I. D. Kargin, *Russ. Chem. Bull.* **2017**, *66*, 828–832. c) A. Rostamkolahi, A. Rostami, F. Koohyar, F. Kiani, *Chem. Pap.* **2013**, *67*, 1433-1441.

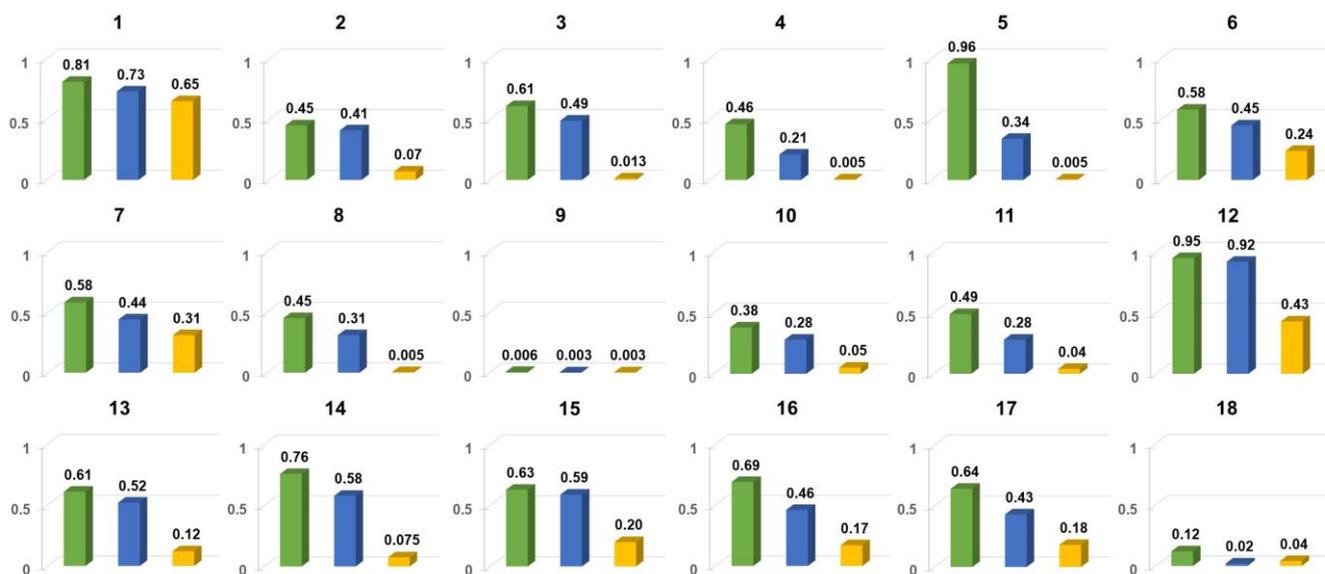


Figure S1. Comparison of ϕ_{fl} for compounds **1-18** in three different solvents: 1,2-dichlorobenzene (DCB) (green), DCM (blue) and ACN (orange). The data for compounds **1**, **2**, **3**, **11** and **12** were taken from the literature: B. Sadowski *et al.* *Chem. Sci.*, 2021,12, 14039-14049.

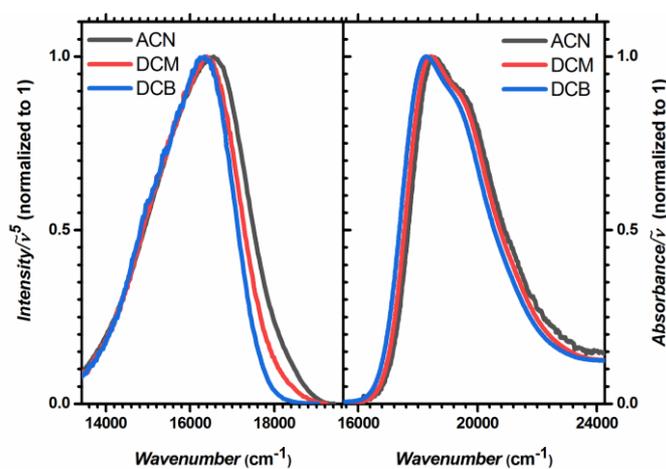


Figure S2. Absorption and emission spectra of **4** in DCB, DCM and ACN.

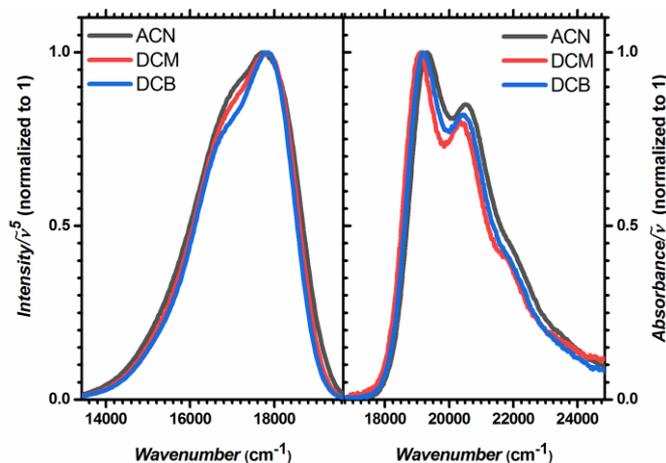


Figure S3. Absorption and emission spectra of **5** in DCB, DCM and ACN.

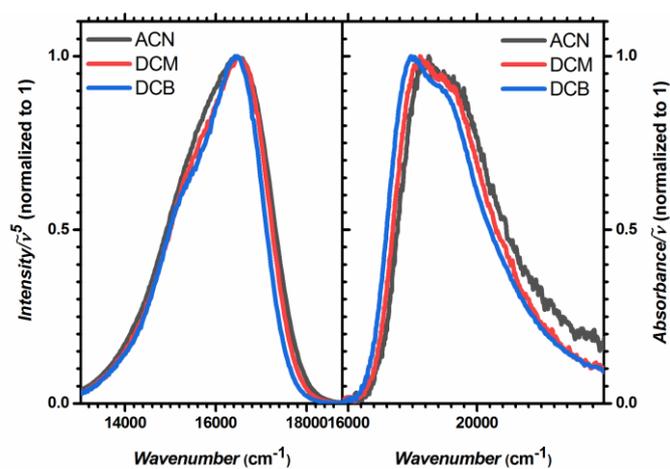


Figure S4. Absorption and emission spectra of **6** in DCB, DCM and ACN.

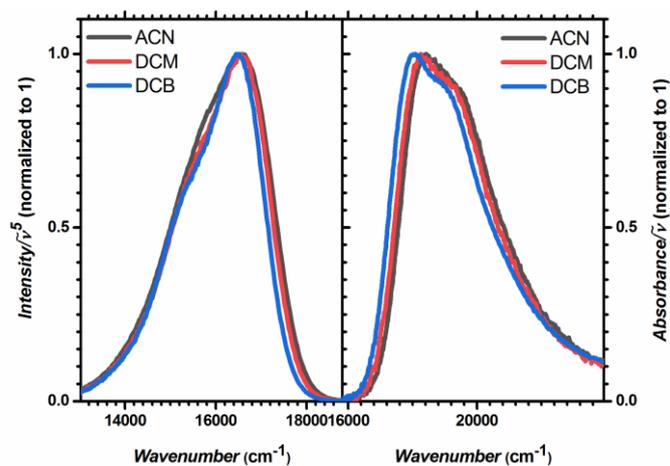


Figure S5. Absorption and emission spectra of **7** in DCB, DCM and ACN.

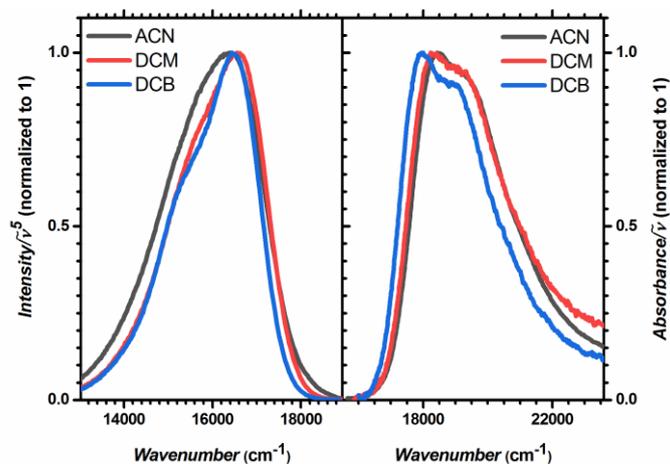


Figure S6. Absorption and emission spectra of **8** in DCB, DCM and ACN.

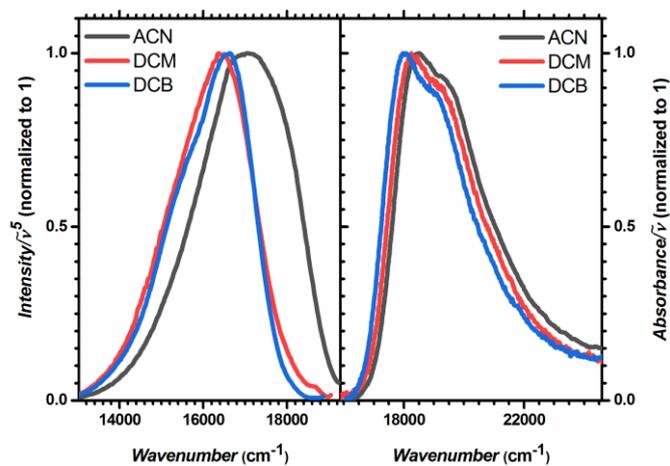


Figure S7. Absorption and emission spectra of **9** in DCB, DCM and ACN.

