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Electronic Supplementary Information

# Structural factors influencing the intramolecular charge transfer and photoinduced electron transfer in tetrapyrazinoporphyrazines

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# Content

## General

All organic solvents were of analytical grade. Anhydrous butanol was stored over magnesium and distilled prior to use. All chemicals for synthesis were obtained from established suppliers (Aldrich, Acros, Merck, TCI Europe) and used as received. Zinc phthalocyanine (ZnPc) was purchased from Aldrich, 5,6-dichloropyrazine-2,3-dicarbonitrile from TCI Europe. TLC was performed on Merck aluminum 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 Engineering Ltd., Southend-on-Sea, Essex, Great Britain). Infrared spectra were measured on a Nicolet 6700 (ATR mode). $^{1}$H and $^{13}$C NMR spectra were recorded on a Varian Mercury Vx BB 300 or VNMR S500 NMR spectrometers. The reported chemical shifts are given relative to Si(CH3)4 and were locked to the signal of the solvent. The elemental analysis was carried out on Automatic Microanalyser EA1110CE (Fisons Instruments S.p.A., Milano, Italy). Matrix assisted laser desorption ionization - time of flight (MALDI-TOF) mass spectra were recorded in positive reflectron mode on a 4800 MALDI TOF/TOF mass spectrometer (AB Sciex, Framingham, MA, USA) in trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile as the matrix. The instrument was calibrated externally with a five-point calibration using Peptide Calibration Mix1 (LaserBio Labs, Sophia-Antipolis, France). The UV/Vis spectra were recorded using a Shimadzu UV-2401PC spectrophotometer. Mg and Zn complexes of **9**, **10a**, **11**, **12a**, **13**, **14a**,[1] **15**[2] and **16**[3,4] and **12eZn**[5] were prepared according to literature. Synthesis of 5,6-bis(*tert*-butylsulfanyl)pyrazine-2,3-dicarbonitrile,[6] 5-chloro-6-phenylpyrazine-2,3-dicarbonitrile[7] and 5-chloro-6-methylpyrazine-2,3-dicarbonitrile[7] also followed published procedures.

## Synthesis

### Synthesis of 5-butylamino-6-phenylpyrazine-2,3-dicarbonitrile (1)

*n*-Butylamine (0.5 ml, 2 mmol) was added in a dropwise manner to a solution of 5-chloro-6-phenylpyrazine-2,3-dicarbonitrile (480 mg, 2 mmol) in THF (40 ml), and the mixture was stirred for 2 h at rt. Salts were removed by filtration and washed with THF. The filtrate was evaporated under reduced pressure. The crude product was crystalized from methanol. Mother liquors were collected, evaporated to dryness and purified by column chromatography on silica gel using hexane/ethylacetate 4:1 as the eluent. Fractions from chromatography were combined with those from crystallization. Yield: 500 mg (90%) of yellow crystals. Mp 138.9-139.8 °C (from methanol). Found: C, 69.29; H, 5.55; N, 25.47. Calc. for $C_{16}H_{15}N_5$: C, 69.29; H, 5.45; N, 25.25%. $\nu_{max}$/cm$^{-1}$ 3430 (NH), 2952, 2859 (aliphCH), 2228 (CN), 1564, 1507, 1450, 1412, 1393, 1359, 1331, 1275, 1232, 1187, 1116, 1079, 1006. $\delta_C$(75 MHz; $CDCl_3$) 151.9, 145.4, 133.5, 131.2, 131.1, 129.8, 127.9, 119.5, 114.5, 113.9, 41.6, 30.6, 20.1, 13.7. $\delta_H$(300 MHz, $CDCl_3$) 7.67-7.55 (5 H, m, ArH), 5.91 (1 H, bs, NH), 3.54-3.43 (2 H, m, C$H_2$-NH), 1.66-1.53 (2 H, m, $CH_2$), 1.38 (2 H, sext, J=7.3 Hz, $CH_2$), 0.95 (3 H, t, J=7.3 Hz, $CH_3$).

### Synthesis of 5-phenyl-6-(phenylamino)pyrazine-2,3-dicarbonitrile (2)

Aniline (0.56 g, 6 mmol) was added to a solution of 5-chloro-6-phenylpyrazine-2,3-dicarbonitrile (480 mg, 2 mmol) in THF (10 ml), and the mixture was heated under reflux for 8 h. Salts were removed by filtration and washed with THF. The filtrate was evaporated under reduced pressure. The crude product was crystalized from methanol. Mother liquors were collected, evaporated to dryness and purified by column chromatography on silica gel using toluene/chloroform 1:1 as the eluent. Fractions from chromatography were combined with those from crystallization. Yield: 543 mg (91%) of yellow crystals. Mp 219-220 °C (from methanol) (lit.,[8] 210-210.5 °C). Found: C, 72.43; H, 3.87; N, 23.57. Calc. for $C_{18}H_{11}N_5$: C, 72.72; H, 3.73; N, 23.56%. $\nu_{max}$/cm$^{-1}$ 3322 (NH), 3064 (ArCH), 2224 (CN), 1602, 1534, 1514, 1493, 1445, 1395, 1301, 1283, 1221, 1130, 1074, 1011. $\delta_C$(75 MHz; $CDCl_3$) 149.3, 146.4, 136.3, 133.1, 131.7, 130.2, 130.1, 129.4, 128.2, 125.8, 121.8, 121.1, 114.0, 113.5. $\delta_H$(300 MHz, $CDCl_3$) 7.79-7.72 (2 H, m, ArH), 7.68-7.62 (3 H, m, ArH), 7.60-7.50 (3 H, m, ArH + NH), 7.45-7.37 (2 H, m, ArH), 7.23 (1 H, tt, $J_1$ = 7.4 Hz, $J_2$ = 1.0 Hz, ArH).

### Synthesis of 5-amino-6-phenylpyrazine-2,3-dicarbonitrile (3)

Ammonia solution (25%, 3.7 ml, 0.05 mol) was added to a solution of 5-chloro-6-phenylpyrazine-2,3-dicarbonitrile (2 g, 8.3 mmol) in THF (150 ml), and the mixture was stirred for 4 h at rt. Salts were removed by filtration and washed with THF. The filtrate was evaporated under reduced pressure. The crude product was crystalized from ethanol/water. Yield: 1.4 g (76%) of yellow crystals. Mp 162.4-163.1 °C (ethanol/water) (lit.,[9] 166-167 °C (toluene)). Found: C, 64.93; H, 3.33; N, 31.41. Calc. for $C_{12}H_7N_5$: C, 65.15; H, 3.19; N, 31.66%. $\nu_{max}$/cm$^{-1}$ 3460, 3340 ($NH_2$), 3210 (aromCH), 2228 (CN), 1621, 1529, 1458, 1445, 1406, 1324, 1278, 1241, 1184, 1133, 1080, 1003. $\delta_C$(75 MHz; acetone-$d_6$) 154.9, 145.7, 135.4, 131.8, 131.4, 129.9, 129.0, 120.7, 115.7, 115.0. $\delta_H$(300 MHz, acetone-$d_6$) 7.82-7.74 (2 H, m, ArH), 7.60-7.52 (3 H, m, ArH), 7.33 (2 H, bs, $NH_2$).

### Synthesis of 5-(10*H*-phenothiazin-10-yl)-6-phenylpyrazine-2,3-dicarbonitrile (4)

Cesium fluoride (1.89 g, 12.4 mmol) was carefully dried at 450 °C (10 min) under reduced pressure (15 mbar) and the flask was filled with argon after cooling down. 5-Chloro-6-phenylpyrazine-2,3-dicarbonitrile (1 g, 4.2 mmol) and phenothiazine (1.24 g, 6.2 mmol) were dissolved in anhydrous DMF (3.5 ml) under argon and added by syringe to cesium fluoride. The mixture was stirred for 5 h at rt and quenched by pouring into distilled water (200 ml).The suspension was stirred for 20 h at rt and filtered. The crude solid product was purified by column chromatography on silica gel using toluene as the eluent ($R_f$ =

0.4). Yield: 806 mg (48%) of yellow crystals. Mp 240.7-243.5 °C. Found: C, 71.25; H, 3.95; N, 17.51. Calc. for $C_{24}H_{13}N_5S$: C, 71.45; H, 3.25; N, 17.36%. $\nu_{max}$/cm$^{-1}$ 3061, 2229, 1580, 1515, 1481, 1460, 1421, 1397, 1313, 1293, 1252. $\delta_C$(125 MHz; $CDCl_3$) 149.1, 147.4, 139.4, 135.7, 132.5, 130.0, 128.3, 127.9, 127.4, 127.3, 127.2, 126.8, 124.6, 123.2, 113.7, 113.3. $\delta_H$(500 MHz, $CDCl_3$) 7.54-7.47 (4 H, m, Ar-H), 7.30 (2 H, dd, $J_1$=7.7 Hz, $J_2$=1.5 Hz, phenyl), 7.20-7.04 (7 H, m, Ar-H).

**Synthesis of 5-[2-(diethylamino)ethylsulfanyl]-6-phenylpyrazine-2,3-dicarbonitrile (5)**

Water solution (3 ml) of 2-diethylaminoethanethiol hydrochloride (388 mg, 2.3 mmol) was stirred with 1M aqueous NaOH solution (4.6 ml, 4.6 mmol) for 15 min at rt. Afterwards, 5-chloro-6-phenylpyrazine-2,3-dicarbonitrile (500 mg, 2.1 mmol) in THF (10 ml) was added and the mixture was stirred for next 15 min at rt. The reaction was diluted with ethylacetate and the organic layer was collected. Subsequently, the organic layer was washed three times with 1% HCl and discarded. The water phase was neutralized by 1M aqueous NaOH to basic pH and washed three times with ethylacetate. The organic layer was separated, dried with sodium sulfate and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using acetone as the eluent ($R_f$ = 0.57). Yield: 370 mg (53%) of yellowish oily liquid. For better stability, the free base was converted to hydrochloride as follows: compound **5** was dissolved in diethylether and bubbled by dry HCl (g). Product that solidified in the flask was collected, washed with diethylether and crystallized from isopropanol to give white solid. Data for **5·HCl**: Mp 158.4-169.2 °C (dec.) (isopropanol). Found: C, 57.29; H, 5.53; N, 18.47. Calc for $C_{18}H_{19}N_5S$·HCl: C, 57.82; H, 5.39; N, 18.73%. $\nu_{max}$/cm$^{-1}$ 2980, 2944, 2238 (CN), 1598, 1505, 1447, 1393, 1336, 1316, 1283, 1226, 1148, 1099, 1030, 1001, 951. $\delta_C$(125 MHz; $D_2O$) 161.7, 157.0, 134.1, 132.6, 131.1, 129.8, 129.4, 127.7, 114.4, 114.2, 49.6, 48.5, 25.1, 9.1. $\delta_H$(500 MHz, $D_2O$) 7.79-7.75 (2 H, m, ArH), 7.71-7.66 (1 H, m, ArH), 7.65-7.60 (2 H, m, ArH), 3.60-3.52 (2 H, m, NC$H_2$CH$_2$), 3.49-3.42 (2 H, m, SCH$_2$), 3.34 (4 H, q, $J$ = 7 Hz, NC$H_2$CH$_3$), 1.37 (6 H, t, $J$ = 7 Hz, CH$_3$). The hydrochloride was converted to free base before further reaction. The solid was dissolved in water, the solution was made slightly basic using aqueous NaOH and extracted 3 times with diethylether. The organic phase was collected, dried ($Na_2SO_4$) and co-evaporated to dryness with toluene.

