Electronic Supplementary Information

Ultrafast Intramolecular Charge Separation in Tetrapyrazinoporphyrazines Controls the Quantum Yields of Fluorescence and Singlet Oxygen

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1. Content

2. Synthesis

General: All organic solvents used for the synthesis were of analytical grade. Anhydrous butanol was stored over magnesium and distilled prior to use. 1,3-Diphenylisobenzofuran (DPBF) for singlet oxygen studies was purchased from Aldrich, anhydrous DMF for synthesis from Across, other organics from Lachema (Czech Republic). Zinc phthalocyanine (ZnPc) was purchased from Eastman Organic Chemicals (New York, USA). Trifluoroacetic acid (TFA) was purchased from Fluka. All these chemicals were used as received without further purification except for zinc acetate (Lachema, Czech Republic) that was dried in a drying gun at 78 °C and under a pressure of 13 mbar for 8 h. TLC was performed on Merck aluminium sheets with silica gel 60 F254. Merck Kieselgel 60 (0.040-0.063 mm) was used for column chromatography. Melting points were measured on an Electrothermal IA9200 Series Digital Melting point Apparatus (Electrothermal Engineeering Ltd., Southend-on-Sea, Essex, Great Britain). Infrared spectra were measured in KBr pellets on a Nicolet Impact 400 IR-Spectrometer. 1H and 13C NMR spectra were recorded on a Varian Mercury – Vx BB 300 instrument (299.95 MHz – 1H and 75.43 MHz – 13C). Chemical shifts reported are given relative to internal $Si(CH_3)_4$. The elementary analysis was carried out on an Automatic Microanalyser EA1110CE (Fisons Instruments S.p.A., Milano, Italy). MALDI-TOF mass spectra were recorded in a negative reflectron mode on a Voyager-DE STR mass spectrometer (Applied Biosystems, Framingham, MA, USA). The instrument was calibrated externally with a five-point calibration using Peptide Calibration Mix1 (LaserBio Labs, Sophia-Antipolis, France). For each sample, 0.5 µl of the mixture was spotted onto the target plate, air-dried and covered with 0.5 µl of a matrix solution consisting of 10 mg of α-cyano-4-hydroxycinnamic acid in 100 µl of 50% ACN.

Compounds **1**[1], **3**[2] and **4**[3] have been prepared according to literature. Compounds **5H** and **11H** were isolated from the reaction mixtures and showed characteristics (R_f values, NMR, UV-vis, IR spectra) identical with the same compounds prepared in our laboratory earlier.[2, 4] Compounds **5Zn**[2] and **11Zn**[4] have been also described before. Therefore, they are not characterized completely, but only some new characteristics are added.

Synthesis of the precursors

5-Diethylamino-6-(*tert*-butylsulfanyl)-pyrazine-2,3-dicarbonitrile (2): 2-methyl-2-propanethiol (550 mg, 6.1 mmol) was stirred for 30 min at room temperature in 1M water solution of NaOH (6.11 mL). Then **1** (1.195 g, 5.09 mmol) in THF (15 mL) was added and stirring continued at room temperature for next 30 min. The solvents were evaporated under reduced pressure and residual water was eliminated by azeotropic distillation with toluene. The product was dissolved in chloroform and undissolved NaCl was filtered out. Crude **2** was purified by flash chromatography with chloroform as an eluent to give yellow solid **2** (1.121 g, 76 %); mp 94-95 °C (Found: C, 57.99; H, 6.86; N, 24.31. Calc. for $C_{14}H_{19}N_5S$: C, 58.10; H, 6,62; N, 24.20%); ν_{max}(KBr)/cm^{-1} 2991, 2967, 2938, 2873, 2361, 2344, 2234 (CN), 2224, 1537, 1503, 1466, 1445, 1436, 1375 and 1359; δ_H(300 MHz; $CDCl_3$; Me_4Si) 3.61 (4 H, q, *J* 7.0, $CH_3C\mathit{H}_2$), 1.58 (9 H, s, CH_3-C), 1.26 (6 H, t, *J* 7.0, $C\mathit{H}_3CH_2$); δ_C(75 MHz, $CDCl_3$, Me_4Si) 151.78, 149.46, 125.36, 118.14, 114.19, 114.63, 51.66, 44.55, 29.90 and 13.09.

General procedure for synthesis of metal-free TPyzPz

Magnesium (3.36 g, 140 mmol) and a small crystal of iodine were refluxed for 4 h in anhydrous butanol (200 mL). Compound **4** (2.72 g, 10 mmol) was added all at once. Compound **3** (3.06 g, 10 mmol) was divided into four parts and added subsequently always after 30 minutes. After the whole amount of **3** was in the reaction, reflux continued for next 3 hours. The mixture was left to cool down and poured into water/ethanol/acetic acid 5:5:1 (600 mL) and stirred for 45 minutes at room temperature. The dark solid was collected and washed thoroughly with hot water and then slightly with methanol.

The product (mixture of **5Mg, 7Mg-11Mg**, 5.7 g) was then purified by column chromatography on silica with chloroform/ethyl acetate 10:1 as a mobile phase. After elimination of impurities the mobile phase was changed to chloroform/ethyl acetate 1:1 to wash out **5Mg, 7Mg-11Mg** from the silica. The mixture of **5Mg, 7Mg-11Mg** (4.7 g) was dissolved in chloroform and stirred for 2.5 h at room temperature with trifluorocacetic acid (5.57 mL, 75 mmol). The solvent was evaporated and the solid was washed with 1% $NaHCO_3$ and then with water. The product was dried thoroughly.

The desired congeners of TPyzPz were separated by column chromatography on silica using a step gradient starting from chloroform/toluene/ethyl acetate 7:7:1 as a first eluent. After the elution of **9H** the eluent was changed to more polar chloroform/ethyl acetate 13:1 and after **10H** was eluted to chloroform/ethyl acetate 5:1. Each obtained solid congener was then washed by methanol and purified separately again with the use of column chromatography. The used mobile phases are mentioned below.

