Chemical Communication

Azaphthalocyanines with fused triazolo rings: formation of sterically stressed constitutional isomers

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Electronic Supplementary Information

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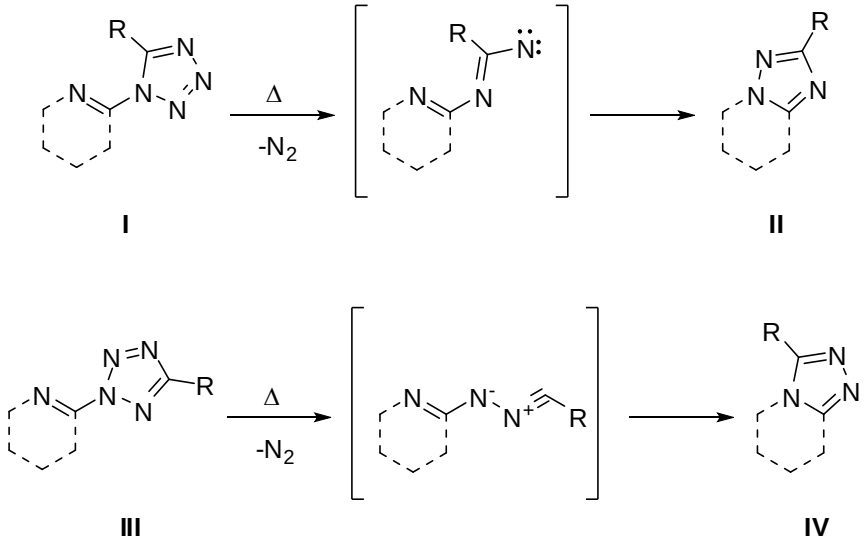
1. REACTION MECHANISM OF FORMATION OF TRIAZOLO-FUSED DERIVATIVES

Generally, 5-Substituted tetrazole carrying the electron-accepting group on its nitrogen atom opens the ring under elevated temperature. This process is followed by the release of nitrogen and, if possible, rearrangement to other heterocycle. Thus, heating the 5-substituted tetrazole containing six membered nitrogen heterocycle, azin-2-yl, attached to its nitrogen atom, was shown to lead to the formation of two possible bicyclic products **II** and **IV** (Scheme S1).[1] If azin-2-yl is attached to N1 of tetrazole, rearrangement of 5-substituted 1-(azin-2-yl)-1*H*-tetrazole (**I**) proceeds to 1*H*-1,2,4-triazole as a part of ortho-fused system (**II**), whereas rearrangement of 5-substituted 2-(azin-2-yl)-2*H*-tetrazole (**III**) proceeds to 4*H*-1,2,4-triazole as a part of ortho-fused heterocycle (**IV**) (Scheme S1). The release of nitrogen from tetrazole and subsequent rearrangements are reported to proceed under elevated temperatures.[1] In case of studied intermediates **4** it occurred under unusually mild conditions at rt.



Scheme S1.