**Synthesis of 5-butoxy-6-chloropyrazine-2,3-dicarbonitrile (6)**

5,6-Dichloropyrazine-2,3-dicarbonitrile (2 g, 10 mmol) was dissolved in butanol (230 ml) and the mixture was cooled down to -10°C using ice/salt bath. 1M aqueous NaOH solution (15 ml, 15 mmol) was added dropwise to the solution. The mixture was stirred at rt for 5 min, the solvents were removed under reduced pressure and the crude mixture was purified several times by column chromatography on silica using toluene:chloroform 2:1 as the eluent. The purification afforded pure compound **6** (92 mg, 4%) as the colorless oily liquid ($R_f$ = 0.56 in toluene:chloroform 1:1) but also inseparable mixture (1 g) with 5,6-dibutoxypyrazine-2,3-dicarbonitrile ($R_f$ (5,6-dibutoxypyrazine-2,3-dicarbonitrile) = 0.51 in toluene:chloroform 1:1). $\nu_{max}$/cm$^{-1}$ 2963, 2875, 2241, 1542, 1523, 1446, 1366, 1352, 1233, 1198, 1146, 1064, 938. $\delta_C$(75 MHz; $CDCl_3$) 157.4, 142.8, 129.1, 123.6, 112.3, 112.2, 70.8, 30.1, 18.9, 13.6. $\delta_H$(300 MHz, $CDCl_3$) 4.54 (2 H, t, $J$ = 7 Hz, OCH$_2$), 1.82 (2 H, p, $J$ = 7 Hz, OCH$_2$C$H_2$), 1.49 (2 H, sext, $J$ = 7 Hz, C$H_2$CH$_3$), 1.24 (t, $J$ = 3.6 Hz, 1H), 1.00 (3 H, t, $J$ = 7 Hz, CH$_3$).

**Synthesis of 5-butoxy-6-[2-(diethylamino)ethylsulfanyl]pyrazine-2,3-dicarbonitrile (7)**

This compound has been synthesized from 5,6-dichloropyrazine-2,3-dicarbonitrile in two steps (one-pot) without complicated isolation of the intermediate **6**. 5,6-Dichloropyrazine-2,3-dicarbonitrile (1 g, 5 mmol) was dissolved in butanol (230 ml) and the mixture was cooled down to -10°C using ice/salt bath. 1M aqueous NaOH solution (9 ml, 9 mmol) was homogenized with butanol (20 ml) and slowly added dropwise to the solution. Subsequently, 2-diethylaminoethanethiol hydrochloride (2.55 g, 15 mmol) was added followed by additional 1M aqueous NaOH (15 ml, 15 mmol). The mixture was stirred at rt for 15 min and the solvents were removed under reduced pressure. The crude mixture was purified by column chromatography on silica gel using ethylacetate:triethylamine 50:1 and impure fractions containing product once more with ethylacetate ($R_f$ = 0.42 in ethylacetate) as the eluents. Yield: 510 mg (30%, based on 5,6-dichloropyrazine-2,3-dicarbonitrile) of yellow oil. $\nu_{max}$/cm$^{-1}$ 2967, 2873, 2812, 2233 (CN), 1520, 1462, 1427, 1380, 1333, 1242, 1196, 1150, 1062, 1012, 941. $\delta_C$(75 MHz; $CD_3OD$) 158.15, 156.41, 126.19, 125.7+9, 114.96, 114.94, 70.45, 51.60, 47.96, 31.44, 27.08, 20.17, 14.01, 11.89. $\delta_H$(300 MHz; $CD_3OD$) 4.49 (2 H, t, $J$ = 6 Hz, OCH$_2$), 3.31-3.27 (2 H, m, NC$H_2$CH$_2$), 2.83-2.76 (2 H, m, SCH$_2$), 2.65 (4 H, q, $J$ = 7 Hz, NC$H_2$CH$_3$), 1.86-1.76 (2 H, m, OCH$_2$C$H_2$), 1.57-1.44 (2 H, m, OCH$_2$CH$_2$C$H_2$), 1.10 (6 H, t, $J$ = 7 Hz, NCH$_2$C$H_3$), 0.98 (3 H, t, $J$ = 7 Hz, CH$_3$.)

**Synthesis of 5-[2-(diethylamino)ethylsulfanyl]-6-methylpyrazine-2,3-dicarbonitrile (8)**

Compound **8** was synthesized similarly to **5** but starting from water solution (10 ml) of 2-diethylaminoethanethiol hydrochloride (953 mg, 5.6 mmol), 1M aqueous NaOH solution (12 ml, 12 mmol) and 5-chloro-6-methylpyrazine-2,3-dicarbonitrile (1 g, 5.6 mmol) in THF (20 ml). Moreover, the reaction turned deep red after mixing all components. Eluent for column chromatography: ethylacetate:triethylamine 30:1. Yield: 1 g (68%) of slightly red oily liquid. The free base was also converted to its hydrochloride. Data for free base **8**: $\nu_{max}$/cm$^{-1}$ 3388, 2975, 2965, 2918, 2875, 2732, 2646, 2527, 2414, 2234, 1686, 1528, 1515, 1465, 1397, 1376, 1335, 1325, 1290, 1281, 1267, 1255, 1208, 1156, 1147, 1101, 1046, 1028, 996, 953, 898, 843, 819, 806, 781, 771. $\delta_C$(75 MHz; acetone-d$_6$) 8.93, 22.14, 24.36, 47.36, 49.42, 114.48, 114.86, 127.97, 131.04, 157.63 a 161.86. $\delta_H$(300 MHz, acetone-d$_6$) 1.44 (6 H, t, $J$ = 7.3 Hz, NCH$_2$C$H_3$), 2.63 (3 H, s, CH$_3$), 3.22-3.36 (4 H, m, NC$H_2$CH$_3$), 3.37-3.43 (2 H, m, SCH$_2$C$H_2$N), 3.84-3.91 (2 H, m, SCH$_2$). Data for **8·HCl**: Mp 156.8-157.2 °C (isopropanol). Found: C, 49.00; H, 5.62; N, 22.45.

Calc for $C_{13}H_{17}N_5S$+HCl: C, 50.07; H, 5.82; N, 22.46%., $\nu_{max}$/cm$^{-1}$ 2964, 2918, 1529, 1515, 1465, 1398, 1375, 1279, 1267, 1209, 1147, 1055, 1026. $\delta_C$(75 MHz; $D_2O$) 9.03, 21.86, 24.24, 48.49, 49.59, 114.28, 114.61, 127.19, 130.73, 158.15 a 162.27. $\delta_H$(300 MHz, $D_2O$) 1.37 (6 H, t, *J* = 7 Hz, $NCH_2CH_3$), 2.62 (3 H, s, $CH_3$), 3.36 (4 H, q, *J* = 7 Hz, $NCH_2CH_3$), 3.44-3.51 (2 H, m, $SCH_2$), 3.60-3.67 ppm (2 H, m, $SCH_2CH_2N$). The hydrochloride was converted to free base before further reaction. The solid was dissolved in water, the solution was made slightly basic using aqueous NaOH and washed 3 times with diethylether. The organic phase was collected, dried ($Na_2SO_4$) and co-evaporated to dryness with toluene.

**General procedure A (for synthesis of metal-free complexes 10fH, 12fH and 14fH)**

Freshly distilled anhydrous butanol (70-80 ml) was refluxed with magnesium turnings (28 eq) and a small crystal of iodine until all magnesium was converted to magnesium butoxide (typically 3 h). Subsequently, 5,6-bis(*tert*-butylsulfanyl)pyrazine-2,3-dicarbonitrile (3 eq) and compound **5**, **7** or **8** (1 eq) were added. The latter was added in the form of free base in butanol (5 ml) solution. The reflux continued for 6 h. Butanol was evaporated under reduced pressure and the mixture of congeners was extracted several times from the excess of magnesium butoxide with dichloromethane/THF mixture (1:1). The solvents were evaporated and the congener of AAAB type was subsequently isolated using column chromatography on silica as the second most intense green fraction. Typically, the product was not pure but contaminated with 2,3,9,10,16,17,23,24-octakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine magnesium(II) (AAAA type congener) that was best removed after conversion to metal-free derivatives. Thus, isolated magnesium complexes (1 eq) were dissolved in THF (25 ml) and *p*-toluenesulfonic acid (20 eq) in THF (5 ml) was added. The reaction was stirred at rt for 2 h followed by evaporation of THF under reduced pressure. The solid was dissolved in dichloromethane and washed 2 times with aqueous $NaHCO_3$ and 2 times with water. The organic phase was collected, dried ($Na_2SO_4$) and evaporated. The crude metal-free derivative was purified using column chromatography on silica (once or twice). The final product was washed with methanol and dried. Details to each synthesis can be found below.

**General procedure B (for synthesis of metal-free complexes 12bH, 12cH and 12dH)**

Freshly distilled anhydrous butanol (50-70 ml) was refluxed with magnesium turnings (28 eq) and a small crystal of iodine until all magnesium was converted to magnesium butoxide (typically 3 h). Subsequently, 5,6-bis(*tert*-butylsulfanyl)pyrazine-2,3-dicarbonitrile (3 eq) and compound **1**, **2** or **4** (1 eq) were added. The reflux continued for 3-16 h. Butanol was evaporated under reduced pressure at the end of the reaction and the solids treated with 50% acetic acid (100 ml) for 30 min. The green solids were collected, washed with water and air dried. The crude product was dissolved in chloroform (20 ml), *p*-toluenesulfonic acid (10 eq) in THF (30 ml) was added and the reaction was stirred for 30 min. The solvents were evaporated under reduced pressure and the solids washed with water and methanol. The congener of AAAB type was subsequently isolated using column chromatography on silica as the second most intense (typically green) fraction. Further purification of isolated fraction by column chromatography was required (once or twice) in order to receive pure product – metal-free tetrapyrazinoporphyrazine. Details to each synthesis of **12b-d** can be found below.