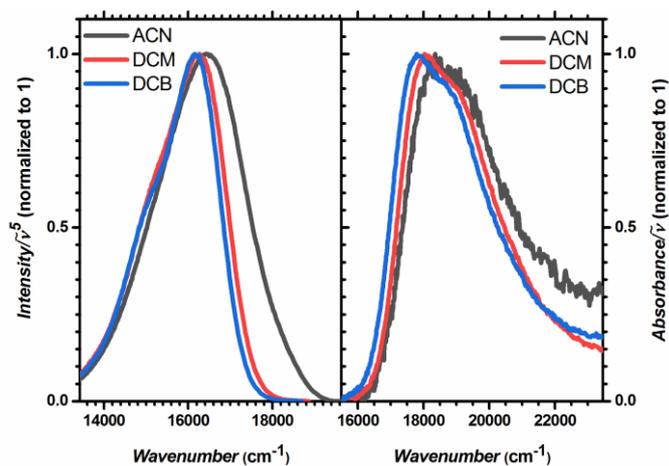


Figure S8. Absorption and emission spectra of **10** in DCB, DCM and ACN.

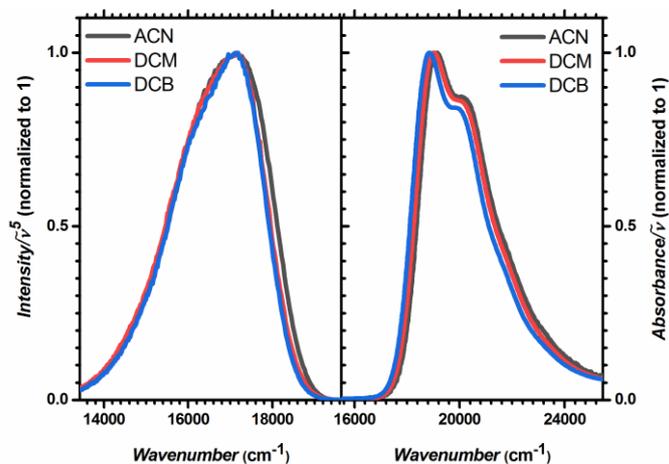


Figure S9. Absorption and emission spectra of **13** in DCB, DCM and ACN.

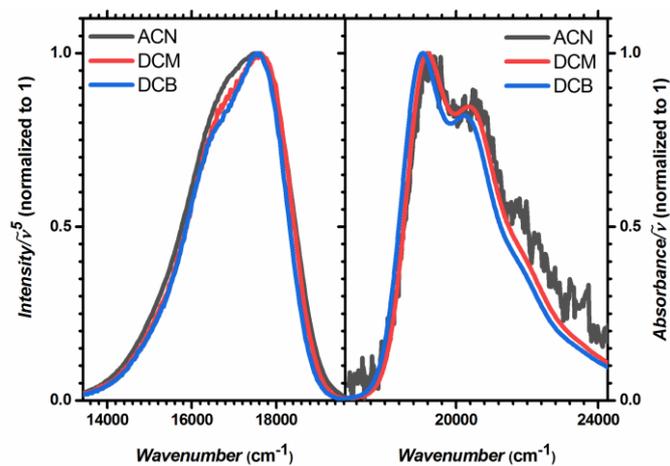


Figure S10. Absorption and emission spectra of **14** in DCB, DCM and ACN.

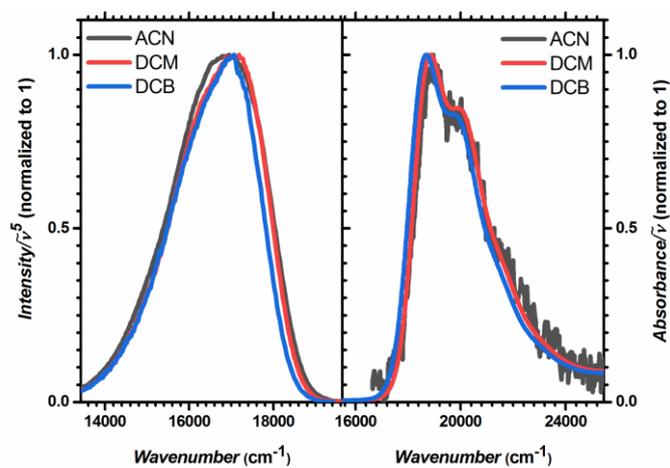


Figure S11. Absorption and emission spectra of **15** in DCB, DCM and ACN.

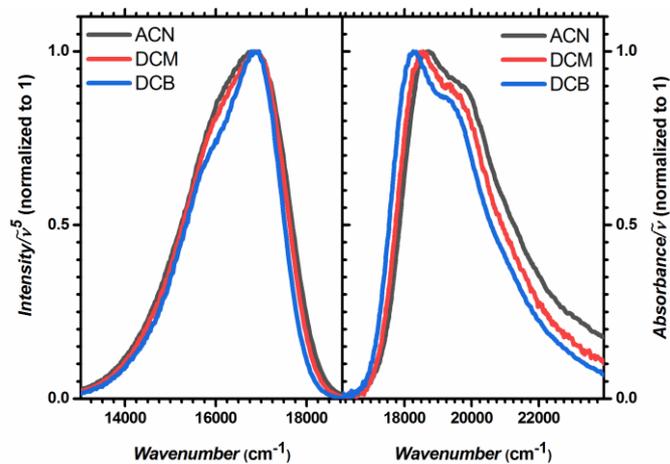


Figure S12. Absorption and emission spectra of **16** in DCB, DCM and ACN.

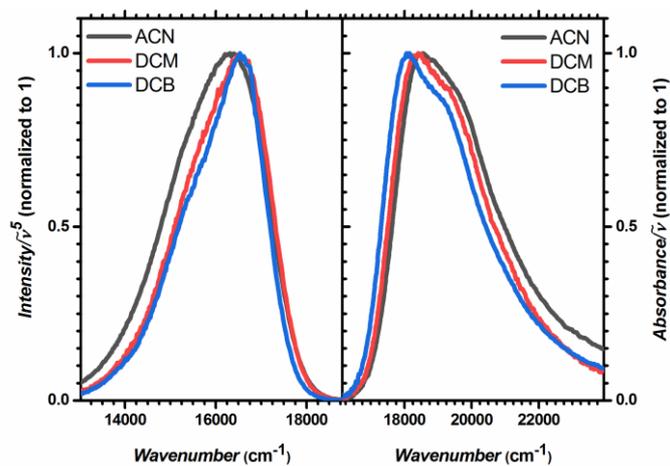


Figure S13. Absorption and emission spectra of **17** in DCB, DCM and ACN.

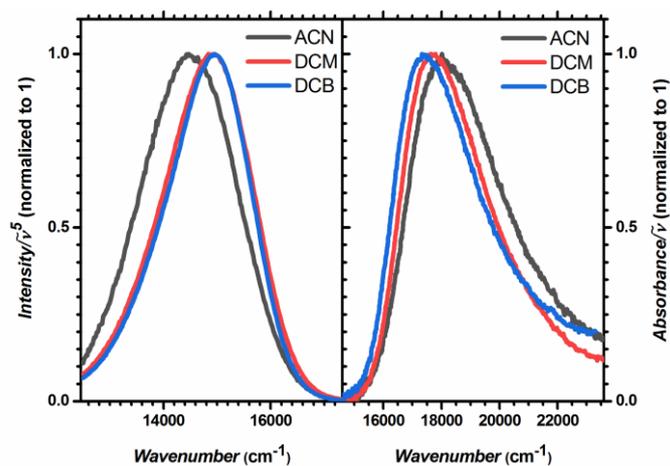


Figure S14. Absorption and emission spectra of **18** in DCB, DCM and ACN.

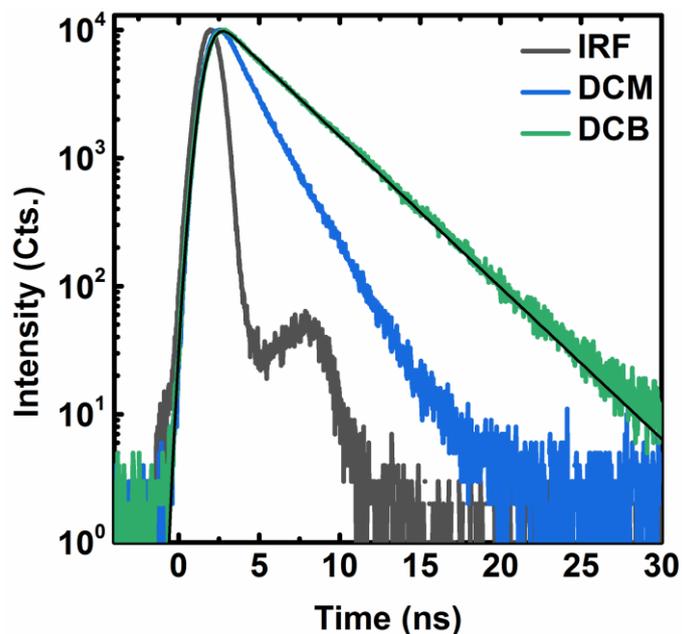


Figure S15. Emission decays of **4** in DCM and DCB. The decays were gated at the indicated wavelengths. The emission lifetimes of **4** in ACN are below IRF (grey curve, 1.5 ns), and thus the emission decays could not be recorded.