Compound 5H: Crude product isolated from a reaction mixture was repurified by column chromatography on silica with chloroform/toluene 1:1 as an eluent to obtain green solid (0.51 g, 8 %) corresponding to compound prepared in our laboratory before. *m/z* (MALDI-TOF) 1227.36 $[M+H]^+$, 1171.30 $[M-C_4H_8+H]^+$, 1115.24 $[M-2\times C_4H_8+H]^+$, 1059.18 $[M-3\times C_4H_8+H]^+$, 1003.12 $[M-4\times C_4H_8+H]^+$, 947.07 $[M-5\times C_4H_8+H]^+$, 890.99 $[M-6\times C_4H_8+H]^+$, 834.93 $[M-7\times C_4H_8+H]^+$, 778.87 $[M-8\times C_4H_8+H]^+$.

Compound 7H: Preparation of this compound was carried out according to the general procedure described above. The crude compound was then purified by column chromatography with the use of chloroform/toluene/ethyl acetate 7:7:1 as an eluent to obtain dark green solid (0.90 g, 15 %); (Found: C, 56.41; H, 6.69; N, 20.67. Calc. for $C_{56}H_{76}N_{18}S_6$: C, 56.35; H, 6.42; N, 21.12%); λ_{max}(THF)/nm 671 (ε/dm^3 mol^{-1} cm^{-1} 104100), 649 (110200), 574 (39300), 470 (41500) and 367 (124000); ν_{max}(KBr)/cm^{-1} 3432, 3305, 2962, 2919, 1522, 1423, 1363, 1279, 1249 and 1142; δ_H(300 MHz, [D$_5$]-pyridine, Me$_4$Si) 4.10 (8 H, q, *J* 6.8, N-CH$_2$), 2.27 (18 H, s, CH$_3$-C), 2.25 (18 H, s, CH$_3$-C), 2.24 (18 H, s, CH$_3$-C), 1.48 (12 H, t, *J* 6.8 Hz, C*H*$_3$CH$_2$); δ_C(75 MHz, [D$_5$]-pyridine, Me$_4$Si) 158.06, 146.13, 145.79, 139.28, 129.40, 128.65, 125.75, 51.94, 51.33, 44.21, 30.86, 30.74, 30.57 and 13.40; *m/z* (MALDI-TOF) 1193.41 [M+H]$^+$, 1137.35 [M-C$_4$H$_8$+H]$^+$, 1081.29 [M-2×C$_4$H$_8$+H]$^+$, 1025.23 [M-3×C$_4$H$_8$+H]$^+$, 969.17 [M-4×C$_4$H$_8$+H]$^+$, 913.11 [M-5×C$_4$H$_8$+H]$^+$, 857.06 [M-6×C$_4$H$_8$+H]$^+$.

Compound 8H: This compound was obtained in good purity from the mixtures of congeners by the general procedure described above and did not need any further purification by column chromatography. Yield 0.26 g (5 %) of blue solid (Found: C, 57.80; H, 6.79; N, 24.00. Calc. for $C_{56}H_{78}N_{20}S_4$: C, 58.00; H, 6.78; N, 24.16%); λ_{max}(THF)/nm 657 (ε/dm^3 mol^{-1} cm^{-1} 126200), 541 (71900) and 369 (126400); ν_{max}(KBr)/cm^{-1} 3447, 3312, 2963, 2929, 2872, 1637, 1522, 1422, 1362, 1276, 1249 and 1155; δ_H(300 MHz, [D$_5$]-pyridine, Me$_4$Si) 4.01 (16 H, q, *J* 4.5, N-CH$_2$), 2.24 (36 H, s, CH$_3$-C), 1.36 (24 H, t, *J* 6.0, C*H*$_3$CH$_2$); δ_C(75 MHz, [D$_5$]-pyridine, Me$_4$Si) 158.33, 154.95, 146.47, 139.89, 138.52, 131.06, 51.14, 44.07, 30.84 and 13.3; *m/z* (MALDI-TOF) 1159.46 [M-H]$^+$, 1103.41 [M-C$_4$H$_8$+H]$^+$, 1047.35 [M-2×C$_4$H$_8$+H]$^+$, 991.30 [M-3×C$_4$H$_8$+H]$^+$, 935.24 [M-4×C$_4$H$_8$+H]$^+$.

Compound 9H: The crude compound was purified by column chromatography with the use of chloroform/toluene/ethyl acetate 7:4:1 as an eluent yielding dark green solid **9H** (0.57 g, 10 %); (Found: C, 58.83; H, 7.05; N, 23.18. Calc. for $C_{56}H_{78}N_{20}S_4$: C, 58.00; H, 6.78; N, 24.16%); λ_{max}(THF)/nm 677 (ε/dm^3 mol^{-1} cm^{-1} 96200), 647 (76700), 465 (38700), 367 (112200) and 545 (39700); ν_{max}(KBr)/cm^{-1} 3447, 3301, 2963, 2927, 2871, 1637, 1522, 1423, 1362, 1342, 1280, 1251, 1158 and 1140; δ_H(300 MHz, [D$_5$]-pyridine, Me$_4$Si) 4.03 (8 H, q, *J* 6.9, N-CH$_2$), 3.89 (8 H, q, *J* 7.0, N-CH$_2$), 2.27 (18 H, s, CH$_3$-C), 2.23 (18 H, s, CH$_3$-C), 1.40 (12 H, t, *J* 7.0, C*H*$_3$CH$_2$), 1,21 (12 H, t, *J*

7.0, C*H*$_3$CH$_2$); δ_C(75 MHz, [D$_5$]-pyridine, Me$_4$Si) 159.96, 158.95, 150.53, 150.46, 143.10, 142.66, 142.11, 141.04, 51.52, 44.10, 42.98, 30.72, 30.64, 29.99, 13.46 and 13.0; *m/z* (MALDI-TOF) 1159.48 $[M+H]^+$, 1181.46 $[M+Na]^+$, 1197.43 $[M+K]^+$, 1103.42 $[M-C_4H_8+H]^+$, 1047.36 $[M-2\times C_4H_8+H]^+$, 991.31 $[M-3\times C_4H_8+H]^+$, 935.24 $[M-4\times C_4H_8+H]^+$.