**General procedure C (for synthesis metal-complexes).**

Metal-free derivative (1 eq) was dissolved in pyridine (3-5 ml) and anhydrous magnesium acetate (10 eq) or zinc acetate (10 eq) was added. The reaction was heated to reflux for 2 h. Solvent was evaporated and the residue washed successively with water. The final product was purified by column chromatography on silica when required. The final product was washed with methanol and dried.

**Synthesis of 2-[2-(diethylamino)ethylsulfanyl]-3-methyl-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine (10fH)**

Synthesis of this compound followed the general procedure A. Details: 1 eq = 2.5 mmol, eluent for magnesium AAAB congener isolation: chloroform:THF:pyridine 16:3:1, eluent for further purification of **10fH** (twice with this eluent): chloroform:THF:methanol 20:2:1. Yield: 330 mg (11%) of dark green solid.
Found: C, 54.86; H, 6.18; N, 19.74. Calc for $C_{55}H_{73}N_{17}S_7$+$H_2O$: C, 54.38; H, 6.22; N, 19.60%. $\lambda_{max}$(THF, 1 μM)/nm 668 (ε/dm$^3$mol$^{-1}$cm$^{-1}$ 143 000), 637 (117 700), 612 (42 100), 586 (28 300), 471 (49 000), 363 (122 200). $\nu_{max}$/cm$^{-1}$ 3295 (centrNH), 2962, 2920, 1653, 1558, 1540, 1522, 1508, 1489, 1473, 1457, 1424, 1362, 1314, 1284, 1250, 1231, 1195, 1140, 1094, 1082, 1016, 969, 843, 750, 716, 696, 674. $\delta_C$(75 MHz; $CDCl_3$/pyridine-$d_5$) 10.09, 22.24, 29.76, 29.79, 29.83, 29.85, 30.01, 30.11, 46.40, 49.99, 50.77, 50.81, 50.82, 50.87, 140.71, 142.36, 153.49, 158.20, 158.50, 159.75 some signals of TPyzPz core were not detected or fused together. $\delta_H$(300 MHz; $CDCl_3$/pyridine-$d_5$) 1.33-1.46 (6 H, m, $NCH_2CH_3$), 2.13 (9 H, s, $SCCH_3$), 2.14 (9 H, s, $SCCH_3$), 2.16-2.23 (36 H, m, $SCCH_3$), 3.12-3.17 (7 H, br m, $ArCH_3$ + $NCH_2CH_3$), 3.37-3.49 (2 H, m, $NCH_2CH_2$), 4.17-4.31 (2 H, m, $SCH_2$). *m/z* (MALDI) 1196.23 $[M+H]^+$. Calc. for $C_{55}H_{73}N_{17}S_7$: 1195.43.

**Synthesis of 2-[2-(diethylamino)ethylsulfanyl]-3-methyl-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine magnesium(II) (10fMg)**

Synthesis of this compound followed the general procedure C. Details: 1 eq = 84 μmol, eluent for chromatography purification: chloroform:THF 5:1. Yield: 72 mg (72%) of dark green solid. Found: C, 52.59; H, 5.67; N, 18.73.Calc. for

$C_{55}H_{71}MgN_{17}S_7$+2$H_2O$: C, 52.63; H, 6.02; N, 18.97%. $\lambda_{max}$(THF, 1 μM)/nm 648 (ε/dm$^3$mol$^{-1}$cm$^{-1}$ 267 300), 589 (35 500), 380 (149 700). $\nu_{max}$/cm$^{-1}$ 2962, 2920, 1656, 1521, 1453, 1393, 1362, 1335, 1257, 1232, 1145, 1092, 1008, 974, 869, 849, 781, 751, 710, 696, 669. $\delta_C$(75 MHz; $CDCl_3$/pyridine-$d_5$) 7.81, 21.90, 29.79, 29.91, 30.20, 30.54, 46.66, 50.08, 50.44, 50.52, 144.28, 144.31, 144.49, 145.29, 150.50, 150.79, 150.90 some signals of TPyzPz core were not detected or fused together. $\delta_H$(300 MHz; $CDCl_3$/pyridine-$d_5$) 1.69 (6 H, t, $J$ = 7 Hz, $NCH_2CH_3$), 2.05 (9 H, s, $SCCH_3$), 2.14 (9 H, s, $SCCH_3$), 2.21 (18 H, s, $SCCH_3$), 2.22 (18 H, s, $SCCH_3$), 3.16 (3H, s, Ar-$CH_3$), 3.51-3.72 (6 H, m, $SCH_2CH_2$ + $NCH_2CH_3$), 4.37-4.84 (2 H, m, $SCH_2$). *m/z* (MALDI-TOF) 1218,19 [M+H]$^+$. Calc. for $C_{55}H_{71}MgN_{17}S_7$: 1217.40.

**Synthesis of 2-[2-(diethylamino)ethylsulfanyl]-3-methyl-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine zinc(II) (10fZn)**

Synthesis of this compound followed the general procedure C. Details: 1 eq = 84 μmol, eluent for chromatography purification: chloroform:THF 5:1. Yield: 86 mg (82%) of dark green solid. Found: C, 51.75; H, 5.87; N, 17.97. Calc. for $C_{55}H_{71}N_{17}S_7Zn$+$H_2O$: C, 51.68; H, 5.76; N, 18.63%. $\lambda_{max}$(THF, 1 μM)/nm 646 (ε/dm$^3$mol$^{-1}$cm$^{-1}$ 284 700), 618sh, 588 (39 000), 455sh, 375 (153 200). $\nu_{max}$/cm$^{-1}$ 2960, 2921, 1658, 1523, 1478, 1452, 1392, 1362, 1327, 1257, 1233, 1143, 1098, 1010, 975, 867, 847, 781, 746, 709, 694. $\delta_C$(75 MHz; $CDCl_3$/pyridine-$d_5$) 10.87, 22.18, 29.72, 29.91, 29.94, 30.03, 30.21, 46.42, 50.21, 50.49, 50.54, 50.61, 143.68, 143.75, 143.79, 143.87, 144.07, 144.37, 147.29, 150.28, 150. 51, 150.91, 151.08, 152.89, 157.47, 157.85, 158.56 some signals of TPyzPz core were not detected or fused together. $\delta_H$(300 MHz; $CDCl_3$/pyridine-$d_5$) 1.64-1.77 (6 H, m, $NCH_2CH_3$), 2.12-2.27 (54 H, m, $SCCH_3$), 3.18 (3 H, s, Ar-$CH_3$), 3.44-3.72 (6 H, br m, 4×$NCH_2CH_3$ + 2×$NCH_2CH_2$), 4.18-4.38 (2 H, br m, $SCH_2$). *m/z* (MALDI-TOF) 1258,13 [M+H]$^+$. Calc. for $C_{55}H_{71}N_{17}S_7Zn$: 1257.34.

**Synthesis of 2-butylamino-3-phenyl-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine (12bH)**

Synthesis of this compound followed the general procedure B with the modification that the crude product was not washed with methanol. Details: 1 eq = 1.3 mmol, reaction time: 16 h, eluent for AAAB congener isolation: toluene:chloroform:ethylacetate 20:10:1, eluent for further purification (twice with this eluent): toluene:chloroform:THF 25:8:1. Yield: 144 mg (10%) of dark green solid. Found: C, 57.54; H, 5.87; N, 19.00. Calc. for: $C_{58}H_{71}N_{17}S_6$+$H_2O$: C, 57.25; H, 6.05; N, 19.57%. $\lambda_{max}$(THF, 1 μM)/nm 674 (ε/dm$^3$mol$^{-1}$cm$^{-1}$ 127 100), 651 (110 000), 617 (39 800), 474 (56 200), 367 (126 400). $\nu_{max}$/cm$^{-1}$ 3441 (secNH), 3300 (centrNH), 2960, 2920 (aliphCH), 1515, 1476, 1452, 1391, 1362, 1312, 1280, 1231, 1140, 1078, 1021, 967. $\delta_C$(75 MHz; $CDCl_3$/pyridine-$d_5$) 159.1, 159.0, 158.8, 158.3, 157.54, 157.47, 154.0, 136.5, 129.2, 128.7, 128.4, 51.0, 50.9, 50.6, 50.5, 41.2, 30.8, 30.15, 30.11, 29.94, 29.86, 20.0, 13.5 some signals of TPyzPz core were not detected or fused together. $\delta_H$(300 MHz; $CDCl_3$/pyridine-$d_5$) 8.25 (2 H, d, $J$ = 7 Hz, ArH-2), 7.77 (2 H, t, $J$ = 7 Hz, ArH-3), 7.68 (1 H, d, $J$ = 7 Hz, ArH-4), 6.91 (1 H, t, $J$ = 6 Hz, NH), 4.25-4.14 (2 H, m, $CH_2$NH), 2.28-2.18 (47 H, m, $CCH_3$+$CH_2$), 2.10 (9 H, s, $CCH_3$), 1.79 (2 H, sext, $J$ = 7 Hz, $CH_2$), 1.25 (3 H, t, $J$ = 7 Hz, $CH_3$). *m/z* (MALDI-TOF) 1197.38 [M]$^+$. Calc. for $C_{58}H_{71}N_{17}S_6$: 1197.44.

**Synthesis of 2-butylamino-3-phenyl-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine magnesium(II) (12bMg)**

Synthesis of this compound followed the general procedure C. No chromatography was required. Details: 1 eq = 25 μmol, Yield: 28 mg (92%) of dark green solid. Found: C, 54.84; H, 5.85; N, 18.22; Calc. for $C_{58}H_{69}MgN_{17}S_6$+3$H_2O$: C, 54.64; H, 5.93; N, 18.68%. $\lambda_{max}$(THF, 1 μM)/nm 658 (ε/dm$^3$mol$^{-1}$cm$^{-1}$ 180 500); 595 (34 000); 382 (153 800). $\nu_{max}$/cm$^{-1}$ 3438 (NH), 2960, 2921 (aliphCH), 1519, 1477, 1392, 1362, 1249, 1143, 1095, 974. $\delta_C$(125 MHz; $CDCl_3$/pyridine-$d_5$) 158.1, 157.14, 157.06, 156.6, 153.4, 152.1, 150.8, 150.5, 149.9, 149.8, 149.7, 149.3, 149.1, 144.6, 144.3, 144.1, 144.0, 143.92, 143.86, 139.3, 136.9, 128.9, 128.6, 128.3, 50.52, 50.48, 50.45, 50.37, 50.36, 41.1, 30.8, 30.22, 30.18, 30.02, 29.97, 19.9, 13.4 some signals of TPyzPz core were not detected or fused together. $\delta_H$(500 MHz; $CDCl_3$/pyridine-$d_5$) 8.21 (2 H, d, $J$ = 7 Hz, ArH-2), 7.71 (2 H, t, $J$ = 7 Hz, ArH-3), 7.67-7.58 (1 H, m, ArH-4, fused with solvent signal), 6.51 (1 H, bs, NH), 4.15 (2 H, broad, $CH_2$NH), 2.31-2.14 (45 H, m, $CCH_3$), 2.14-1.99 (11 H, m, $CCH_3$+$CH_2$), 1.72 (2 H, broad, $CH_2$), 1.19 (3 H, t, $J$ = 7 Hz, $CH_3$). *m/z* (MALDI-TOF) 1219.31 [M]$^+$, 1242.29 [M+Na]$^+$, 1258.26 [M+K]$^+$. Calc. for $C_{58}H_{69}MgN_{17}S_6$: 1219.41.