2. SYNTHESIS

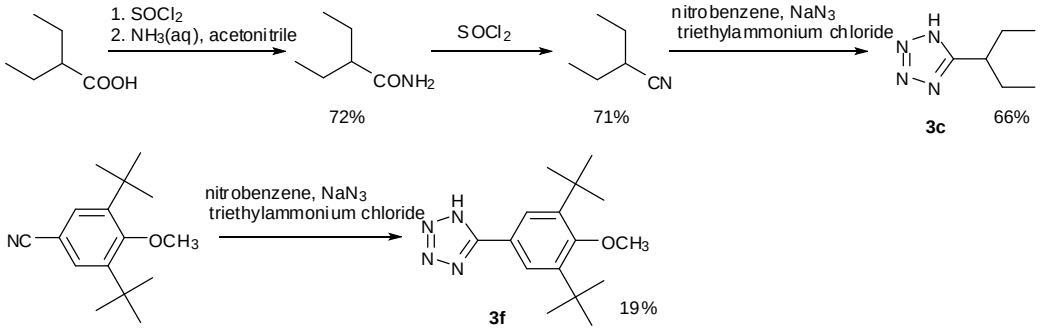
General

All organic solvents used 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) and used as received. 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 Electrothermal IA9200 Series Digital Melting Point apparatus (Electrothermal Engineeering Ltd., Southend-on-Sea, Essex, Great Britain). Infrared spectra were measured on Nicolet 6700 (ATR mode). ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury Vx BB 300 or VNMR S500 NMR spectrometer. Chemical shifts were reported as δ values in parts per million (ppm) and were indirectly referenced to tetramethylsilan (TMS) *via* the solvent signal. The elemental analysis was carried out on Automatic Microanalyser EA1110CE (Fisons Instruments S.p.A., Milano, Italy). The UV/vis spectra were recorded using a Shimadzu UV-2401PC spectrophotometer. Electrospray ionization mass spectroscopic (ESI MS) experiments were performed using LCQ Advantage Max (Thermo Finnigan, San Jose, USA) equipped with an ESI source. Mass spectra of the samples were obtained by direct infusion of each sample in a solvent system methanol/water/HCOOH 50/50/0.1 into the detector. Atmospheric pressure chemical ionization (APCI) was obtained using Agilent 500 Ion Trap LC/MS (Agilent Technologies, Santa Clara, California, USA) by direct infusion of the sample in methanol into the detector. Matrix assisted light desorption ionization – time of flight (MALDI-TOF) mass spectra were recorded in positive reflectron mode on a Voyager-DE STR mass spectrometer (Applied Biosystems, 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). High resolution (HR) MALDI-TOF mass spectra were obtained using the same instrument but each spot was further calibrated internally after addition of metal-free azaphthalocyanine with peripheral camphorquinone units[2] to the mass of its monomer (*m/z* 954.5030 $[M]^+$) and dimer that appeared in the mass spectrum as well (*m/z* 1909.0061 $[2M]^+$). Compound **2** was prepared according to published literature.[3]

Synthesis of 5-substituted tetrazoles

5-Substituted tetrazoles **3a**, **3b**, **3d** and **3e** were prepared according to literature.[4] Compounds **3c** and **3f** were synthesized according to Scheme S2.



Scheme S2. Synthesis of tetrazoles **3c** and **3f**.

2-Ethylbutanamide

2-Ethylbutanamide was prepared according to known procedure with few modifications.[5] 2-Ethylbutyric acid (37 g, 0.32 mol) was dissolved in thionyl chloride (30 ml) and heated in oil bath for 1 h at 100 °C. Afterwards, thionyl chloride was distilled off. The residue was dissolved in acetonitrile (50 ml) and added dropwise to aqueous ammonia (26 %, 150 ml) at 0 °C and then left to stir for 1 h. Reaction mixture was then extracted with ethyl acetate (3 × 100 mL), the organic phase was washed with 5 % Na_2CO_3 (2 × 100 ml), dried over Na_2SO_4 and concentrated. 2-Ethylbutanamide was prepared in sufficient purity and was used in a following reaction without further purification.

Yield: 26 g (72 %); isolated as colorless crystals

δ_H (300 MHz, $CDCl_3$) 0.91 (t, 6H, J = 7.4 Hz, CH_3), 1.38-1.69 (m, 4H, CH_2), 1.89-2.06 (m, 1H, CH), 5.76 (s, 1H, NH), 6.14 (s, 1H, NH).

δ_C (75 MHz, $CDCl_3$) 11.93, 25.58, 50.43, 178.85.

2-Ethylbutanenitrile

2-Ethylbutanamide (19.5 g, 0.17 mol) was dissolved in thionyl chloride (20 ml) and heated for 2 h at 100 °C. Then, the reaction mixture was distilled, taking the fraction with boiling point from 144-146 °C.

Yield: 11.6 g (71 %); isolated as colorless liquid

δ_H (300 MHz, $CDCl_3$) 1.07 (t, 6H, J = 7.4 Hz, CH_3), 1.62 (p, 4H, J = 7.6 Hz, CH_2), 2.40 (p, 1H, J = 7.1 Hz, CH).

δ_C (75 MHz, $CDCl_3$) 11.53, 25.09, 34.91, 122.08.

*5-(Pentan-3-yl)-1H-tetrazole (**3c**)*

2-Ethylbutanenitrile (2.0 g, 20.5 mmol), sodium azide (2.66 g, 41 mmol) and triethylamine hydrochloride (5.64 g, 41 mmol) were heated in nitrobenzene (50 ml) for 14 h under controlled microwave irradiation at 100 °C (infrared probe). Then, the reaction mixture was extracted with 5 % Na_2CO_3 (3 × 30 ml), aqueous phase was washed with diethylether (3 × 30 ml) and slowly acidified to pH = 1-2 with hydrochloric acid (evolution of CO_2). Then, the aqueous solution was saturated with NaCl and extracted by ethyl acetate (4 × 50 ml). Ethyl acetate was dried over Na_2SO_4 and evaporated. The crude product was purified by filtration through silica gel (washed with chloroform, eluted by ethyl acetate).