Compound 10H: The crude compound was purified by column chromatography with the use of chloroform/toluene/ethyl acetate/acetone 40:10:3:2 as an eluent to obtain purple solid **10H** (0.38 g, 7 %) (Found: C, 58.81; H, 7.19; N, 26.92. Calc. for $C_{56}H_{80}N_{22}S_2$ + 1H$_2$0: C, 58.82; H, 7.23; N, 26.95%); λ_{max}(THF)/nm 67 (ε/dm^3 mol^{-1} cm^{-1} 94100), 653 (87900), 528 (63600) and 368 (118300); ν_{max}(KBr)/cm^{-1} 3447, 3309, 2965, 2930, 2871, 1637, 1477, 1423, 1376, 1341, 1280, 1250, 1159 and 1140; δ_H(300 MHz, [D$_5$]-pyridine, Me$_4$Si) 4.01 (8H, q, *J* 6.9, N-CH$_2$), 3.95 – 3.79 (16 H, m, N-CH$_2$), 2.22 (18 H, s, CH$_3$-C), 1.38 (12 H, t, *J* 7.0, C*H*$_3$CH$_2$), 1.26 – 1.11 (24 H, m, C*H*$_3$CH$_2$); δ_C(75 MHz, [D$_5$]-pyridine, Me$_4$Si) 158.16, 156.22, 152.41, 150.83, 150.77, 145.63, 143.86, 141.52, 140.17, 139.53, 138.32, 51.09, 44.15, 42.98, 30.83, 13.41, 13.15 and 13.00; *m/z* (MALDI-TOF) 1125.57 $[M+H]^+$, 1147.55 $[M+Na]^+$, 1163.52 $[M+K]^+$, 1069.52 $[M-C_4H_8+H]^+$, 1013.45 $[M-2\times C_4H_8+H]^+$.

Compound 11H: The crude compound was purified by column chromatography with chloroform/acetone 1:1 as an eluent to obtain violet solid (0.31 g, 6 %) corresponding to compound prepared in our laboratory before.[4] λ_{max}(THF)/nm 680 (ε/dm^3 mol^{-1} cm^{-1} 103100), 650 (75700), 515 (67500) and 367 (115600). *m/z* (MALDI-TOF) 1091.65 $[M+H]^+$, 1113.62 $[M+Na]^+$, 1129.59 $[M+K]^+$, 1063.64 $[M-C_2H_4+H]^+$.

Compound 6H: The preparation of this compound was carried out similarly to the general procedure described above. In this case, compound **2** (0.5 g, 1.7 mmol) reacted with compound **3** (1.6 g, 5.2 mmol). A crude mixture of magnesium complexes was not purified but directly treated with trifluorocacetic acid. Desired **6H** was then separated by column chromatography with chloroform/toluene/ethyl acetate 7:7:1 as an eluent to obtain green solid (0.44 g, 21 %); (Found: C, 55.75; H, 6.33; N, 18.81. Calc. for $C_{56}H_{75}N_{17}S_7$: C, 55.55; H, 6.24; N, 19.67%); ν_{max}(KBr)/cm^{-1} 3448, 3302, 2961, 2919, 2862, 1521, 1458, 1452, 1404, 1363, 1314, 1278, 1246, 1232, 1194 and 1141; δ_H(300 MHz, [D$_5$]-pyridine, Me_4Si) 4.11 (4 H, q, *J* 6.2, N-CH_2), 2.27 (45 H, s, C-CH_3), 2.24 (9 H, s, C-CH_3), 2.22 (9 H, s, C-CH_3), 1.76 (6 H, t, *J* 6.8, C*H*$_2$$CH_3$); δ_C(75 MHz, [D$_5$]-pyridine, Me_4Si) 51.42, 30.84, 29.99 and 13.62 (aromatic signals not detected); *m/z* (MALDI-TOF) 1210.37 [M+H]$^+$, 1154.31 [M-C_4H_8+H]$^+$, 1098.25 [M-2×C_4H_8+H]$^+$, 1042.19 [M-3×C_4H_8+H]$^+$, 986.13 [M-4×C_4H_8+H]$^+$, 930.07 [M-5×C_4H_8+H]$^+$, 874.01 [M-6×C_4H_8+H]$^+$, 818.00 [M-7×C_4H_8+H]$^+$.

General procedure for synthesis of Zinc TPyzPz

A solution of appropriate metal-free dye (**5H-11H**) (0.1 mmol) and dry zinc(II) acetate (128 mg, 0.70 mmol) in dimethylformamide (DMF)/toluene 1:1 was heated at 160 °C for 2 hours. The excess of toluene was evaporated. Water (10 ml) was added to a fine green suspension in the rest of DMF, and the product was filtered and washed thoroughly with water and methanol. Crude zinc TPyzPz was sorbed to a small amount of silica (1.5 g) and washed with methanol on a glass frit. The product on silica was then dried up, poured on a silica column and purified by chromatography. The mixtures of chloroform/ethyl acetate in different ratios were used as eluents according to lipophilicity of the congeners. The eluents for each compound are described below. Solvents were then evaporated and pure zinc TPyzPz were washed with methanol and put into a drying pistol to remove residual solvents.

Compound 5Zn: λ_{max}(THF)/nm 650 (ε/dm^3 mol^{-1} cm^{-1} 312400), 624 (41900), 590 (41100) and 378 (154800); *m/z* (MALDI-TOF) 1289.33 [M+H]$^+$, 1311.33 [M+Na]$^+$, 1327.30 [M+K]$^+$, 1233.29 [M-C_4H_8+H]$^+$.