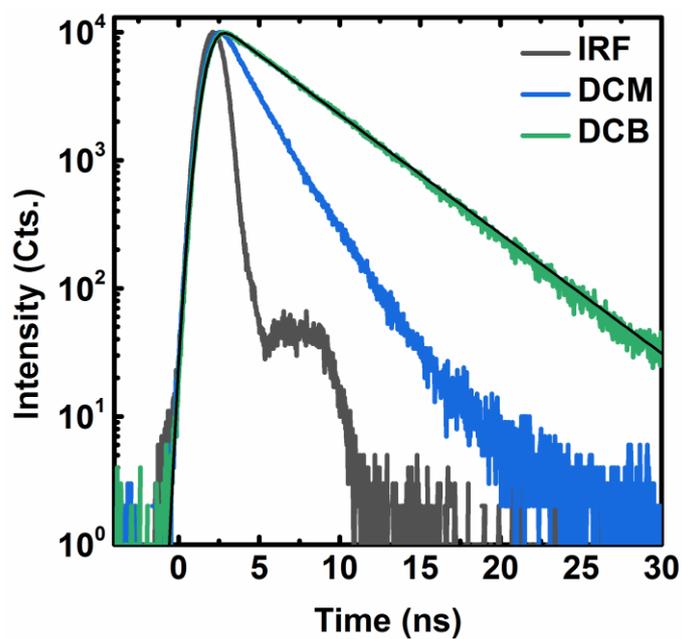


Figure S16. Emission decays of **5** in DCB and DCM. The emission lifetimes of **5** in ACN are below IRF (grey curve, 1.5 ns), and thus the emission decays could not be recorded.

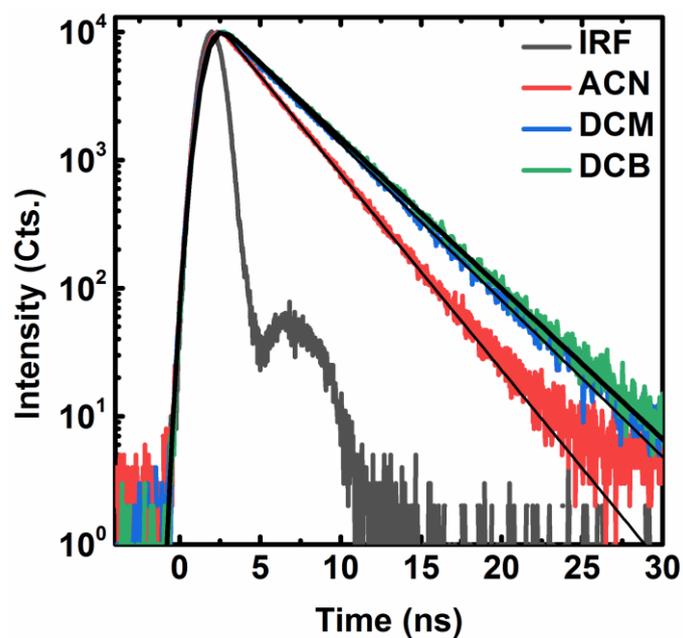


Figure S17. Emission decays of **6** in DCB, DCM and ACN.

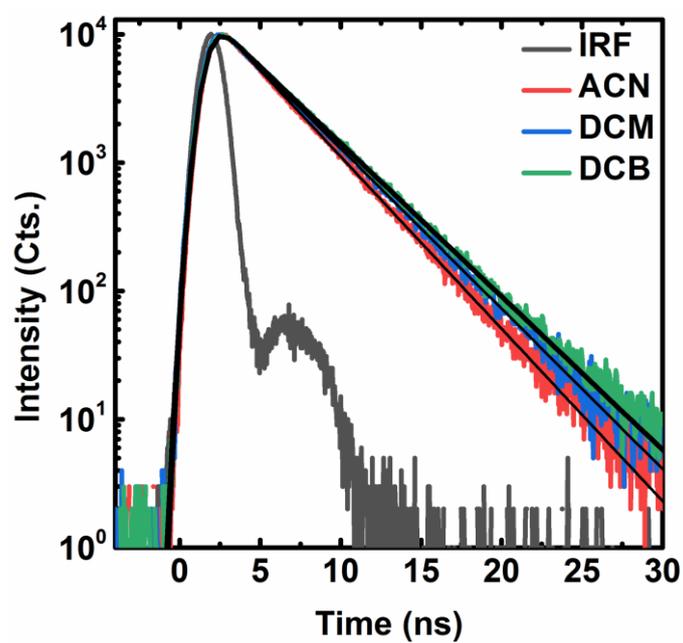


Figure S18. Emission decays of **7** in DCB, DCM and ACN.

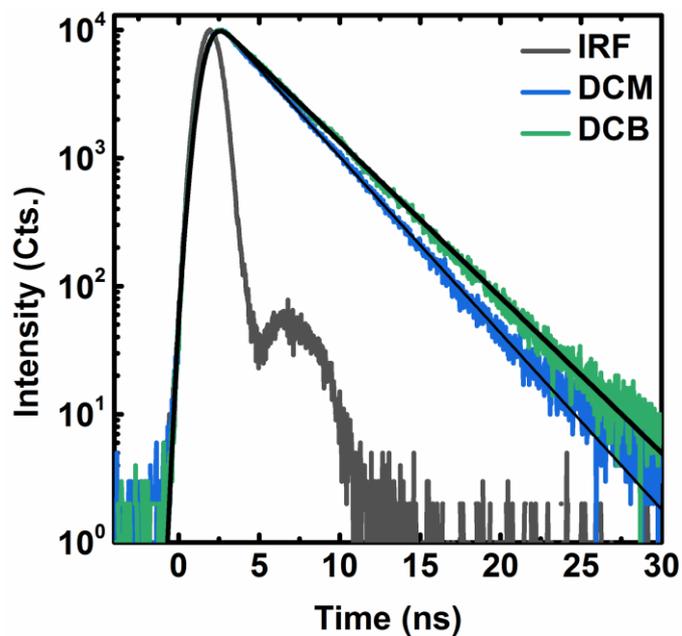


Figure S19. Emission decays of **8** in DCB and DCM. The emission lifetime of **8** in ACN is below IRF (grey curve, 1.5 ns), and thus the emission decays could not be recorded.

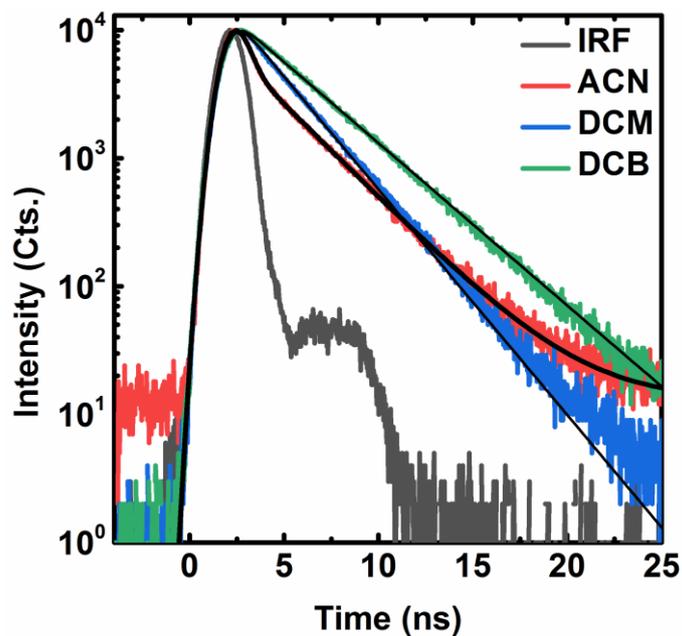


Figure S20. Emission decays of **10** in DCB, DCM and ACN.

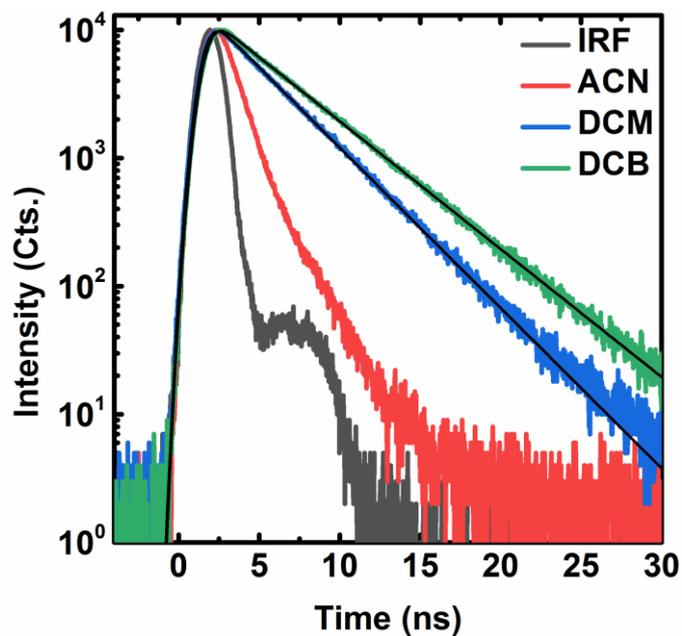


Figure S21. Emission decays of **13** in DCB, DCM and ACN.