Yield: 1.9 g (66 %); isolated as white solid

m.p. 96.8-98.9 °C

Found: C, 51.28; H, 8.98; N, 39.85 %. Calc. for $C_6H_{12}N_4$: C, 51.41; H, 8.63; N, 39.97 %

ν_{max}/cm^{-1} 3122, 2973, 2950, 2935, 2913, 2874, 2849, 2791, 2745, 2689, 2626, 2592, 2467, 1566, 1541, 1468, 1458, 1434, 1375, 1331, 1264, 1244, 1105, 1084, 1050, 984, 930, 915, 880, 830, 786 and 711

δ_H (300 MHz, DMSO) 0.72 (t, 6H, J = 7.4 Hz, CH_3), 1.53-1.83 (m, 4H, CH_2), 2.79-2.97 (m, 1H, CH).

δ_C (75 MHz, DMSO) 11.54, 26.34, 38.11, 158.85.

*5-(3,5-di(tert-butyl)-4-methoxyphenyl)-1H-tetrazole (**3f**)*

3,5-Di(*tert*-butyl)-4-methoxybenzonitrile (490 mg, 2 mmol) prepared according to literature[6], sodium azide (169 mg, 2.6 mmol) and triethylamine hydrochloride (358 mg, 2.6 mmol) were heated in nitrobenzene (25 ml) for 6 h under controlled microwave irradiation at 120 °C (infrared probe). Then, the reaction mixture was extracted with 3 % NaOH (3 × 15 ml), aqueous phase was washed with diethylether (2 × 15 ml) and slowly acidified to pH = 1-2 with hydrochloric acid. Product was filtered under reduced pressure and dried on air.

Yield: 109 mg (19 %); isolated as white solid

m.p. 231.2-233.2 °C (dec.)

Found: C, 66.53; H, 8.75; N, 19.59 %. Calc. for $C_{16}H_{24}N_4O$: C, 66.64; H, 8.39; N, 19.43 %

ν_{max}/cm^{-1} 3091, 3025, 2973, 2960, 2231 (CN), 1817, 1764, 1594, 1485, 1464, 1408, 1396, 1358, 1263, 1230, 1205, 1171, 1120, 1002, 926, 912, 891, 885, 815, 798, 757, 722 and 657.

δ_H (300 MHz, DMSO) 1.42 (s, 18H, CH_3), 3.65 (s, 3H, OCH_3), 7.98 (s, 2H, ArH),

δ_C (75 MHz, DMSO) 161.80, 155.07, 144.74, 125.74, 118.69, 64.70, 35.88, 31.90.

Synthesis of compounds 5 and 6

5-Substituted tetrazole **3** (1.5 mmol) was dissolved in THF (5 ml) and stirred at ambient temperature. Subsequently, NaH (60 mg of 60 % dispersion in mineral oil, 1.5 mmol) was

added. After the evolution of gas was finished, the solution of compound **2** (305 mg, 1.3 mmol) in THF (2 ml) was added in several portions. The reaction mixture was stirred at ambient temperature for 48-72 h, until TLC showed full conversion (mobile phases are mentioned below). After completion of the reaction, THF was evaporated and the residue was dissolved in ethyl acetate (30 ml) and washed with water (3 × 30 ml). The organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The products **5** and **6** (or only **6** when **5** is produced only in trace amounts) were purified by column chromatography on silica. Advanced NMR experiments of compounds **5c** and **6c** confirmed or refused, respectively, important spatial correlations in the structure of these derivatives (Figures S1 and S2).