**Synthesis of 2-butylamino-3-phenyl-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine zinc(II) (12bZn)**

Synthesis of this compound followed the general procedure C. No chromatography was required. Details: 1 eq = 25 μmol, Yield: 20 mg (64%) of dark green solid. Found: C, 52.99; H, 5.57; N, 17.73. Calc. for $C_{58}H_{69}N_{17}S_6Zn$+3$H_2O$: C, 52.93; H, 5.74; N, 18.09%. $\lambda_{max}$(THF, 1 μM)/nm 656 (ε/dm$^3$mol$^{-1}$cm$^{-1}$ 160 600), 593 (30 800), 376 (130 000). $\nu_{max}$/cm$^{-1}$ 3438 (NH), 2959, 2922 (aliphCH), 1519, 1477, 1391, 1362, 1315, 1248, 1143, 1097, 975. $\delta_C$(75 MHz; $CDCl_3$/pyridine-$d_5$) 158.4, 157.9, 157.5, 157.4, 157.1, 157.0, 153.6, 152.6, 151.2, 151.0, 150.4, 150.3, 150.2, 149.7, 149.5, 149.4, 144.2, 143.9, 143.8, 143.6, 143.51, 143.48, 139.0, 136.9, 128.9, 128.6, 128.3, 50.58, 50.55, 50.51, 50.46, 41.2, 30.8, 30.18, 30.15, 29.99, 29.94, 19.9, 13.4 one signal of TPyzPz core was not detected or fused together with another one. $\delta_H$(300 MHz; $CDCl_3$/pyridine-$d_5$) 8.20 (2 H, d, $J$ = 7 Hz, ArH-2), 7.72 (2 H, t, $J$ = 7 Hz, ArH-3), 7.67-7.57 (1 H, m, ArH-4, fused with solvent signal), 6.59 (1 H, t, $J$ = 6 Hz, NH), 4.20 (2 H, q, $J$ = 7 Hz, $CH_2$NH), 2.28-2.19 (45 H, m, $CCH_3$), 2.13-2.02 (11 H, m, $CCH_3$+$CH_2$), 1.75 (2 H, sext, $J$ = 7 Hz,

$CH_2$), 1.20 (3 H, t, *J* = 7 Hz, $CH_3$). *m/z* (MALDI-TOF) 1259.23 $[M]^+$, 1282.22 $[M+Na]^+$, 1289.19 $[M+K]^+$. Calc. for $C_{58}H_{69}N_{17}S_6Zn$: 1259.35.

**Synthesis of 2-phenyl-3-phenylamino-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine (12cH)**

Synthesis of this compound followed the general procedure B. Details: 1 eq = 1.5 mmol, reaction time: 8 h, eluent for AAAB congener isolation: toluene:chloroform:THF 75:10:1, eluent for further purification: toluene:chloroform:THF 50:25:1. Yield: 149 mg (8%) of dark green solid. Found: C, 58.58; H, 5.62; N, 19.04. Calc. for $C_{60}H_{67}N_{17}S_6+H_2O$: C, 58.27; H, 5.62; N, 19.25%. $\lambda_{max}$(THF, 1 μM)/nm 676 (ε/$dm^3mol^{-1}cm^{-1}$ 140 800), 650 (100 100), 619 (42 700), 479 (54 100), 366 (122 700). $\nu_{max}$/$cm^{-1}$ 3413 (secNH), 3294 (centrNH), 2959, 2917 (aliphCH), 1599, 1518, 1494,1440, 1362, 1278, 1221, 1136, 1077, 1013. $\delta_C$(75 MHz; $CDCl_3$/pyridine-$d_5$) 158.84, 158.48, 158.39,157.86, 157.71, 150.39, 146.2, 138.85, 136.34, 129.33, 128.76, 128.63, 128.31, 119.3,50.82, 50.75, 50.64, 50.54, 50.51, 50.39, 30.09, 30.00, 29.79 some signals of TPyzPz core were not detected or fused together. $\delta_H$(300 MHz; $CDCl_3$/pyridine-$d_5$) 8.46 (1 H, bs, NH), 8.33 (2 H, d, *J* = 8 Hz, ArH), 8.26 (2 H, d, *J* = 7 Hz, ArH), 7.83-7.60 (5 H, m, ArH, fused with solvent signal), 7.33 (1 H, t, *J* = 7 Hz, ArH), 2.19 (9 H, s, $CH_3$), 2.17-2.14 (36 H, 2×s, $CH_3$), 2.09 (9 H, s, $CH_3$). *m/z* (MALDI-TOF) 1217.36 $[M]^+$, 1240.35 $[M+Na]^+$, 1256.32 $[M+K]^+$. Calc. for $C_{60}H_{67}N_{17}S_6$: 1217.41.

**Synthesis of 2-phenyl-3-phenylamino-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine magnesium(II) (12cMg)**

Synthesis of this compound followed the general procedure C. Eluent for chromatography purification:chloroform:THF 10:1. Details: 1 eq = 37 μmol, Yield: 44 mg (94%) of dark green solid. Found: C, 54.26; H, 5.41; N, 18.00. Calc for $C_{60}H_{65}MgN_{17}S_6+5H_2O$: C, 54.14; H, 5.68; N, 17.89%. $\lambda_{max}$(THF, 1 μM)/nm 657 (ε/$dm^3mol^{-1}cm^{-1}$ 192 000), 596 (34 500), 383 (138 600). $\nu_{max}$/$cm^{-1}$ 3413 (NH), 2961, 2919 (aliphCH), 1599, 1515, 1496, 1441,1363, 1248, 1144, 1093. $\delta_C$(75 MHz; $CDCl_3$/pyridine-$d_5$) 150.2, 149.4, 128.8, 128.6, 128.4,119.6, 50.56, 50.51, 50.40, 50.32, 30.29, 30.23, 30.02, 29.96 some signals of TPyzPz core were not detected or fused together. $\delta_H$(300 MHz; $CDCl_3$/pyridine-$d_5$) 8.51-8.38 (3 H, m, ArH + NH), 8.27 (2 H, d, *J* = 7 Hz, ArH), 7.80-7.72 (2 H, m, ArH), 7.71-7.62 (3 H, m, ArH, fused with solvent signal), 7.35 (1 H, t, *J* = 7 Hz, ArH), 2.28 (9 H, s, $CH_3$), 2.26-2.24 (18 H, 2×s, $CH_3$), 2.23 (18 H, s, $CH_3$), 2.10 (9 H, s, $CH_3$). *m/z* (MALDI-TOF) 1239.35 $[M]^+$. Calc. for $C_{60}H_{65}MgN_{17}S_6$: 1239.38.

**Synthesis of 2-phenyl-3-phenylamino-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine zinc(II) (12cZn)**

Synthesis of this compound followed the general procedure C. Details: 1 eq = 37 μmol, Yield: 47 mg (99%) of dark green solid. Found: C, 54.80; H, 5.40; N, 17.76. Calc. for $C_{60}H_{65}N_{17}S_6Zn+2H_2O$: C, 54.67; H, 5.28; N, 18.06%. $\lambda_{max}$(THF, 1 μM)/nm 655 (ε/$dm^3mol^{-1}cm^{-1}$ 251 000), 594 (40 200), 378 (150 300). $\nu_{max}$/$cm^{-1}$ 3417 (NH), 2961, 2918 (aliphCH), 1600, 1518, 1496, 1441, 1363, 1249,1143, 975. $\delta_C$(75 MHz; $CDCl_3$/pyridine-$d_5$) 158.48,157.91, 157.64, 157.59, 157.35, 157.18, 151.41, 151.04, 150.67, 150.35, 150.26,150.23, 150.15, 150.03, 147.90, 145.02, 144.13, 143.89, 143.83, 143.72, 143.62,140.92, 139.07, 136.54, 129.28, 128.80, 128.56, 128.37, 119.72, 50.59, 50.55, 50.45,50.37, 30.23, 30.15, 29.97, 29.92 some signals of TPyzPz core were not detected or fused together. $\delta_H$(300 MHz; $CDCl_3$/pyridine-$d_5$) 8.51-8.43 (3 H, m, ArH + NH), 8.26 (2 H, d, *J* = 7 Hz, ArH), 7.76 (2 H, t, *J* = 7 Hz, ArH), 7.72-7.62 (3 H, m, ArH, fused with solvent signal), 7.35 (1 H, t, *J* = 7 Hz, ArH), 2.29 (9 H, s, $CH_3$), 2.25 (9 H, s, $CH_3$), 2.24 (9 H, s, $CH_3$), 2.23 (18 H, s, $CH_3$), 2.11 (9 H, s, $CH_3$). *m/z* (MALDI-TOF) 1279.29 $[M]^+$, 1302.27 $[M+Na]^+$, 1318.25 $[M+K]^+$. Calc. for $C_{60}H_{65}N_{17}S_6Zn$: 1279.32.