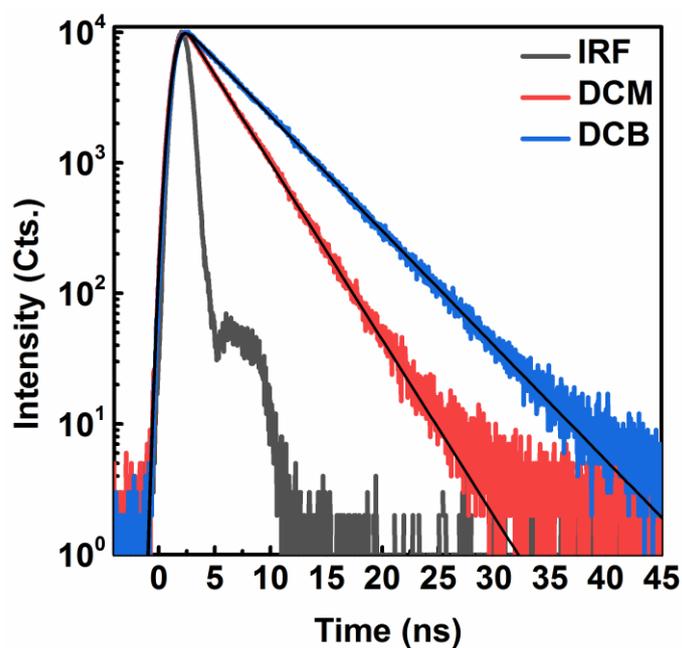


Figure S22. Emission decays of **14** in DCB and DCM. The emission lifetime of **14** in ACN is below IRF (grey curve, 1.5 ns), and thus the emission decay could not be recorded.

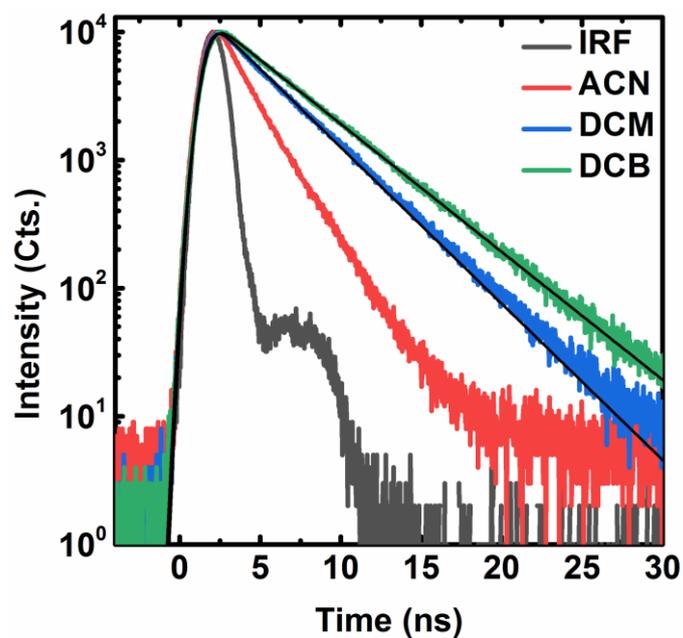


Figure S23. Emission decays of **15** in DCB, DCM and ACN.

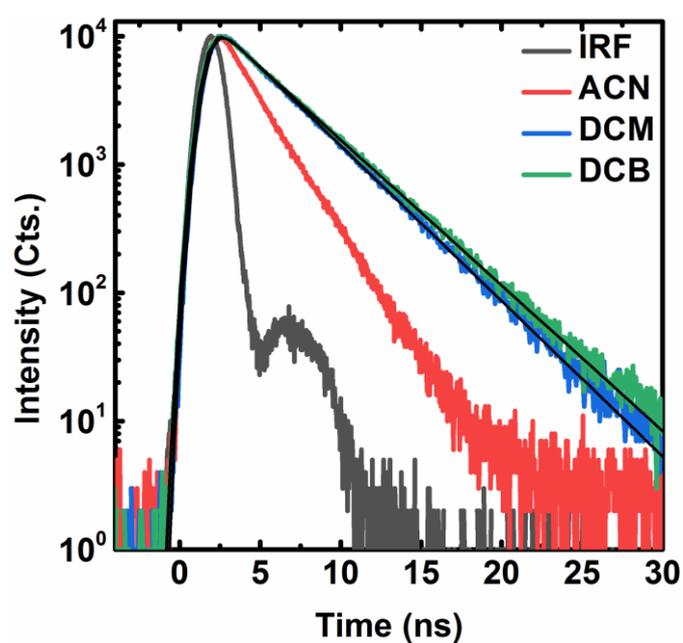


Figure S24. Emission decays of **16** DCB, DCM and ACN.

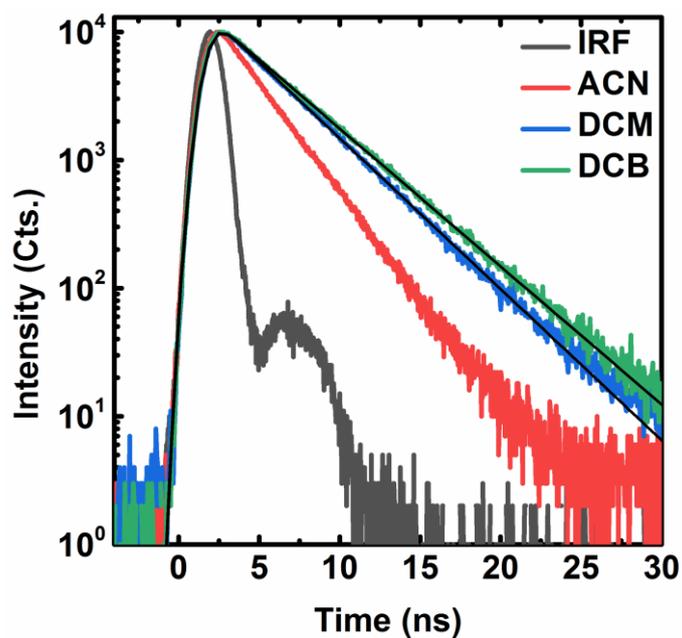


Figure S25. Emission decays of **17** in DCB, DCM and ACN.