Compound 6Zn: Chloroform/ethyl acetate 25:1 as an eluent yielded green solid **6Zn** (0.11 g, 89 %); (Found: C, 52.00; H, 5.85; N, 18.00. Calc. for $C_{56}H_{73}N_{17}S_7Zn$ + $1H_20$: C, 52.05; H, 5.85; N, 18.43%); λ_{max}(THF)/nm 652 (ε/dm^3 mol^{-1} cm^{-1} 244800), 592 (37000) and 375 (148600); ν_{max}(KBr)/cm^{-1} 3428, 2962, 2919, 2862, 1637, 1517, 1457, 1394, 1363, 1286, 1252 and 1146; δ_H(300 MHz, [D$_5$]-pyridine, Me$_4$Si) 4,03 (4 H, q, *J* 6.9, N-CH$_2$), 2.25 (45 H, s, CH$_3$-C), 2.22 (9 H, s, CH$_3$-C), 2.19 (9 H, s, CH$_3$-C), 1.64 (6 H, t, *J* 6.8, C*H$_3$*CH$_2$); δ_C(75 MHz, [D$_5$]-pyridine, Me$_4$Si) 158.95, 158.51, 158.45, 158.39, 158.06, 156.21, 152.98, 152.82, 152.77, 151.95, 151.40, 151.31, 151.12, 150.81, 150.78, 145.43, 145.10, 145.02, 144.95, 144.79, 144.73, 142.47, 51.42, 51.38, 51.31, 50.60, 45.17, 30.94, 30.78 and 13.56; *m/z* (MALDI-TOF) 1272.30 [M+H]$^+$, 1294.27 [M+Na]$^+$, 1310.24 [M+K]$^+$, 1216.23 [M-C$_4$H$_8$+H]$^+$, 1160.17 [M-2×C$_4$H$_8$+H]$^+$, 1104.11 [M-3×C$_4$H$_8$+H]$^+$, 1048.05 [M-4×C$_4$H$_8$+H]$^+$, 991.99 [M-5×C$_4$H$_8$+H]$^+$.

Compound 7Zn: Chloroform/ethyl acetate 20:1 as an eluent yielded green solid **7Zn** (0.094 g, 79 %); (Found: C, 52.73; H, 6.02; N, 19.45. Calc. for $C_{56}H_{74}N_{18}S_6Zn$ + 1H$_2$0: C, 52.75; H, 6.01; N, 19.77%); λ_{max}(THF)/nm 654 (ε/dm^3 mol^{-1} cm^{-1} 195900), 595 (37200) and 376 (147800); ν_{max}(KBr)/cm^{-1} 3428, 2963, 2922, 1518, 1422, 1363, 1253 and 1149; δ_H(300 MHz, [D$_5$]-pyridine, Me$_4$Si) 4,00 (8 H, q, *J* 6.8, N-CH$_2$), 2.25 (18 H, s, CH$_3$-C), 2.24 (18 H, s, CH$_3$-C), 2.24 (18 H, s, CH$_3$-C), 1.36 (12 H, t, *J* 6.8, CH$_3$*CH$_2$*); δ_C(75 MHz, [D$_5$]-pyridine, Me$_4$Si) 158.90, 158.24, 157.96, 153.81, 151.58, 145.23, 144.83, 144.60, 143.09, 51.33, 51.29, 43.95, 30.78, 30.75 and 13.34; *m/z* (MALDI-TOF) 1255.35 [M+H]$^+$, 1277.34 [M+Na]$^+$, 1293.31 [M+K]$^+$, 1199.29 [M-C$_4$H$_8$+H]$^+$.

Compound 8Zn: Chloroform/ethyl acetate 15:1 as an eluent to give green blue solid **8Zn** (0.114 g, 95 %); (Found: C, 54.05; H, 6.34; N, 21.96. Calc. for $C_{56}H_{76}N_{20}S_4Zn$ + 1H$_2$0: C, 54.20; H, 6.34; N, 22.57%); λ_{max}(THF)/nm 664 (ε/dm^3 mol^{-1} cm^{-1} 165500), 648 (109500), 611 (39100) and 374 (133800); ν_{max}(KBr)/cm^{-1} 3428, 3397, 2964, 2929, 2872, 1636, 1519, 1420, 1363, 1295, 1253 and 1157; δ_H(300 MHz, [D$_5$]-pyridine, Me$_4$Si) 3.98 (16 H, q, *J* 6.8, N-CH$_2$), 2.24 (36 H, s, CH$_3$-C), 1.36 (24 H, t, *J* 6.8 Hz, C*H$_3$*CH$_2$); δ_C(75 MHz, [D$_5$]-pyridine, Me$_4$Si) 158.23, 152.50, 149.68, 145.07, 142.83, 51.15, 43.87, 30.79 and 13.3; MS (MALDI-TOF): *m/z*: 1221.42 $[M+H]^+$, 1243.39 $[M+Na]^+$, 1259.37 $[M+K]^+$, 1165.36 $[M-C_4H_8+H]^+$, 1109.29 $[M-2\times C_4H_8+H]^+$, 1053.23 $[M-3\times C_4H_8+H]^+$;

Compound 9Zn: Chloroform/ethyl acetate 13:1 as an eluent to give dark green blue solid **9 Zn** (0.112 g, 93 %); (Found: C, 53.91; H, 6.33; N, 22.23. Calc. for $C_{56}H_{76}N_{20}S_4Zn + 1H_20$: C, 54.20; H, 6.34; N, 22.57%); λ_{max}(THF)/nm 654 (ε/dm^3 mol^{-1} cm^{-1} 212700), 594 (37500) and 375 (140600); ν_{max}(KBr)/cm^{-1} 3432, 2964, 2928, 2873, 1637, 1516, 1424, 1363, 1303, 1254 and 1158; δ_H(300 MHz, [D$_5$]-pyridine, Me_4Si) 4.01 (8 H, q, *J* 6.7, N-CH$_2$), 3.87 (8 H, q, *J* 6.8, N-CH$_2$), 2.24 (18 H, s, CH$_3$-C), 2.22 (18 H, s, CH$_3$-C), 1.38 (12 H, t, *J* 6.7, C*H*$_3$CH$_2$), 1.17 (12 H, t, *J* 6.8, C*H*$_3$CH$_2$); δ_C(75 MHz, [D$_5$]-pyridine, Me_4Si) 158.60, 157.55, 154.05, 152.71, 150.04, 149.16, 144.88, 144.43, 143.63, 142.73, 51.21, 51.18, 44.02, 42.89, 30.83, 30.75, 13.46 and 13.00; *m/z* (MALDI-TOF) 1221.39 $[M+H]^+$, 1243.38 $[M+Na]^+$, 1259.36 $[M+K]^+$.