**Synthesis of 2-(10*H*-phenothiazin-10-yl)-3-phenyl-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine (12dH)**

Synthesis of this compound followed the general procedure C with the modification that compound **4** was added into the reaction mixture in three portions each after 30 min. Details: 1 eq = 2 mmol, reaction time: 3 h, eluent for AAAB congener isolation: toluene:THF 50:1, eluent for further purification (twice): toluene:THF 50:1. Yield: 171 mg (7%) of dark green solid. Found: C, 59.44; H, 5.15; N, 17.00. Calc for $C_{66}H_{69}N_{17}S_7+H_2O$: C, 59.03; H, 5.33; N, 17.73%. $\lambda_{max}$(THF, 1 μM)/nm 673 (ε/$dm^3mol^{-1}cm^{-1}$ 140 300), 645 (101 600), 486 (53 500), 367 (113 900). $\nu_{max}$/$cm^{-1}$ 3300, 2961, 2918, 1518, 1479, 1459, 1362, 1312, 1278, 1252, 1231, 1140, 1081, 1017, 968. $\delta_C$(75 MHz; $CDCl_3$/pyridine-$d_5$) 160.50, 160.42, 160.12, 160.08, 158.09, 153.14, 152.69, 140.36, 143.18, 141.24, 141.19, 138.59, 128.93, 128.83, 128.76, 127.92, 127.55, 127.32, 124.97, 122.28, 51.67, 51.55, 51.39, 30.71, 30.64, 30.57, 30.34 92 some signals of TPyzPz core were not detected or fused together. $\delta_H$(300 MHz; $CDCl_3$/pyridine-$d_5$) 8.69 (2 H, d, *J*= 8 Hz, Ar-H), 8.33 (2 H, d, *J* = 7 Hz, Ar-H), 7.57-7.49 (2 H, m, Ar-H), 7.47-7.38 (3 H, m, Ar-H), 7.37-7.30 (2 H, m, Ar-H), 7.23-7.13 (2 H, m, Ar-H), 2.34 (9 H, s, $CH_3$ ), 2.18-2.13 (27 H, m, $CH_3$), 2.11 (18 H, s, $CH_3$). *m/z* (MALDI-TOF) 1323.39 $[M]^+$, 1346.37 $[M+Na]^+$, 1362.35 $[M+K]^+$. Calc. for $C_{66}H_{69}N_{17}S_7$: 1323.40.

**Synthesis of 2-(10*H*-phenothiazin-10-yl)-3-phenyl-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine magnesium(II) (12dMg)**

Synthesis of this compound followed the general procedure C. Eluent for chromatography purification: toluene:THF 20:1. Details: 1 eq = 38 μmol, Yield: 50 mg (99%) of dark green solid. Found: C, 56.86; H, 4.45; N, 16.84. Calc. for

$C_{66}H_{67}MgN_{17}S_7$+3$H_2O$: C, 56.58; H, 5.25; N, 16.99%. $\lambda_{max}$(THF, 1 μM)/nm 654 (ε/dm$^3$mol$^{-1}$cm$^{-1}$ 228 100), 594 (33 300), 383 (133 900). $\nu_{max}$/cm$^{-1}$ 2960, 2918, 1585, 1518, 1479, 1461, 1362, 1247, 1145, 1106, 1084, 974. $\delta_C$(75 MHz; $CDCl_3$/pyridine-$d_5$) 158.32, 158.28, 157.81, 157.54, 157.44, 153.70, 152.32, 151.88, 151.43, 150.25, 146.45, 144.57, 144.46, 144.38, 142.46, 137.47, 131.72, 130.45, 129.42, 128.71, 128.10, 127.32, 126.73, 126.54, 124.04, 120.63, 116.85, 50.66, 50.60, 50.53, 50.44, 50.33, 30.17, 30.11, 29.99 some signals of TPyzPz core were not detected or fused together. $\delta_H$(300 MHz; $CDCl_3$/pyridine-$d_5$) 8.22-8.15 (2 H, m, Ar-H), 8.10-8.02 (2 H, m, Ar-H), 7.53-7.22 (9 H, m, 9H, Ar-H), 2.33-2.12 (45 H, m, $CH_3$), 1.97 (9 H, s, 9H, $CH_3$). *m/z* (MALDI-TOF) 1345.33 [M]$^+$, 1368.33 [M+Na]$^+$, 1384.32 [M+K]$^+$. Calc. for $C_{66}H_{67}MgN_{17}S_7$: 1345.37,

**Synthesis of 2-(10*H*-phenothiazin-10-yl)-3-phenyl-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine zinc(II) (12dZn)**

Synthesis of this compound followed the general procedure C. Eluent for chromatography purification: toluene:THF 20:1. Details: 1 eq = 44 μmol, Yield: 57 mg (92%) of dark green solid. Found: C, 54.14; H, 4.88; N, 15.72. calc. for $C_{66}H_{67}N_{17}S_7Zn$+5$H_2O$: C, 53.62; H, 5.25; N, 16.11. $\lambda_{max}$(THF, 1 μM)/nm 652 (ε/dm$^3$mol$^{-1}$cm$^{-1}$ 238 700), 592 (34 700), 379 (133 200). $\nu_{max}$/cm$^{-1}$ 2961, 2918, 1583, 1519, 1479, 1458, 1362, 1247, 1143, 1108, 1092, 975. $\delta_C$(75 MHz; $CDCl_3$/pyridine-$d_5$) 159.79, 159.73, 159.34, 159.07, 155.12, 153.36, 152.96, 151.80, 145.12, 145.02, 144.91, 143.43, 138.52, 132.77, 131.46, 130.57, 129.82, 129.20, 128.50, 128.39, 127.81, 127.62, 125.42, 125.17, 121.75, 117.92, 51.79, 51.69, 51.59, 51.49, 31.01 some signals of TPyzPz core were not detected or fused together. $\delta_H$(300 MHz; $CDCl_3$/pyridine-$d_5$) 8.28-8.16 (2 H, m, Ar-H), 8.12-7.99 (2 H, m, Ar-H), 7.56-7.17 (9 H, m, Ar-H), 2.44-2.10 (45 H, m, $CH_3$), 1.96 (9 H, s, $CH_3$). *m/z* (MALDI-TOF) 1385.35 [M]$^+$, 1424.32 [M+K]$^+$. Calc. for $C_{66}H_{67}N_{17}S_7Zn$: 1385.31.

**Synthesis of 2-[2-(diethylamino)ethylsulfanyl]-3-phenyl-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine (12fH)**

Synthesis of this compound followed the general procedure A. Details: 1 eq = 0.77 mmol, eluent for magnesium AAAB congener isolation: chloroform:THF:pyridine 20:2:1, eluent for further purification of **12fH** (twice): chloroform:THF 20:1. Yield: 130 mg (13%) of dark green solid. Found: C, 56.93; H, 6.21; N, 18.77. Calc. for $C_{60}H_{75}N_{17}S_7$: C, 57.25; H, 6.01; N, 18.92%. $\lambda_{max}$(THF, 1 μM)/nm 671 (ε/dm$^3$mol$^{-1}$cm$^{-1}$ 190 300), 641 (154 400), 615 (50 400), 589 (35 800), 478 (66 200), 368 (152 300). ). $\nu_{max}$/cm$^{-1}$ 3290 (centrNH), 2963, 2918, 1519, 1452, 1363, 1315, 1280, 1231, 1141vs, 1081, 1015, 968, 955. $\delta_C$(75 MHz; $CDCl_3$/pyridine-$d_5$) 160.88, 160.15, 159.73, 158.99, 154.86, 147.22, 144.77, 143.36, 141.46, 141.08, 137.92, 130.19, 128.69, 51.82, 51.77, 51.66, 51.62, 50.94, 47.32, 30.95, 30.81, 30.66, 11.41 some signals of TPyzPz core were not detected or fused together. $\delta_H$(300 MHz; $CDCl_3$/pyridine-$d_5$) 8.48-8.38 (2 H, m, ArH), 7.88-7.72 (3 H, m, ArH), 4.29-4.15 (2 H, m, $SCH_2$), 3.43-3.33 (2 H, m, NC*H*$_2$CH$_2$), 3.17-2.96 (4 H, m, NC*H*$_2$CH$_3$), 2.23 (9 H, s, SCCH$_3$), 2.21 (9 H, s, SCCH$_3$), 2.20 (27 H, s, SCCH$_3$), 2.14 (9 H, s, SCCH$_3$), 1.32 (6 H, t, *J* = 7 Hz, $CH_3$). *m/z* (MALDI-TOF) 1258.23 [M+H]$^+$. Calc. for $C_{60}H_{75}N_{17}S_7$: 1257.44.

**Synthesis of 2-[2-(diethylamino)ethylsulfanyl]-3-phenyl-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine magnesium(II) (12fMg)**

Synthesis of this compound followed the general procedure C. Details: 1 eq = 32 μmol, eluent for chromatography purification: dichloromethane:THF 5:1. Yield: 40 mg (98%) of dark green solid. Found: C, 54.70; H, 5.94; N, 17.81. Calc. for $C_{60}H_{73}MgN_{17}S_7$+2$H_2O$: C, 54.71; H, 5.89; N, 18.08%. $\lambda_{max}$(THF, 1 μM)/nm 652 (ε/dm$^3$mol$^{-1}$cm$^{-1}$ 295 000), 626 (37 900), 591 (38 700), 383 (158 100). $\nu_{max}$/cm$^{-1}$ 2962, 2919, 1521, 1474, 1457, 1395, 1362, 1248, 1144vs, 1095, 975. $\delta_C$(75 MHz; $CDCl_3$/pyridine-$d_5$) 159.24, 158.37, 157.88, 154.32, 151.99, 151.77, 151.44, 151.14, 150.66, 150.52, 145.38, 145.25, 145.19, 138.03, 130.03, 128.69, 51.50, 51.34, 51.26, 50.78, 47.33, 31.28, 31.07, 30.90, 30.85, 11.39 some signals of TPyzPz core were not detected or fused together. $\delta_H$(300 MHz; $CDCl_3$/pyridine-$d_5$) 8.34 (2 H, d, *J* = 7 Hz, ArH), 7.83-7.67 (3 H, m, ArH), 4.35-4.03 (2 H, m, $SCH_2$, overlapped with signal of residual water), 3.47-3.23 (2 H, m, NC*H*$_2$CH$_2$), 3.21-2.92 (4 H, m, NC*H*$_2$CH$_3$), 2.29 (18 H, s, SCCH$_3$), 2.27 (18 H, s, SCCH$_3$), 2.19 (9 H, s, SCCH$_3$), 2.12 (9 H, s, SCCH$_3$), 1.43-1.21 (6 H, m, $CH_3$). *m/z* (MALDI-TOF) 1280.19 [M+H]$^+$. Calc. for $C_{60}H_{73}MgN_{17}S_7$: 1279.41.