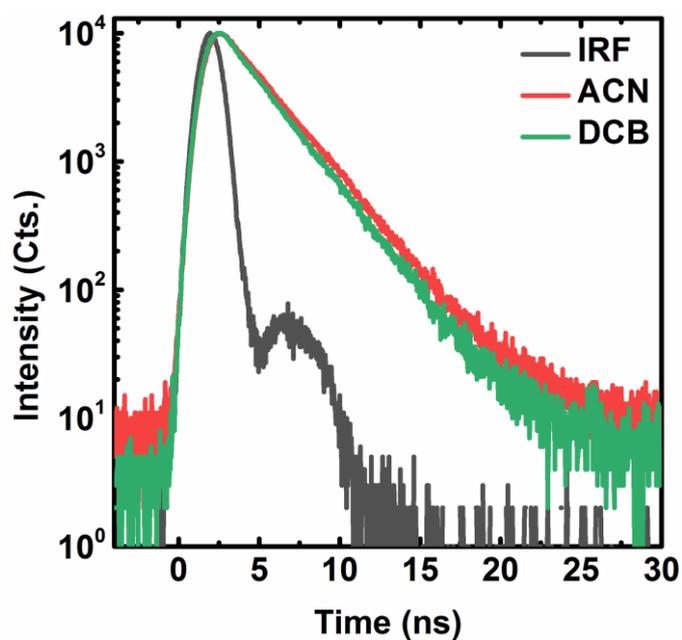


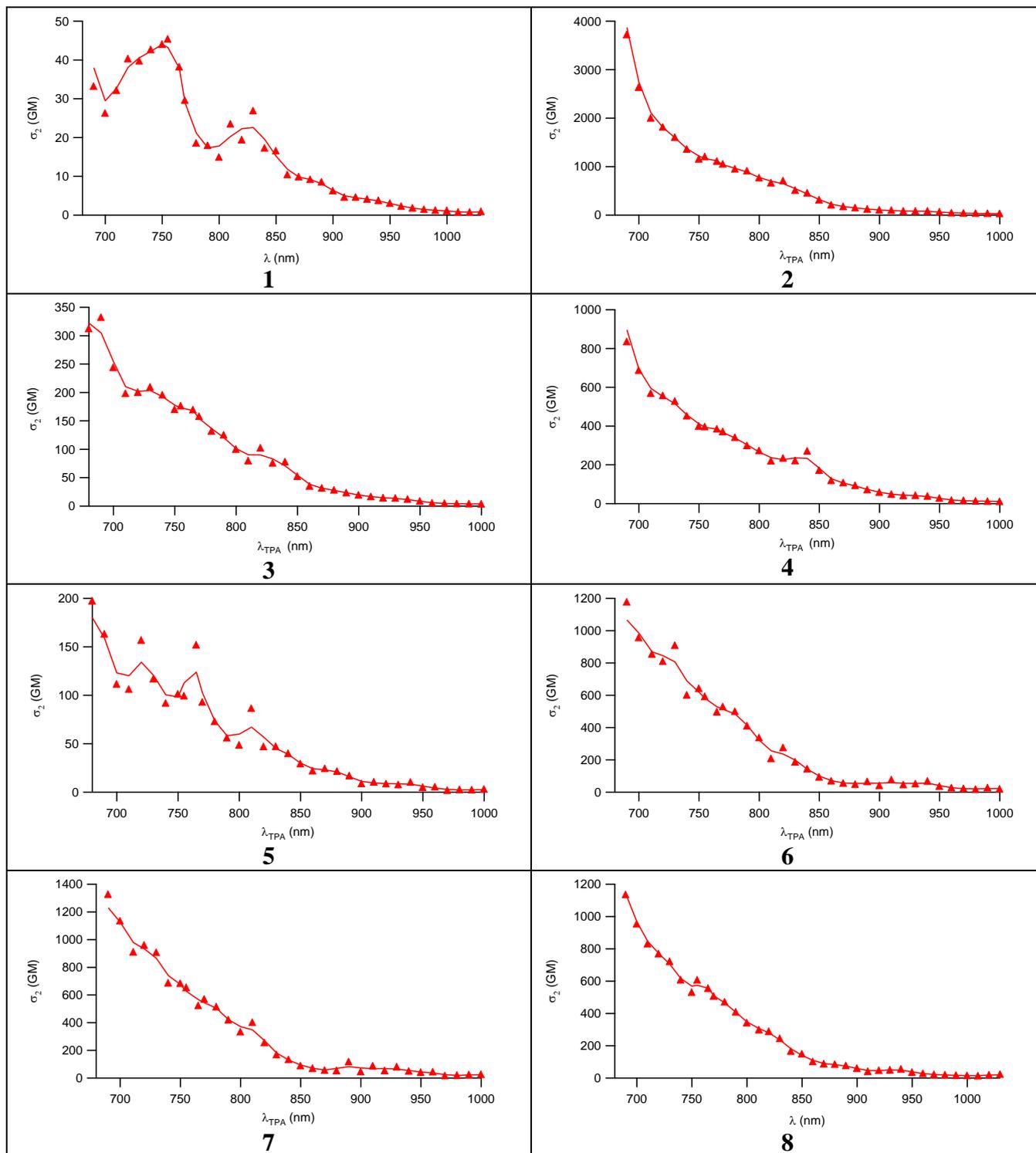
Figure S26. Emission decays of **18** in DCB and ACN. The emission lifetime of **18** in DCM is below IRF (grey curve, 1.5 ns), and thus the emission decays could not be recorded.

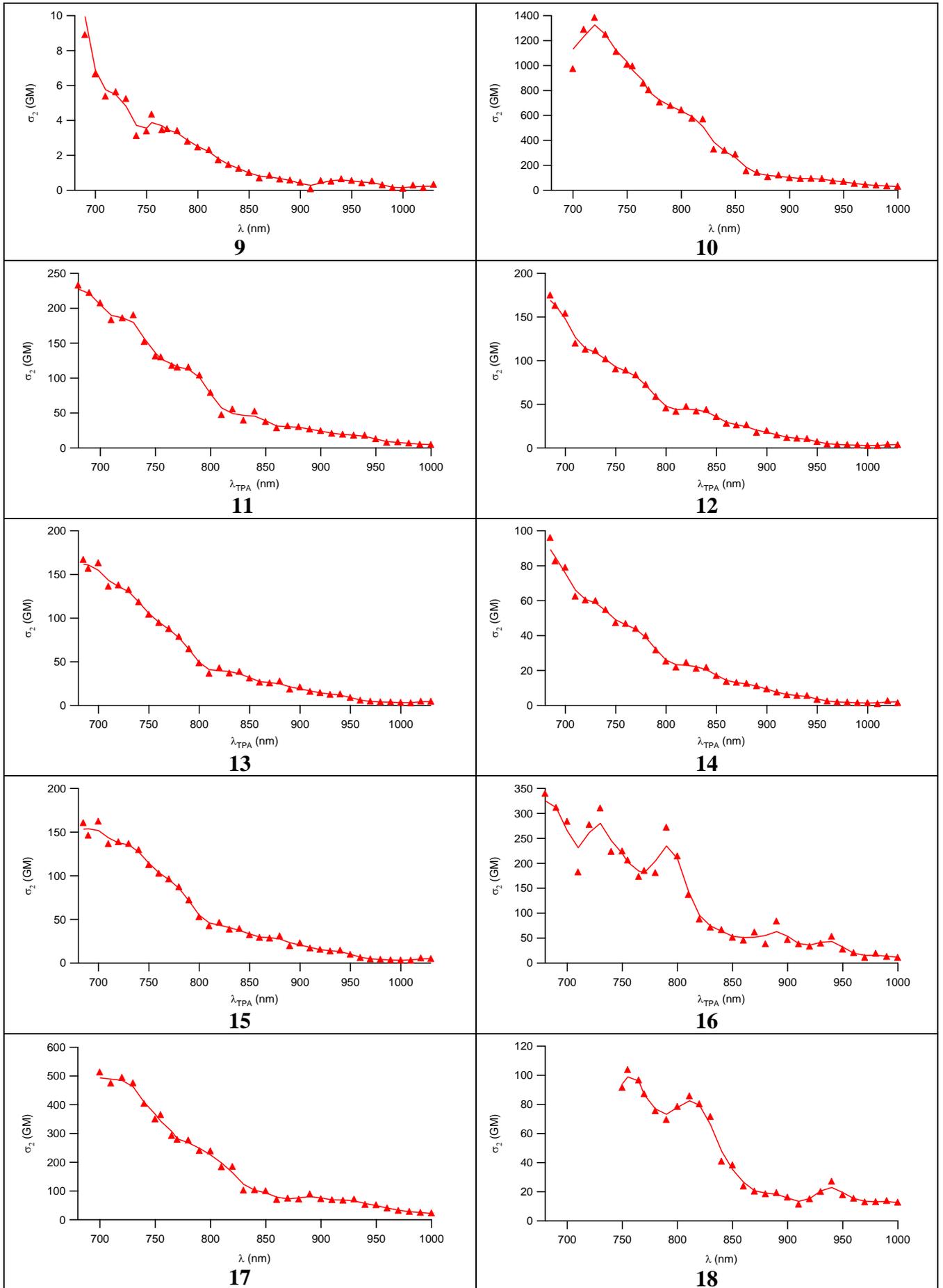
3. Two-photon absorption measurements

Table S2. Two-photon absorption data of compounds **1-18** in DCM.

Compound	λ_{2PA} / nm	σ_2 / GM
1	830	27
	750	44
2	<690	>3718
3	820	102
	730	209
	<680	312
4	840	270
	<690	>835
5	810	86
	765	152
	720	157
	<680	>197
6	730	908
	<690	>1177
7	810	401
	<690	>1326
8	<690	>1134
9	755	4.3
	720	5.6
	<690	>9
10	720	1384
11	770	115
	720	186
	<680	>233
12	820	47
	<685	>175
13	820	43
	<685	>167
14	820	25
	<685	>96
15	820	46
	<685	\geq 161
16	940	53
	890	84
	790	272
	730	310
	<680	>340
17	890	89
	<700	\geq 513
18	940	27
	810	86
	755	104

Table S3. Two-photon absorption spectra of compounds **1-18** in DCM.





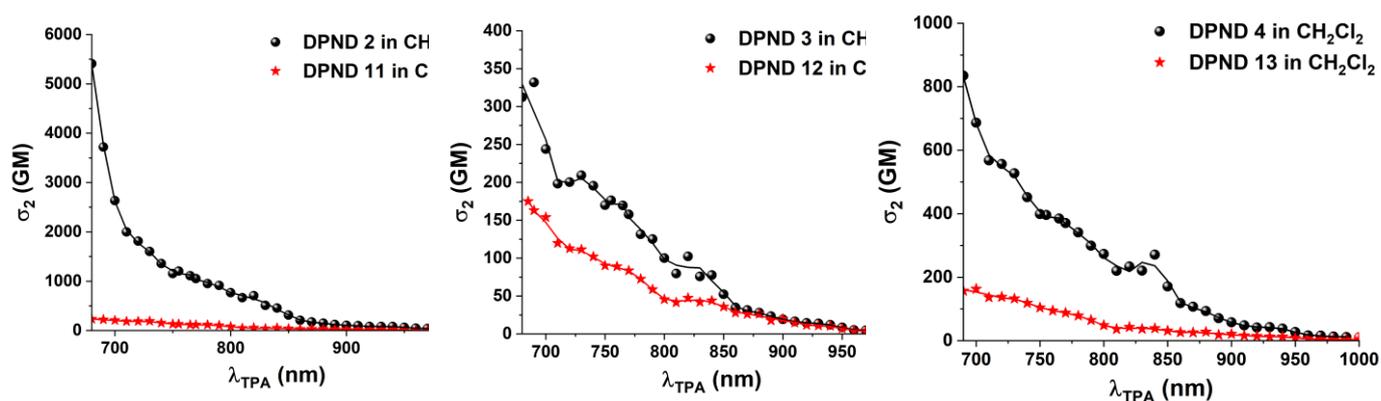


Figure S27. Effect of the position of the NO₂ group (*ortho* vs. *para* derivatives) on 2PA.