Compound 10Zn: Chloroform/ethyl acetate 10:1 as an eluent to give dark green solid **10Zn** (0.119 g, 93%); (Found: C, 55.25; H, 6.57; N, 25.57. Calc. for $C_{56}H_{78}N_{22}S_2Zn + 1H_20$: C, 55.73; H, 6.68; N, 25.53%); λ_{max}(THF)/nm 656 (ε/dm^3 mol^{-1} cm^{-1} 170900), 598 (33300), 527 (28200) and 374 (129900); ν_{max}(KBr)/cm^{-1} 3432, 2966, 2930, 2872, 1637, 1517, 1423, 1376, 1342, 1292, 1254 and 1160; δ_H(300 MHz, [D$_5$]-pyridine, Me_4Si) 4.00 (8 H, q, *J* 6.6, N-CH$_2$), 3.94 – 3.80 (16 H, m, N-CH$_2$), 2.22 (18 H, s, CH$_3$-C), 1.36 (12 H, t, *J* 6.6, C*H*$_3$CH$_2$), 1.26 – 1,10 ppm (24 H, m, C*H*$_3$CH$_2$); δ_C(75 MHz, [D$_5$]-pyridine, Me_4Si) 157.86, 152.84, 152.72, 151.35, 148.98, 144.64, 143.38, 143.22, 142.43, 51.05, 43.97, 42.96, 42.85, 30.80, 13.44, 13.12 and 12.99; *m/z* (MALDI-TOF) 1187.54 $[M+H]^+$, 1209.50 $[M+Na]^+$, 1225.48 $[M+K]^+$, 1131.46 $[M-C_4H_8+H]^+$, 1075.39 $[M-2\times C_4H_8+H]^+$.

Compound 11Zn: λ_{max}(THF)/nm 654 (ε/dm^3 mol^{-1} cm^{-1} 189700), 596 (33400), 505 (37900) and 374 (126700); *m/z* (MALDI-TOF) 1153.55 $[M+H]^+$, 1175.54 $[M+Na]^+$, 1191.51 $[M+K]^+$, 1125.53 $[M-C_2H_4+H]^+$.

3. Spectral Methods

UV-vis and steady-state fluorescence. The UV-vis spectral measurements were carried out with a UV-2401PC spectrophotometer, Shimadzu Europa GmbH (Duisburg, Germany). A slit width of the instrument was set to 0.2 nm giving the wavelength accuracy of ± 0.3 nm. The fluorescence emission was monitored using an AMINCO-Bowman Series 2 luminescence spectrometer (SLM-Aminco, Urbana, IL, USA) and Fluorolog 3 spectrometer (Horiba Jobin Yvon).

Time-resolved fluorescence. Time-resolved fluorescence measurements using a time-correlated single photon counting method were performed on a Fluorolog 3 spectrometer (Horiba Jobin Yvon). The excitation wavelength was 405 nm (laser diode NanoLED-405LH, pulse duration 750ps, repetition rate 1 MHz) and emission was recorded at the maxima of corresponding fluorescence emission spectra using a cooled TBX-05-C photon detection module. Additionally, a 590 nm cut-on filter was used to eliminate scattered light. The data were collected till the peak value reached 10000 counts. The decay curves were fitted to exponential functions using an iterative reconvolution procedure of the DAS6 software (v. 6.4, Horiba Jobin Yvon, 2009).

Electrochemistry: Electrochemical experiments were performed using an Autolab PGSTAT20 potentiostat (Eco Chemie, The Netherlands) at room temperature (22 ^{o}C). Compounds (typically 1.7×10^{-3} M) were dissolved in pyridine (Aldrich, anhydrous) containing 0.1 M tetrabutylammonium tetrafluoroborate (Aldrich) as a supporting electrolyte. The experimental setup consisted of a 3 mm glassy carbon working electrode, Pt counter electrode, and a saturated calomel reference electrode (SCE) that was separated from the bulk solution by a fritted glass bridge. Dissolved oxygen in solutions was removed by vigorous purging with N_2. All values are referenced to SCE; ferrocene used as an internal standard has a half-wave potential $E_{½}$ (Fc/Fc^+) = 0.51 V *vs.* SCE.

Femtosecond transient absorption. Femtosecond pulses were obtained from a 1 kHz femtosecond laser system (Integra-I, Quantronix). The output pulses have ~130 fs width, an average energy of ~2 mJ/pulse, and a central wavelength of 790 nm. The pulses were divided into two paths serving as excitation and probe pulses. Excitation pulses centered at 395 nm were generated by frequency doubling the primary output in a BBO crystal, while a white-light continuum obtained by focusing a fraction of the 790-nm pulses into a 0.2 cm sapphire plate was used for probing. The time delay between pump and probe pulses was introduced by a computer-controlled delay stage driven by a stepper motor with precision of 5 fs. For signal detection, the probe beam and an identical reference beam that does not overlap with the excitation beam were focused onto the entrance slit of a spectrograph, which than dispersed both beams onto a dual photodiode array detection system (ExciPro, CDP Systems). Each array contained 1024 photodiodes and allowed a spectral range of ~240 nm to be measured in each laser shot. For each delay, 300-400 spectra were averaged to improve signal/noise ratio. A 1-mm path length rotating quartz cuvette spinning at a rate ensuring that each excitation pulse hits a fresh sample was used for measurements. The mutual orientation of the excitation and probe beams was set to magic angle (54.7°).

Analysis of time resolved spectra. All kinetic traces collected by the diode-array detection system were fitted globally. This approach allows more precise determination of the time constants of the excited state processes and, more importantly, assignment of spectral profiles of the intermediate excited state species.[5] The data were fitted to a sum of exponentials, including numerical deconvolution of the FWHM of the response function, and a fourth degree polynomial describing the chirp. The fitting procedure used general linear regression for the amplitudes of the exponentials and the Nelder-Mead simplex method for the rate constants, the FWHM and the chirp polynomial. To visualize the excited state dynamics, we assume that the excited molecule evolves according to a sequential, irreversible scheme A → B, B → C, C → D… The arrows represent increasingly slower monoexponential processes and the time constants of these processes correspond to lifetimes of the species A, B, C, D… The spectral profiles of the species are called evolution-associated difference spectra (EADS), and although they do not correspond to the pure spectra of the excited-state species, they provide valuable information about the time evolution of the whole system.[5]

Singlet oxygen and fluorescence quantum yields. Quantum yields of singlet oxygen formation (Φ_Δ) were determined according to a previously published procedure[6] using the decomposition of 1,3-diphenylisobenzofuran (DPBF). Zinc phthalocyanine (ZnPc) was used as a reference ($\Phi_\Delta = 0.61$ in pyridine[7], $\Phi_\Delta = 0.58$ in toluene[7]). Absorption of the dyes in the Q-band area was set approximately to 0.1.