**Synthesis of 2-[2-(diethylamino)ethylsulfanyl]-3-phenyl-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine zinc(II) (12fZn)**

Synthesis of this compound followed the general procedure C. Details: 1 eq = 32 μmol, eluent for chromatography purification: dichloromethane:THF 15:1. Yield: 40 mg (95%) of dark green solid. Found: C, 53.24; H, 5.69; N, 17.41. Calc. for $C_{60}H_{73}N_{17}S_7Zn$+2$H_2O$: C, 53.06; H, 5.71; N, 17.53%. $\lambda_{max}$(THF, 1 μM)/nm 650 (ε/dm$^3$mol$^{-1}$cm$^{-1}$ 237 800), 590 (32 300), 378 (126 900). $\nu_{max}$/cm$^{-1}$ 2961, 2919, 1521, 1454, 1362, 1249, 1144vs, 1095, 975, 961. $\delta_C$(75 MHz; $CDCl_3$/pyridine-$d_5$) 159.66, 158.96, 158.79, 158.58, 154.77, 152.39, 152.21, 151.94, 151.74, 151.57, 151.31, 151.19, 150.38, 148.30, 145.66, 145.08, 144.95, 144.89, 144.84, 144.75, 138.21, 130.12, 128.84, 51.71, 51.69, 51.60, 51.56, 51.55, 51.38, 51.07, 47.47, 31.28, 31.14, 31.00, 30.97, 30.83, 30.80, 11.86 some signals of TPyzPz core were not detected or fused together. $\delta_H$(300 MHz; $CDCl_3$/pyridine-$d_5$) 8.37-8.28 (2 H, m, ArH), 7.80-7.65 (3 H, m, ArH), 4.27-4.09 (2 H, m, $SCH_2$), 3.42-3.26 (2 H, m, NC*H*$_2$CH$_2$), 3.11-2.91 (4 H, m, NC*H*$_2$CH$_3$), 2.31-2.17 (45 H, m, SCCH$_3$), 2.12 (9 H, s, SCCH$_3$), 1.39-1.21 (6 H, m, $CH_3$). *m/z* (MALDI-TOF) 1320.15 [M+H]$^+$. Calc. for $C_{60}H_{73}N_{17}S_7Zn$: 1319.36.

**Synthesis of 2-butoxy-3-[2-(diethylamino)ethylsulfanyl]-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine (14fH)**

Synthesis of this compound followed the general procedure A. Details: 1 eq = 1.44 mmol, eluent for magnesium AAAB congener isolation: chloroform:THF:pyridine 10:2:1, eluent for further purification of **14fH** (twice): chloroform:THF:triethylamine 200:10:1. Yield: 550 mg (30%) of dark green solid. Found: C, 53.72; H, 6.22; N, 18.03. Calc. for $C_{58}H_{79}N_{17}OS_7$+2$H_2O$: C, 53.97; H, 6.48; N, 18.45%., $\lambda_{max}$(THF, 1 μM)/nm 668 (ε/dm$^3$mol$^{-1}$cm$^{-1}$ 153 800), 637 (126 600), 586 (30 500), 461 (52 900), 364 (127 300). $\nu_{max}$/cm$^{-1}$ 3300 (centrNH), 2962, 1522, 1457, 1396, 1362, 1286, 1232, 1141, 1097, 1082, 1017, 969. $\delta_C$(75 MHz; $CDCl_3$/pyridine-$d_5$) 159.88, 159.11, 158.28, 158.12, 158.00, 143.23, 141.22, 68.47, 51.82, 51.45, 51.41, 51.09, 47.24, 31.11, 31.03, 30.88, 30.80, 30.70, 30.67, 19.66, 14.27, 11.72 some signals of TPyzPz core were not detected or fused together. $\delta_H$(300 MHz; $CDCl_3$/pyridine-$d_5$) 5.19 (2 H, t, $J$ = 7 Hz, $OCH_2$), 4.18-4.10 (2 H, m, $SCH_2$, overlapped with signal of residual water), 3.39 (2 H, t, $J$ = 7 Hz, $NCH_2CH_2$), 3.07-2.94 (4 H, m, $NCH_2CH_3$), 2.36-2.11 (56 H, m, $SCCH_3$ + $OCH_2CH_2$), 1.98-1.83 (2 H, m, $OCH_2CH_2CH_2$), 1.37-1.25 (9 H, m, $CH_3$). *m/z* (MALDI-TOF) 1254.37 [M+H]$^+$. Calc. for $C_{58}H_{79}N_{17}OS_7$: 1254.47.

**Synthesis of 2-butoxy-3-[2-(diethylamino)ethylsulfanyl]-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine magnesium(II) (14fMg)**

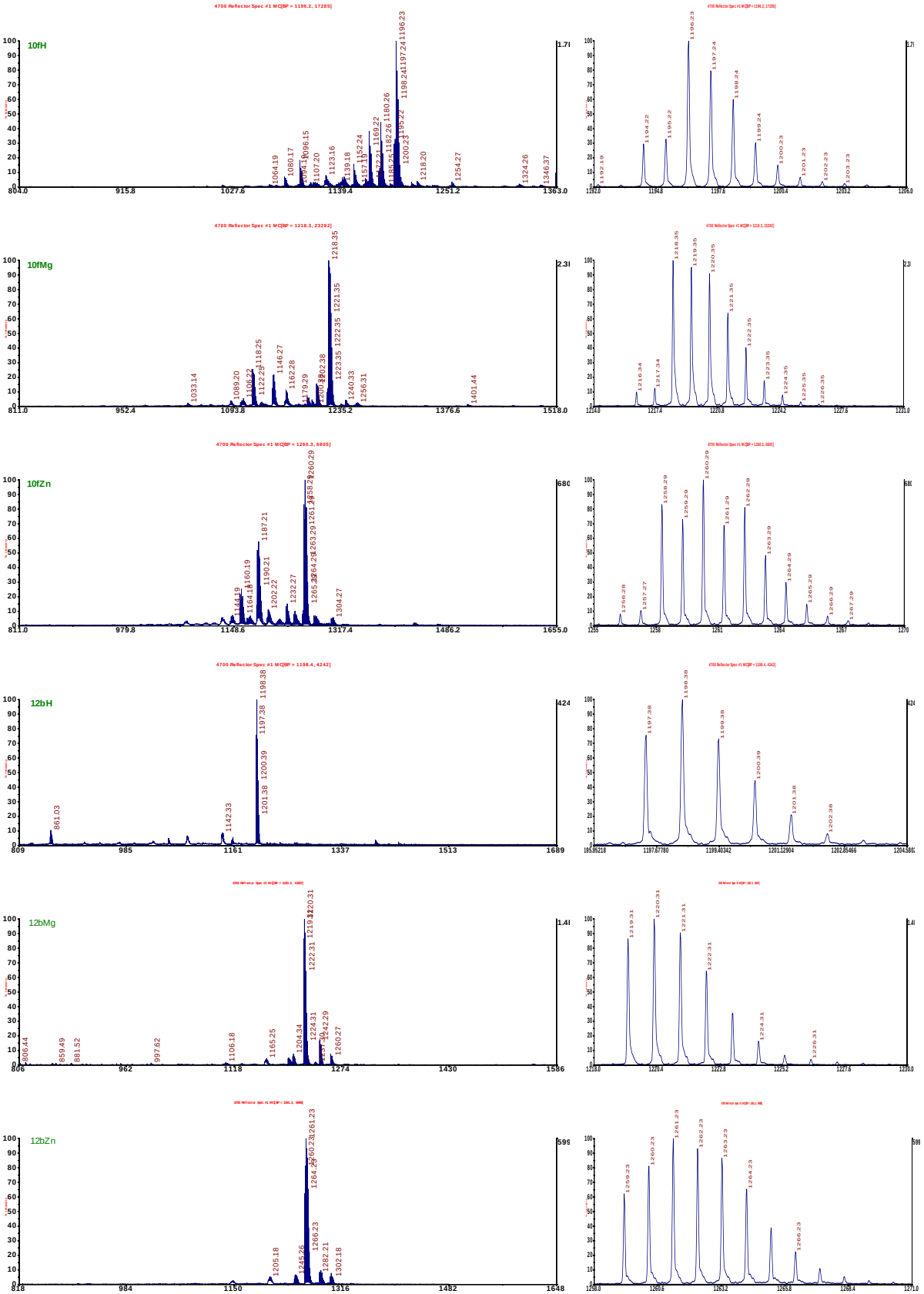
Synthesis of this compound followed the general procedure C. Details: 1 eq = 0.20 mmol, eluent for chromatography purification: chloroform:THF:triethylamine 100:5:1. Yield: 140 mg (55%) of dark green solid. Found: C, 53.32; H, 5.94; N, 18.00. Calc. for $C_{58}H_{77}MgN_{17}OS_7$+2$H_2O$: C, 53.05; H, 6.22; N, 18.13%. $\lambda_{max}$(THF, 1 μM)/nm 648 (ε/dm$^3$mol$^{-1}$cm$^{-1}$ 267 700), 588 (40 200), 382 (168 100). $\nu_{max}$/cm$^{-1}$ 2958, 2920, 1521, 1457, 1395, 1362, 1338, 1249, 1234, 1144, 1093, 1031, 974. $\delta_C$(125 MHz; $CDCl_3$/pyridine-$d_5$) 158.93, 158.19, 158.17, 158.00, 157.71, 151.31, 151.26, 151.04, 151.00, 150.86, 150.47, 145.21, 145.06, 145.04, 144.96, 144.17, 144.10, 68.28, 51.40, 51.30, 51.26, 51.23, 47.24, 31.19, 31.12, 31.06, 30.86, 30.85, 30.82, 30.81, 19.63, 14.15, 11.84 some signals of TPyzPz core were not detected or fused together. $\delta_H$(500 MHz; $CDCl_3$/pyridine-$d_5$) 5.22 (2 H t, $J$ = 7 Hz, $OCH_2$), 4.25-4.07 (2 H, m, $SCH_2$, overlapped with signal of residual water), 3.45-3.30 (2 H, m, $NCH_2CH_2$), 3.13-2.87 (4 H, m, $NCH_2CH_3$), 2.31-2.08 (56 H, m, $SCCH_3$ + $OCH_2CH_2$), 1.85 (2 H, sext, $J$ = 7 Hz, $OCH_2CH_2CH_2$), 1.42-1.27 (6 H, m, $NCH_2CH_3$), 1.24 (3 H, t, $J$ = 7 Hz, $CH_3$). *m/z* (MALDI-TOF) 1276.34 [M+H]$^+$. Calc. for $C_{58}H_{77}MgN_{17}OS_7$: 1275.44