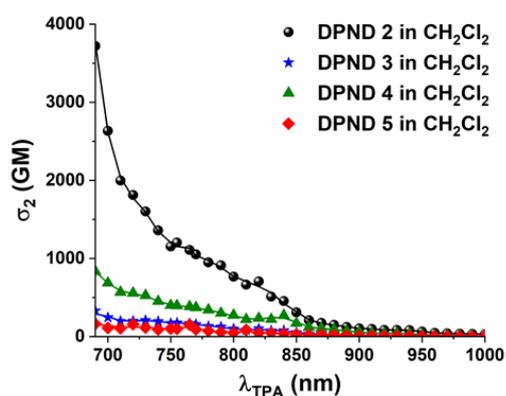


Figure S28. Influence of the presence of an additional substituent in *meta* position with respect to the *para* NO₂ group on 2PA.

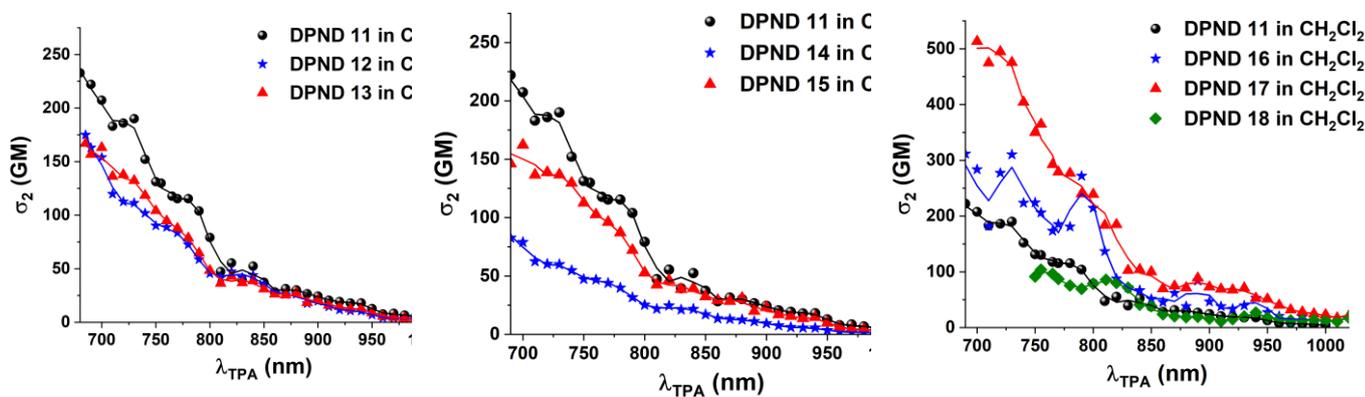