Fluorescence quantum yields (Φ_F) were determined by the comparative method using ZnPc as a reference ($\Phi_F = 0.20$ in pyridine[7]). Absorption of the dyes in the Q-band was always below 0.05. The fluorescence quantum yields were calculated according to the following equation:

$$\Phi_F^S = \Phi_F^R \left(\frac{F^S}{F^R} \right) \left(\frac{1-10^{-A^R}}{1-10^{-A^S}} \right) \left(\frac{n^S}{n^R} \right)^2$$

where F is the integrated area under the emission spectrum, A is absorbance at excitation wavelength (608 nm) and n is the refractive index of the solvent. Superscripts R and S correspond to the reference and sample, respectively.

4. Results

Thin layer chromatography of 5Zn, 7Zn-11Zn and 5H, 7H-11H

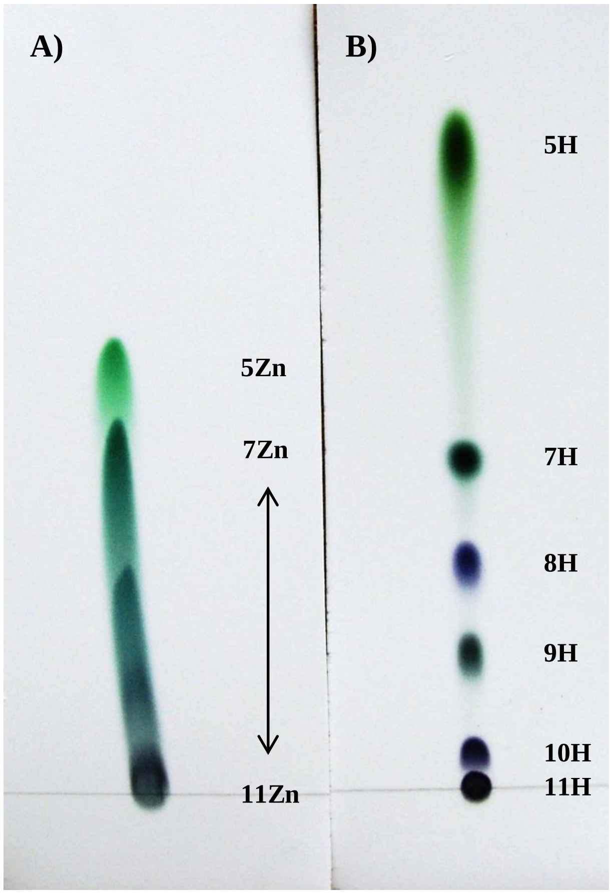

Figure S1: Comparison of the series **5Zn, 7Zn-11Zn** (A) and **5H, 7H-11H** (B). Both TLC were performed with chloroform/toluene/ethylacetate 7:7:1 as an eluent. Note the strong tailing of metal complexes.

UV-vis absorption

Figures S2-S8. Q-bands of **5Zn-11Zn** in different solvents: pyridine (red line), toluene (blue line), toluene with 1% (v/v) pyridine (green line).