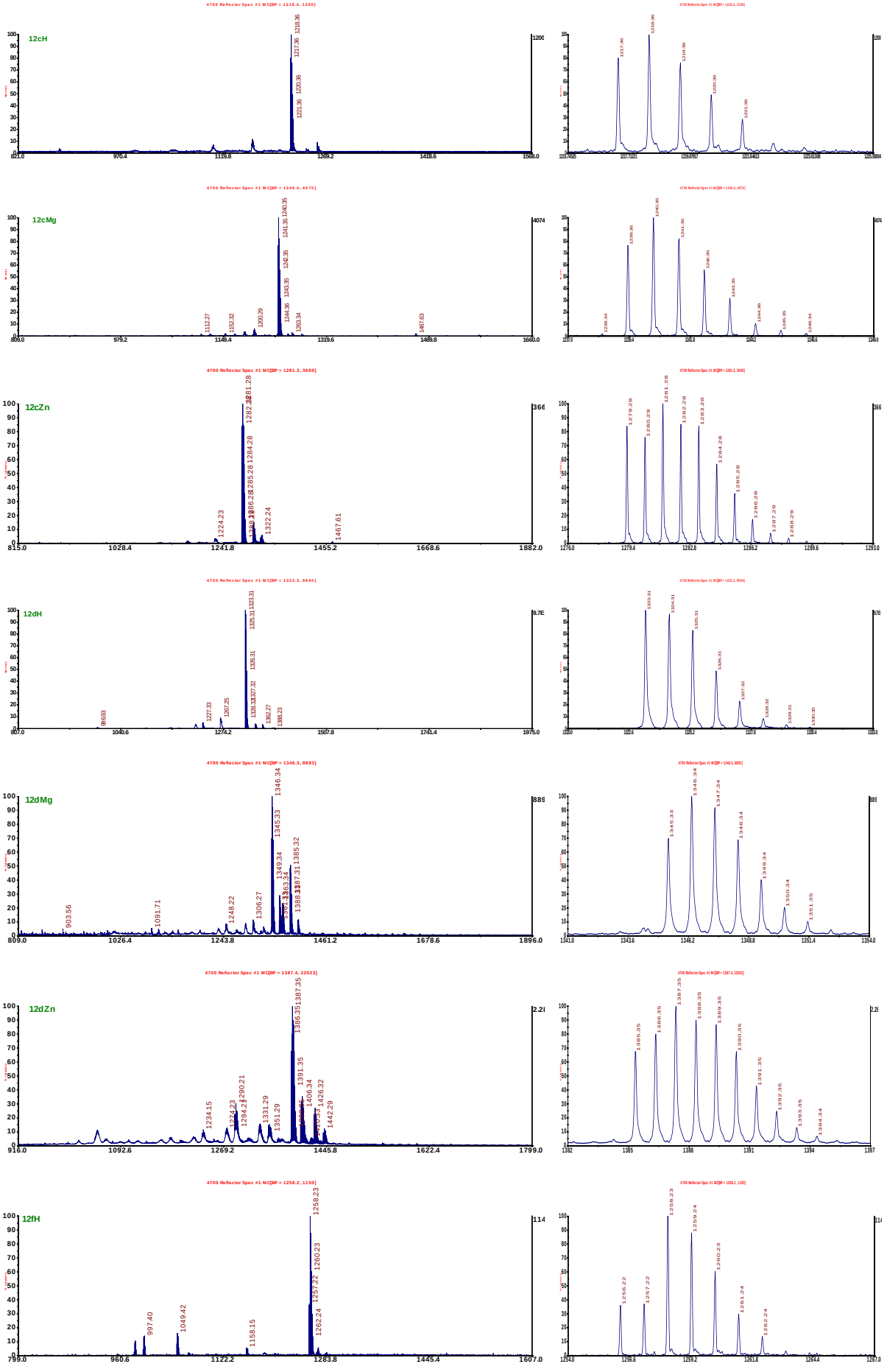
**Synthesis of 2-butoxy-3-[2-(diethylamino)ethylsulfanyl]-9,10,16,17,23,24-hexakis(*tert*-butylsulfanyl)-1,4,8,11,15,18,22,25-octaazaphthalocyanine zinc(II) (14fZn)**

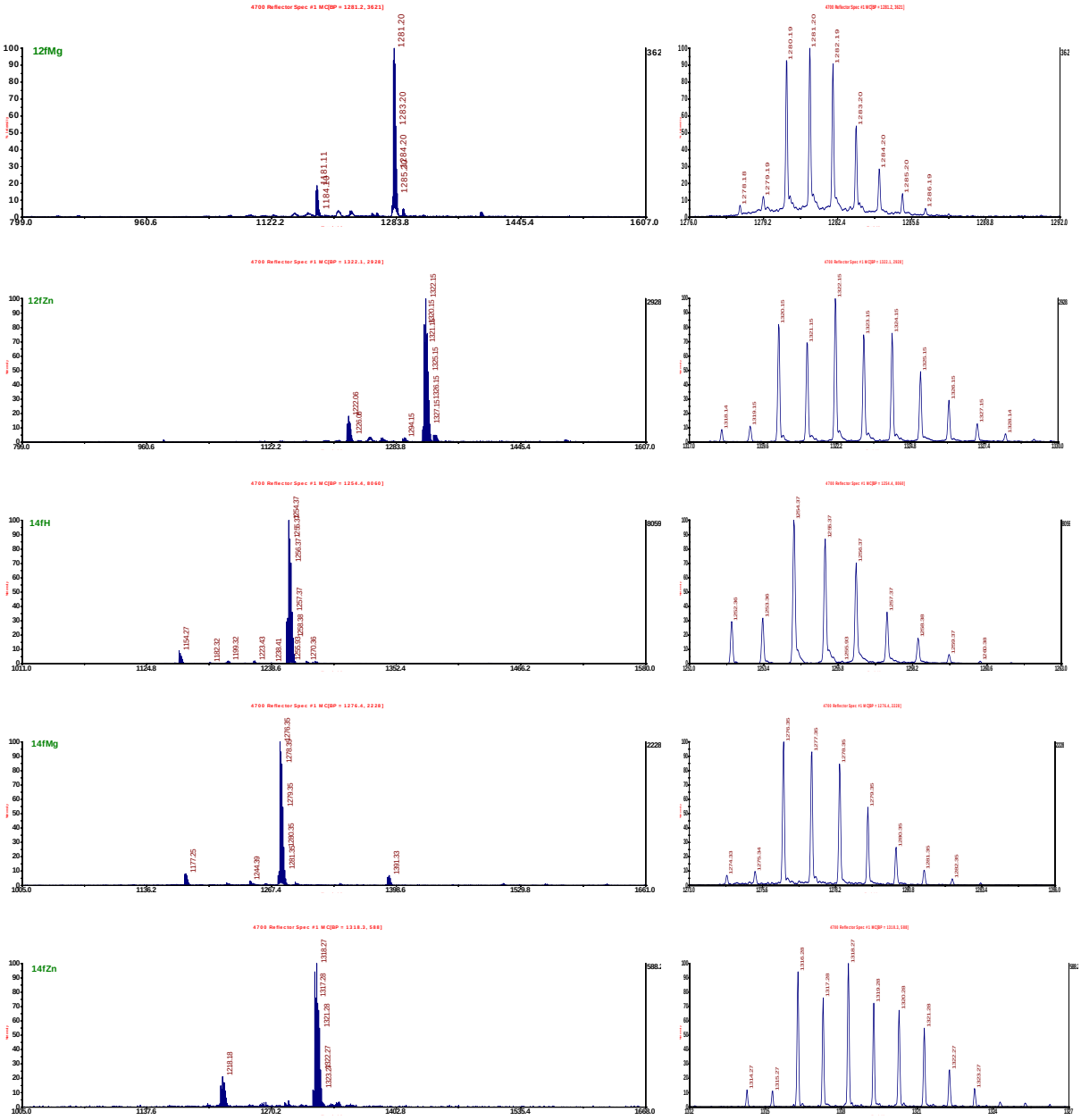
Synthesis of this compound followed the general procedure C. Details: 1 eq = 0.20 mmol, eluent for chromatography purification: chloroform:THF:triethylamine 100:5:0.25.Yield: 220 mg (84%) of dark green solid. Found: C, 52.03; H, 5.93; N, 17.48. Calc. for $C_{58}H_{77}N_{17}OS_7Zn$+$H_2O$: C, 52.14; H, 5.96; N, 17.82%. $\lambda_{max}$(THF, 1 μM)/nm 646 (ε/dm$^3$mol$^{-1}$cm$^{-1}$ 262 700), 586 (38 500), 376 (150 200). $\nu_{max}$/cm$^{-1}$ 2960, 2921, 1519, 1453, 1392, 1362, 1338, 1248, 1144, 1098, 1034, 976. $\delta_C$(75 MHz; $CDCl_3$/pyridine-$d_5$) 159.20, 158.62, 158.60, 158.21, 158.11, 151.71, 151.67, 151.42, 151.21, 150.81, 150.77, 144.78, 144.65, 144.61, 144.59, 144.56, 143.80, 68.36, 51.49, 51.39, 51.36, 50.97, 47.21, 31.12, 31.07, 30.99, 30.82, 30.79, 19.62, 14.14, 11.79 some signals of TPyzPz core were not detected or fused together. $\delta_H$(500 MHz; $CDCl_3$/pyridine-$d_5$) 5.23 (2 H t, $J$ = 7 Hz, $OCH_2$), 4.24-4.16 (2 H, m, $SCH_2$, overlapped with signal of residual water), 3.45-3.34 (2 H, m, $NCH_2CH_2$), 3.12-2.94 (4 H, m, $NCH_2CH_3$), 2.32-2.15 (56 H, m, $SCCH_3$ + $OCH_2CH_2$), 1.85 (2 H, sext, $J$ = 7 Hz, $OCH_2CH_2CH_2$), 1.40-1.28 (6 H, m, $NCH_2CH_3$), 1.23 (3 H, t, $J$ = 7 Hz, $CH_3$). *m/z* (MALDI-TOF) 1316.28 [M+H]$^+$. Calc. for $C_{58}H_{77}N_{17}OS_7Zn$: 1315.38

## Mass spectra

Mass spectra of metal-free, Mg and Zn complexes of **10f**, **12b**, **12c**, **12d**, **12f** and **14f**. Corresponding figure on right is enlarged area of isotopic cluster.




12cH
12cMg
12cZn
12dH
12dMg
12dZn
12fH


12fMg
12fZn
14fH
14fMg
14fZn

**Fluorescence spectra**

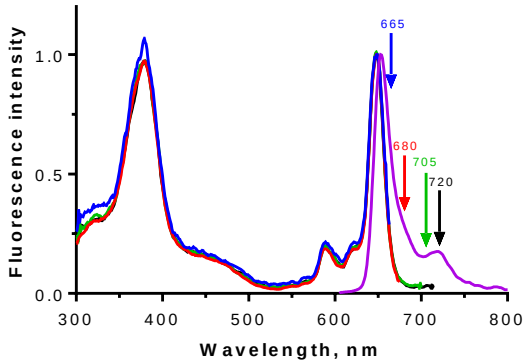



**Figure S1**. Fluorescence emission (magenta) and excitation spectra of compound **14fMg** in THF. Excitation spectra were collected while monitoring emission at different wavelengths: $\lambda_{em}$ = 665 nm (blue), $\lambda_{em}$ = 680 nm (red), $\lambda_{em}$ = 705 nm (green) and $\lambda_{em}$ = 720 nm (black). The spectra were normalized. Emission spectra were corrected for instrument response.