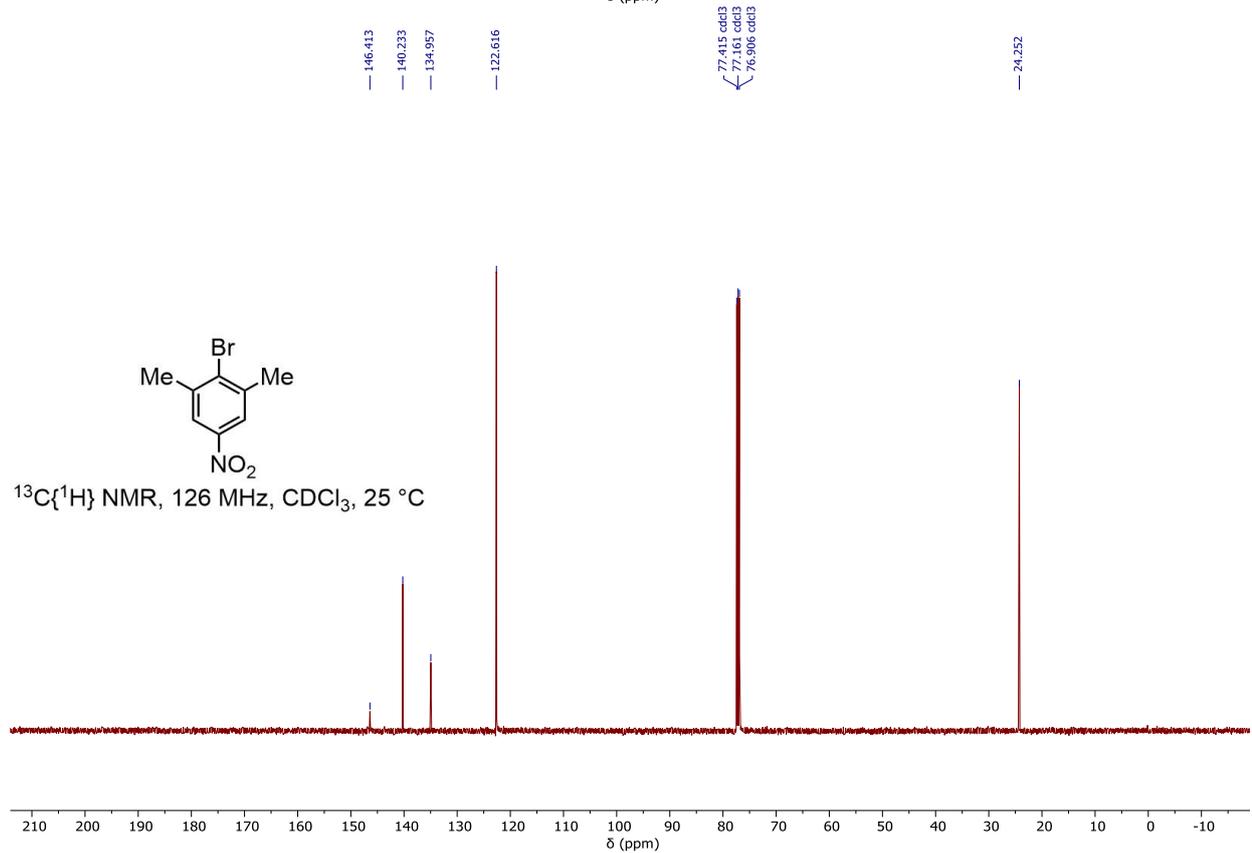
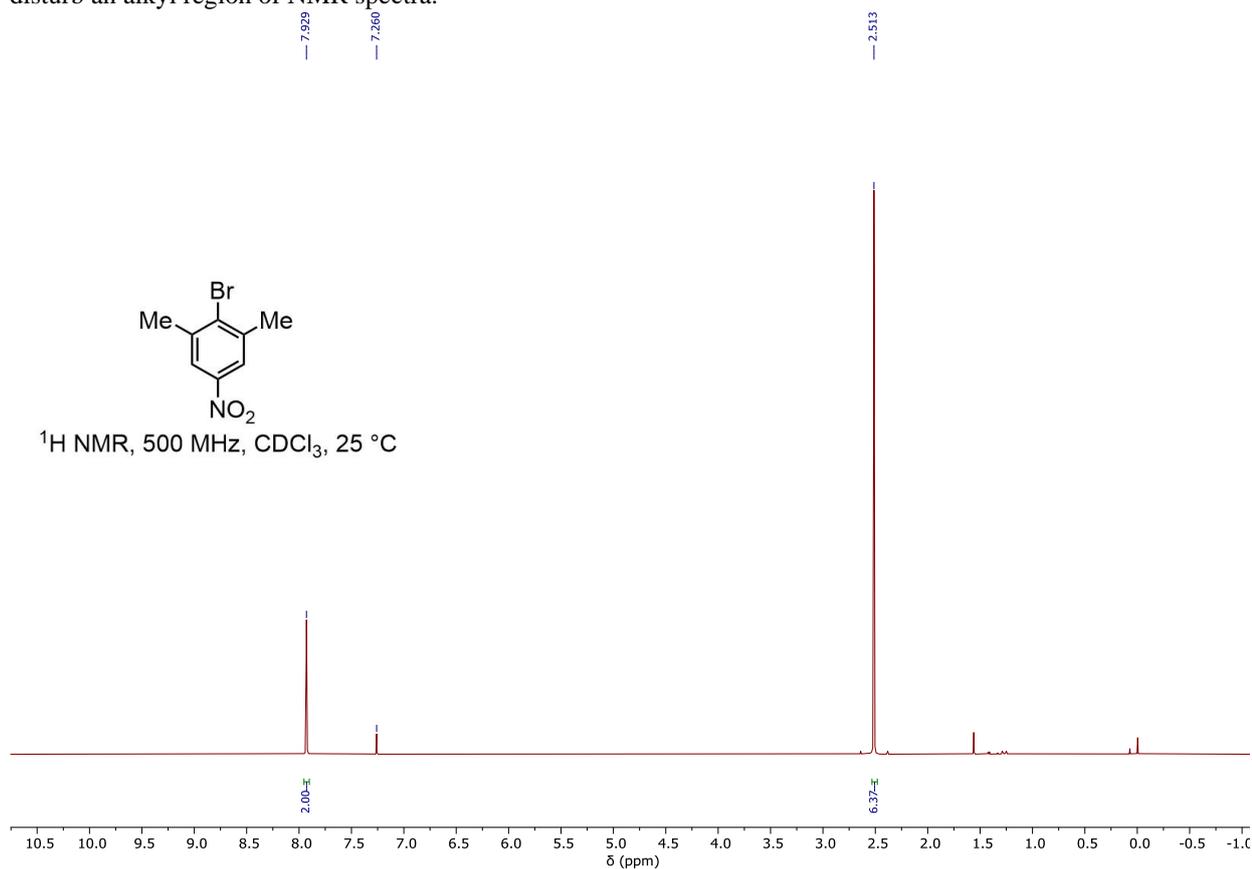
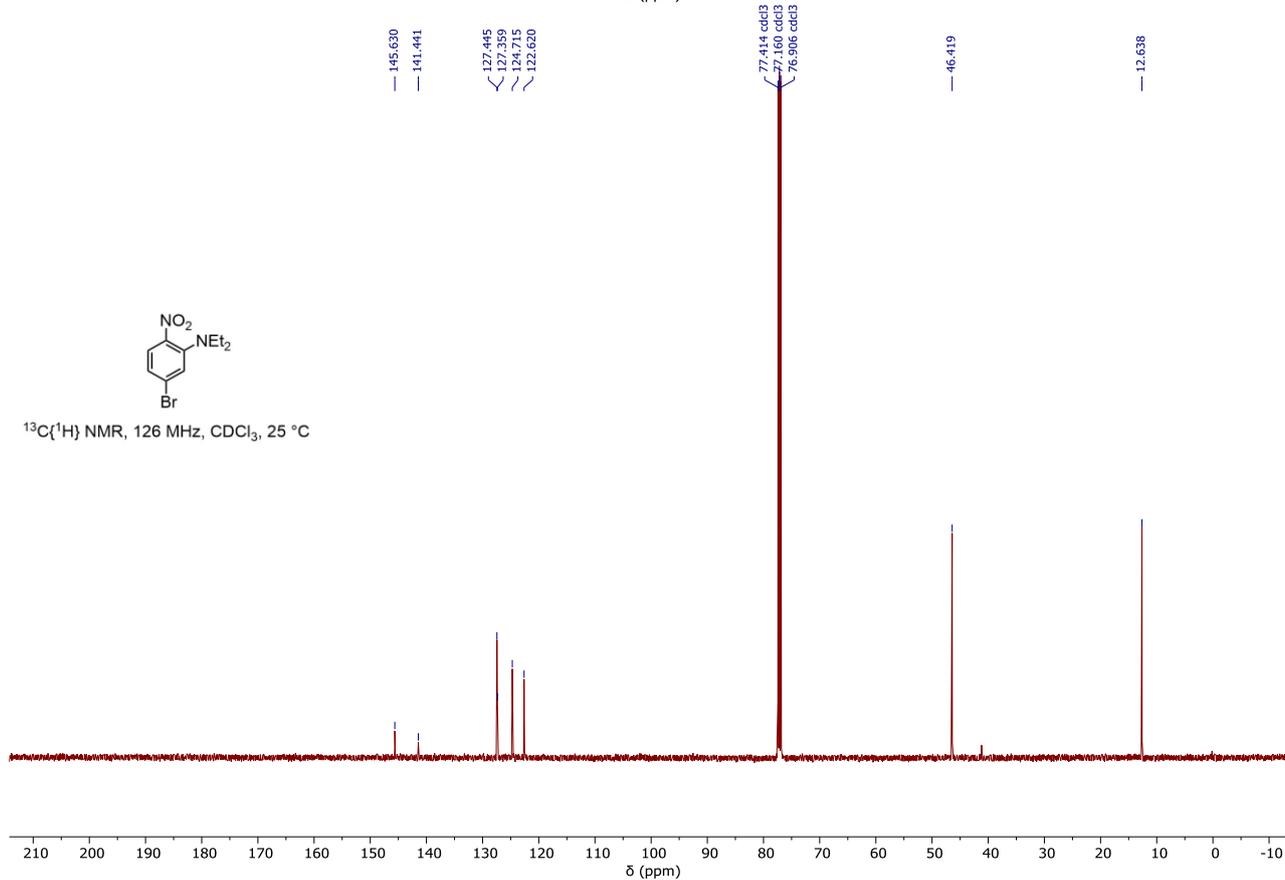
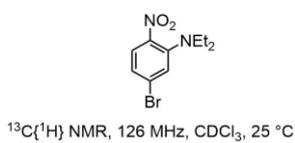
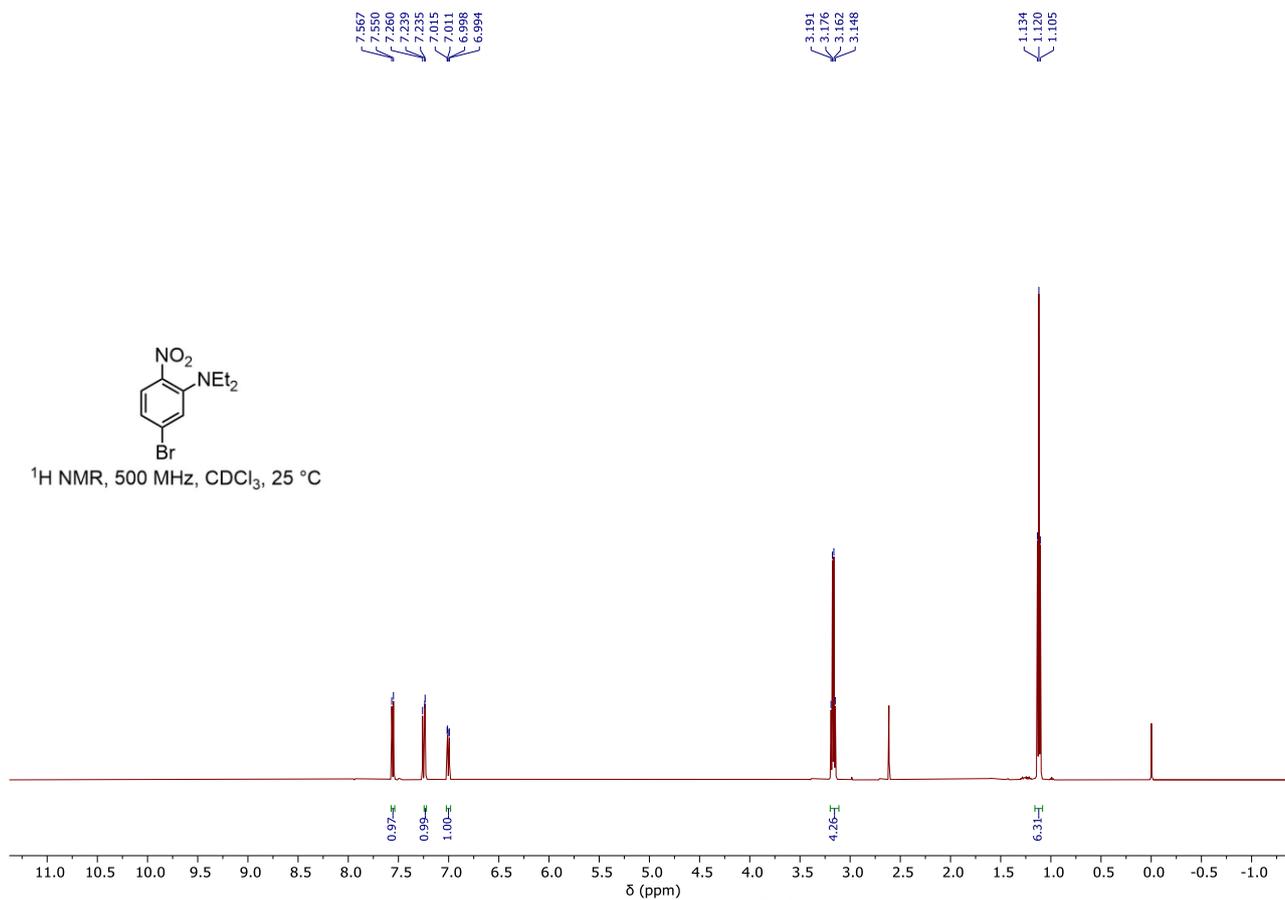
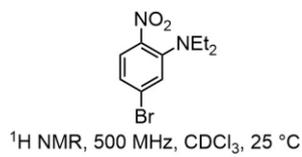