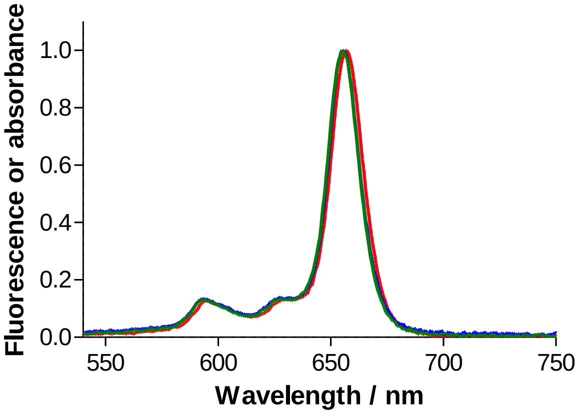

Figure S2: Compound **5Zn**

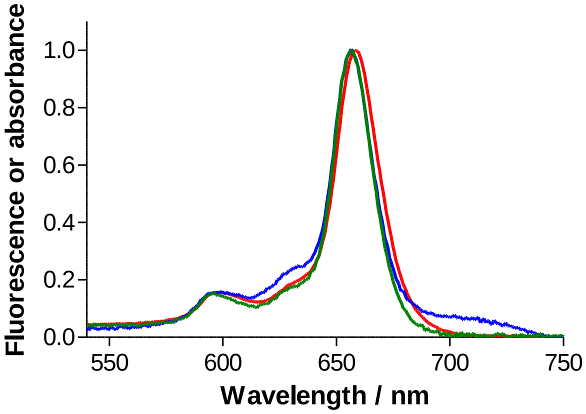

Figure S3: Compound **6Zn**

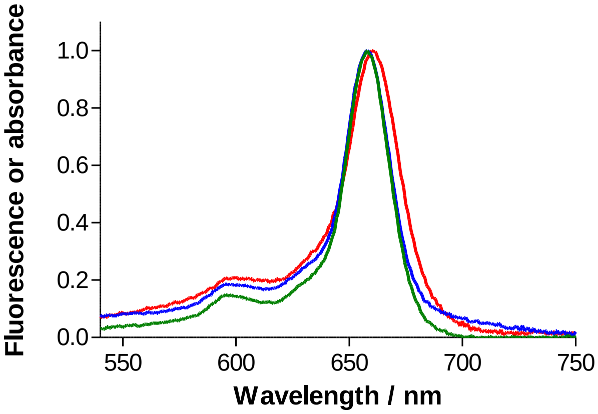

Figure S4: Compound **7Zn**

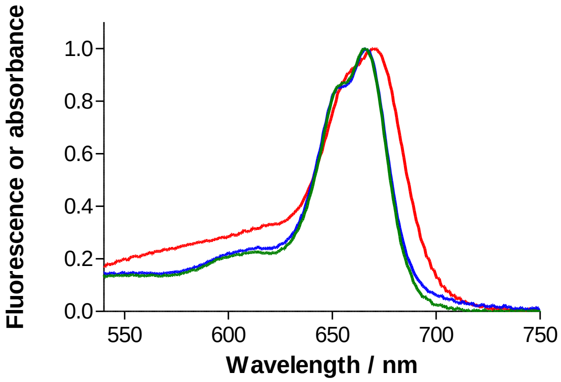

Figure S5: Compound **8Zn**

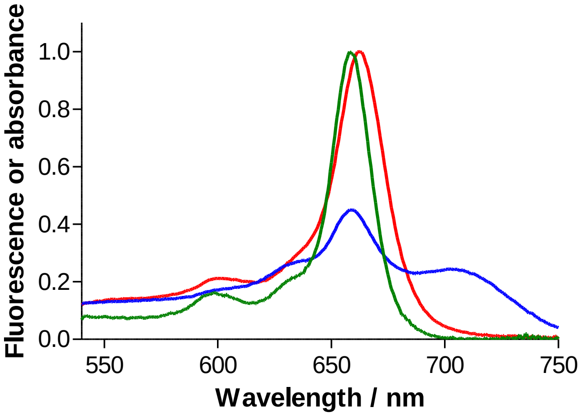

Figure S6: Compound **9Zn**

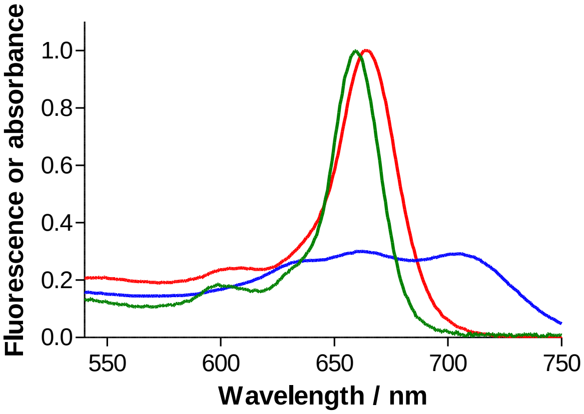

Figure S7: Compound **10Zn**

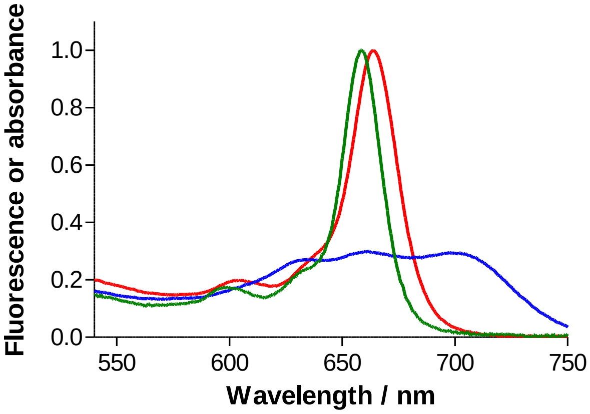

Figure S8: Compound **11Zn**

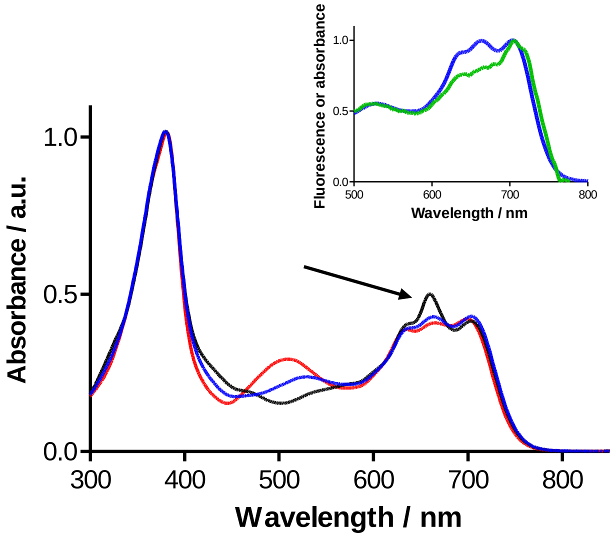

Figure S9. Absorption spectra of **9Zn** (black), **10Zn** (blue) and **11Zn** (red) in toluene normalized to the same absorption of the Soret band. The spectra show the presence of J-dimers. Arrow indicates the band of residual monomer in the absorption spectrum. The contribution of this band decreases in line **9Zn** > **10Zn** > **11Zn**. Inset: absorption (blue) and excitation spectra (green, emission at 810 nm) of **10Zn** in toluene normalized at 703 nm. Emission at 810 nm is attributed to J-dimer (see also Figure S10 C); monomer emission is negligible at this wavelength.

Titration of toluene solution of 9Zn and 10Zn with pyridine

Stock solutions of TPyzPz were prepared in toluene (cca 5 μM). For each titration, 2.5 mL of appropriate stock solution was transferred into a quartz optical cell (10 × 10 mm). The absorption and emission spectra were measured. The aliquots of toluene/1 % pyridine (v/v) were added into the cell and absorption and emission spectra were measured again. The spectral changes correspond to the formation of J-dimers as described for **11Zn** previously.[8]