## Absorption spectra

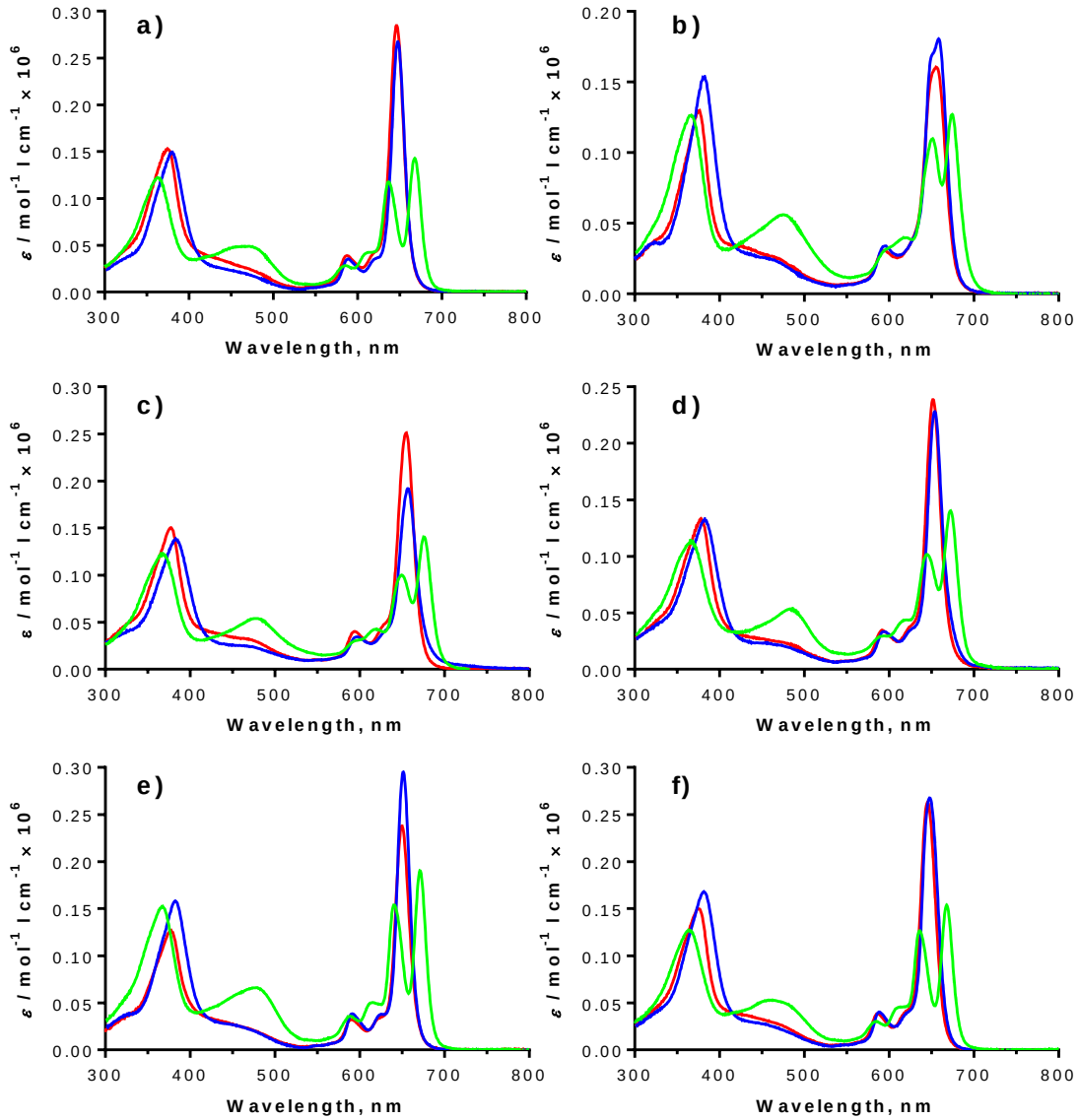



**Figure S2**. Absorption spectra of metal-free (green), magnesium (blue) and zinc (red) complexes of **10f** (a), **12b** (b), **12c** (c), **12d** (d), **12f** (e) and **14f** (f) in THF. Concentration of the solutions was 1 μM.

**Correlations with Hammett substituents constants**

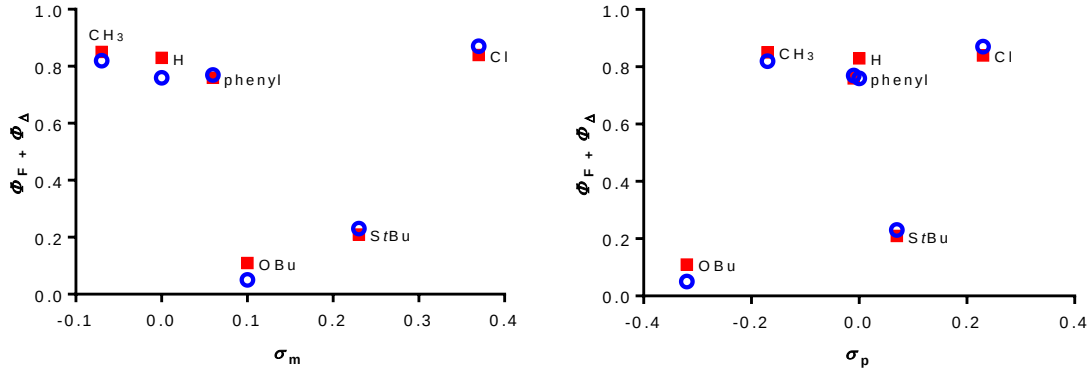



**Figure S3**. Correlations between $\Phi_\Delta + \Phi_F$ of TPyzPzs and Hammett constants $\sigma_m$ and $\sigma_p$ of the substituent in the *ortho* position to the donor. Zinc complexes (red squares), magnesium complexes (blue circles).

**Table S1**. Hammett substituents constants for selected substituents. Data taken from ref. [10].

| Substituent | $\sigma_m$ | $\sigma_p$ |
|---|---|---|
| Cl | 0.37 | 0.23 |
| $CH_3$ | -0.07 | -0.17 |
| H | 0 | 0 |
| phenyl | 0.06 | -0.01 |
| $SCH(CH_3)_2$[a] | 0.23 | 0.07 |
| OBu | 0.1 | -0.32 |

[a]this value was used for S*t*Bu substituent as it was the closest available substituent from the cited reference.

## Electrochemistry

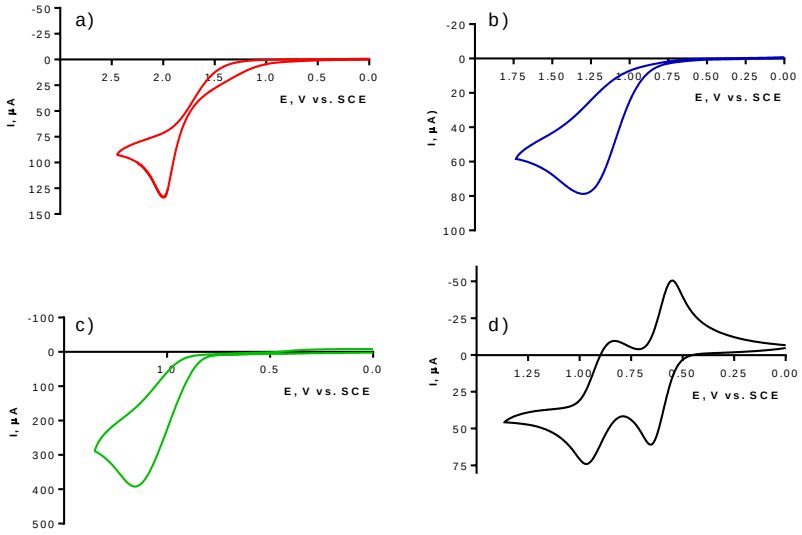



**Figure S4**. Cyclic voltammograms (acetonitrile, 100 mV/s, 0.1 M tetrabutylammonium hexafluorophosphate, 25 °C) of *n*-butylamine (a, red), *N*,*N*-diethylamine (b, blue), aniline (c, green) and phenothiazine (d, black).

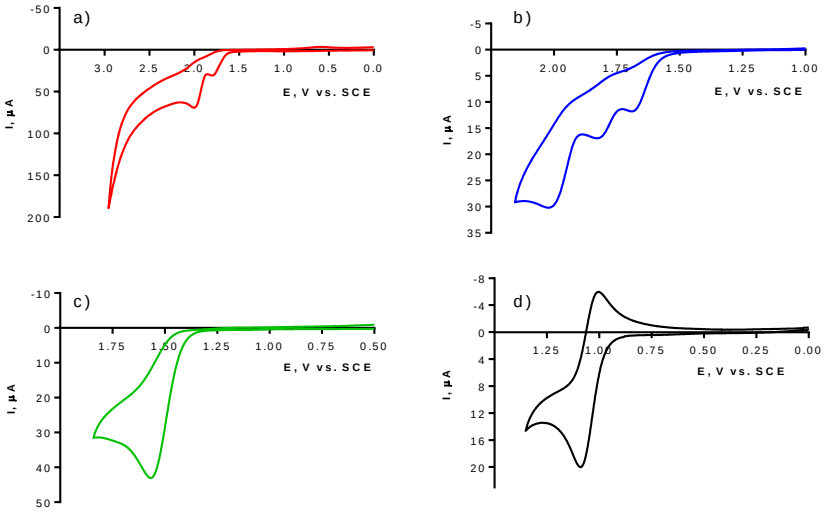



**Figure S5**. Cyclic voltammograms (acetonitrile, 100 mV/s, 0.1 M tetrabutylammonium hexafluorophosphate, 25 °C) of compound **1** (a, red), 5-diethylamino-6-phenylpyrazine-2,3-dicarbonitrile (b, blue), compound **2** (c, green) and compound **4** (d, black, only first oxidation showed).

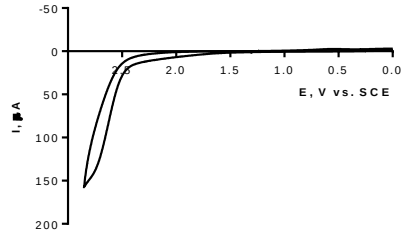



**Figure S6**. Cyclic voltammogram (acetonitrile, 100 mV/s, 0.1 M tetrabutylammonium hexafluorophosphate, 25 °C) of 5-chloro-6-phenylpyrazine-2,3-dicarbonitrile. No oxidation was observed up to 2.8 V vs. SCE.

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