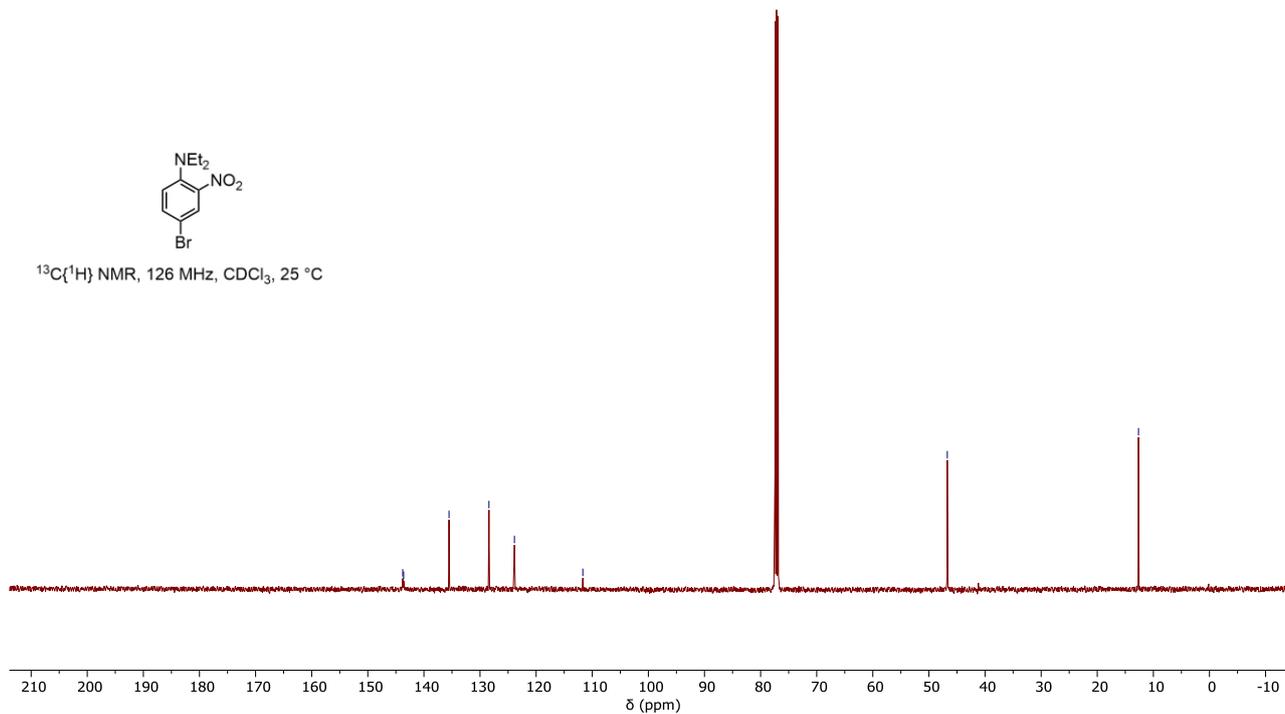
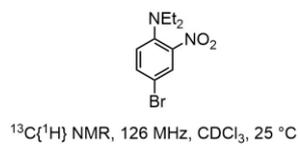
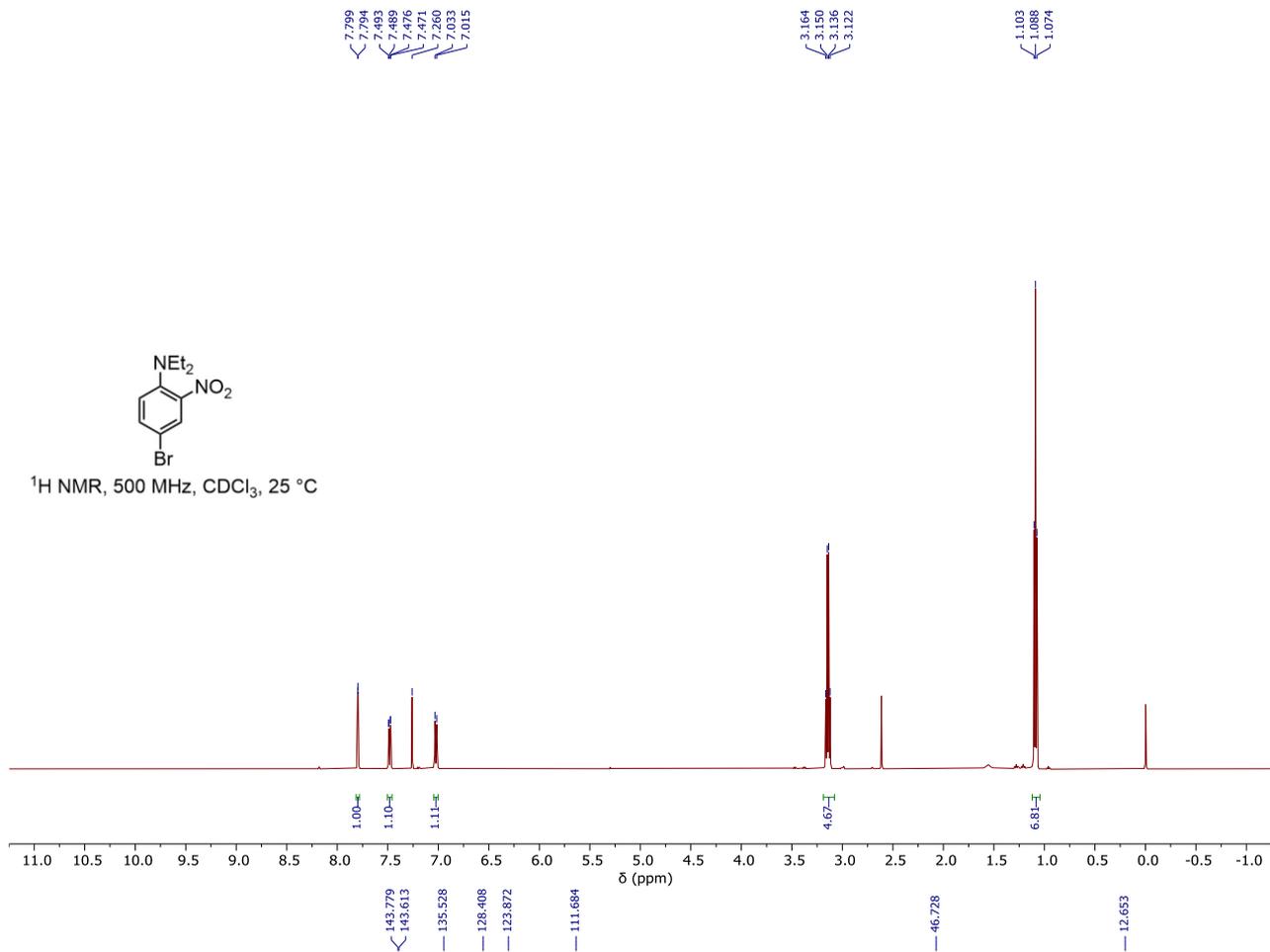
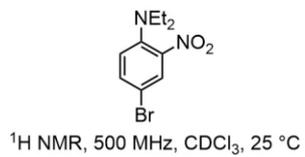
Figure S29. Influence of the presence of an additional substituent in *ortho*, *para* or *ortho'* position for *meta* NO₂ derivatives on 2PA.

4. ^1H and ^{13}C NMR spectra of new compounds.

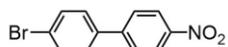
Note: despite the fact that the samples were dried overnight under high vacuum at 70 °C there are traces of solvents that disturb an alkyl region of NMR spectra.



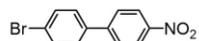
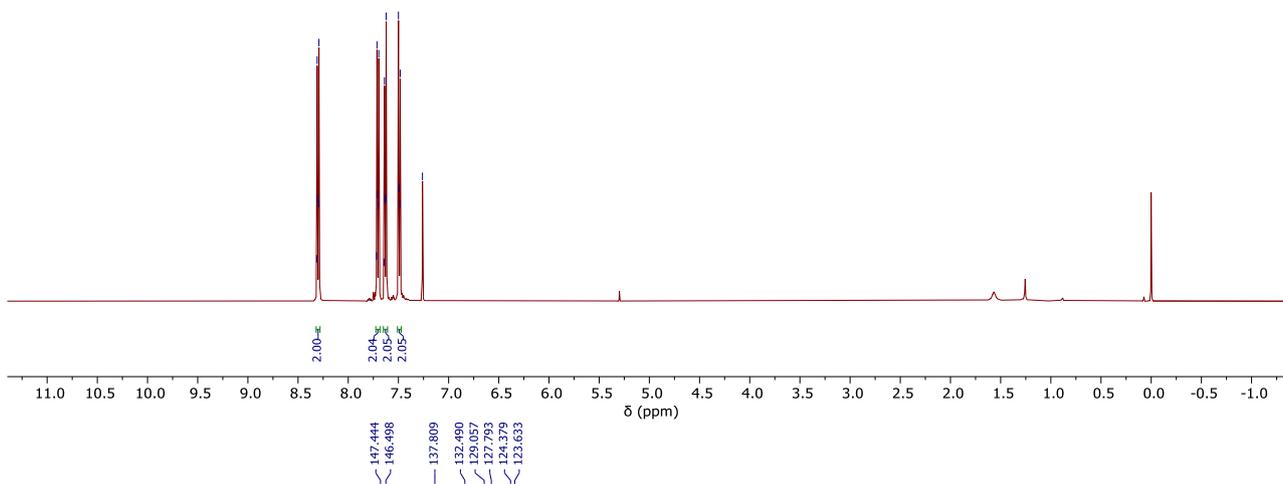




8.314
8.310
8.306
8.296
8.292
7.719
7.714
7.710
7.706
7.698
7.694
7.639
7.635
7.626
7.622
7.500
7.496
7.482
7.260



^1H NMR, 500 MHz, CDCl_3 , 25 °C



$^{13}\text{C}\{^1\text{H}\}$ NMR, 126 MHz, CDCl_3 , 25 °C