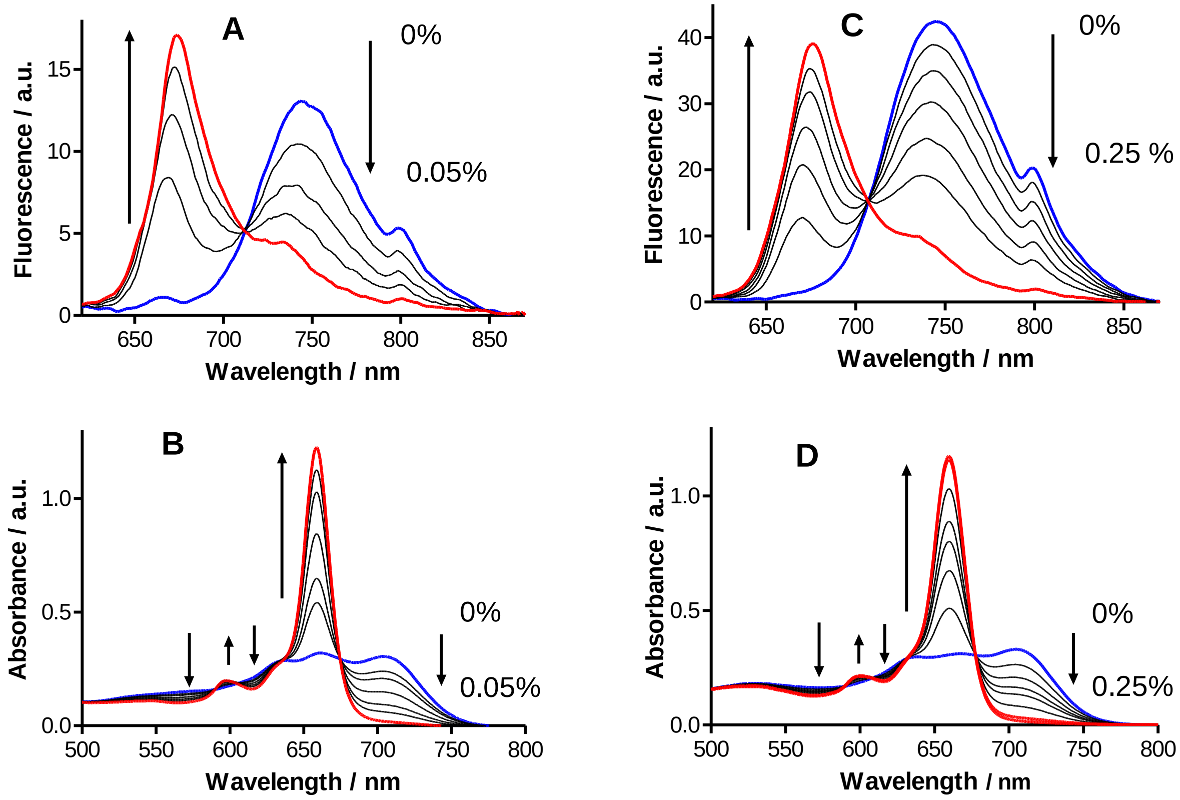

Figure S10. Changes in emission (A, C) and absorption (B, D) spectra of **9Zn** (A, B) and **10Zn** (C, D) in toluene after addition of pyridine. Excitation was at 605 nm (isosbestic point). The spectrum of monomer is a red curve, spectrum of J-dimer (in pure toluene) is blue. Note the small band in emission spectrum of **9Zn** (A) in pure toluene (blue line) at 663 nm. It arises from residual monomer and is in good accordance with the observations in absorption spectra (see Fig. S9). Arrows indicate spectral changes with the increasing concentration of pyridine (v/v).

Dependence of fluorescence quantum yields on the number of donor centers

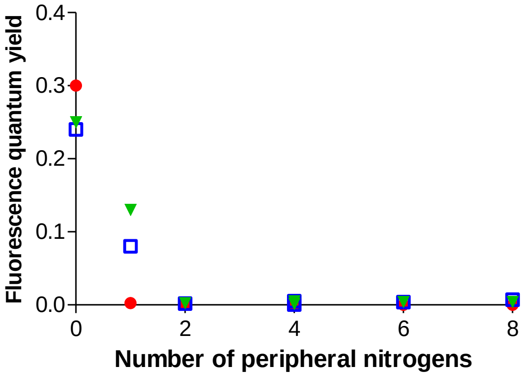

Figure S11: Fluorescence quantum yields in relation to the number of peripheral *N*,*N*-diethylamino substituents (i.e., compounds **5Zn-11Zn**) in pyridine (red ●), toluene (blue □) and toluene with 1% (v/v) of pyridine (green ▼).

Titration of DMSO solution of 6Zn with sulphuric acid

2.0 mL of stock solution of **6Zn** in DMSO (1.5 μM) was transferred into a quartz optical cell (10 × 10 mm), defined amount of concentrated sulphuric acid was added and absorption and emission spectra were measured. Excitation wavelength was 599 nm. The fluorescence emission spectra were corrected for changes in intensity caused by changes in absorption at excitation wavelength. The absorption spectra were corrected for the changes caused by dilution. Figure S12 shows the changes in the absorption spectra during titration of **6Zn** from 6% v/v sulphuric acid to 20% v/v. The absorption spectra did not change at sulphuric acid concentration below 6% v/v. Similar spectra can be drawn also for **5Zn**.

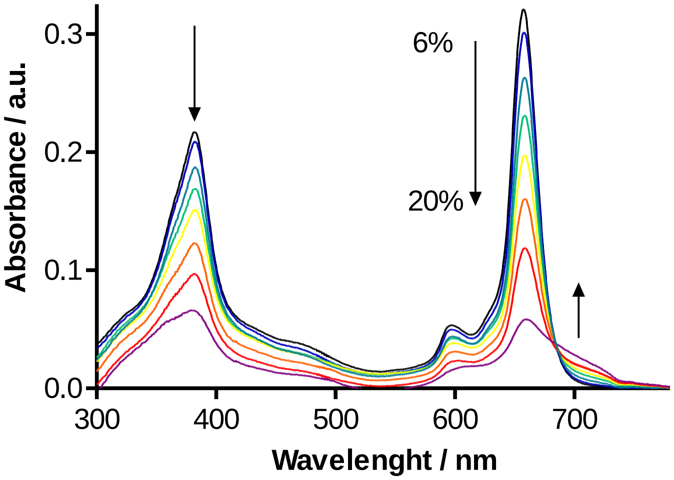

Figure S12. Changes in the absorption spectra of **6Zn** in DMSO during titration by sulphuric acid from 6% v/v to 20% v/v.

5. References

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