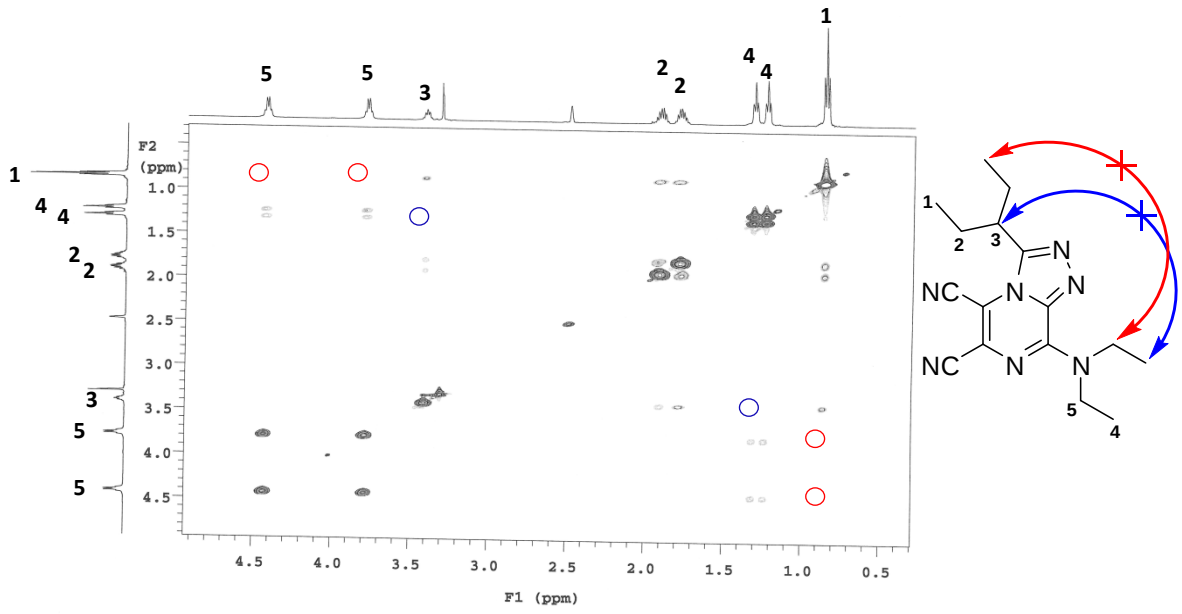


Figure S1: No correlations in NOESY spectrum of **6c** between hydrogens of *N*,*N*-diethylamino group and pentan-3-yl substituent suggest no spatial interaction and significant distance of these groups.

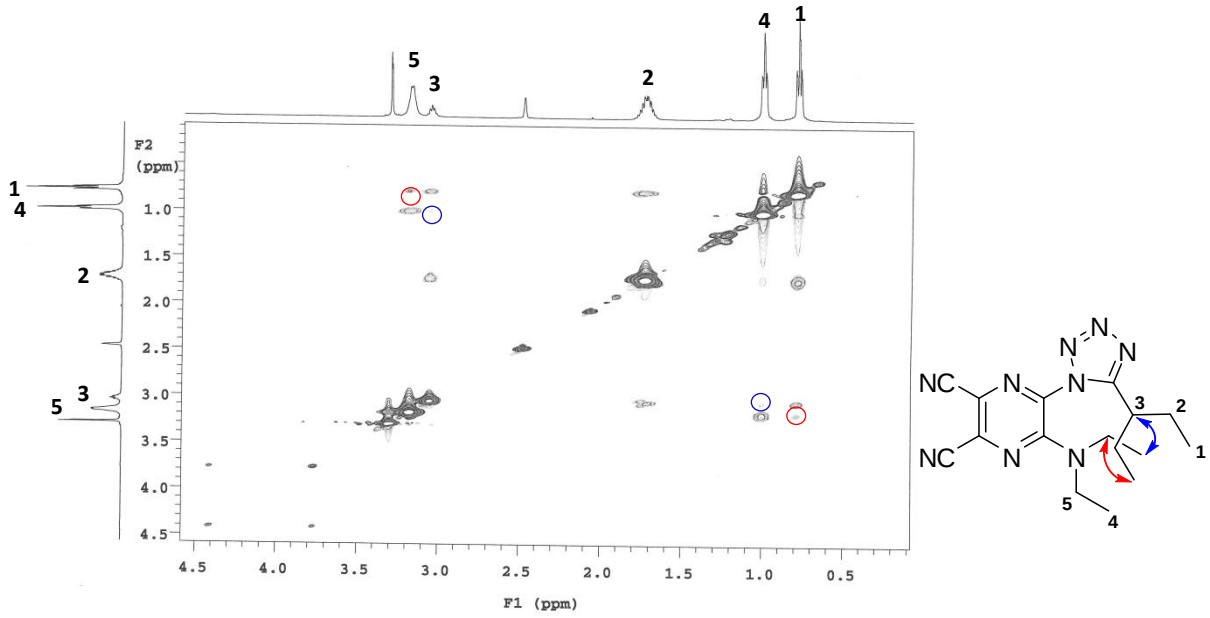


Figure S2: Free rotation of 5-(pentan-3-yl)-1H-tetrazol-1-yl substituent around single bond brings *N*,*N*-diethylamino group and pentan-3-yl substituent close each other resulting thus in significant correlations in NOESY spectrum of **5c**.

*5-(diethylamino)-6-(5-methyl-1H-tetrazol-1-yl)pyrazine-2,3-dicarbonitrile (**5a**)*

Mobile phase: hexane/ethyl acetate/triethylamine, 20:10:1. Yield: 30 % isolated as yellow oil.

ν_{max}/cm^{-1} 2982, 2231, 1568, 1521, 1435, 1384, 1357, 1287, 1188, 1158, 1129, 1098, 1078, 1035, 986, 875, 792, 708, 685 and 659

δ_H (500 MHz, DMSO) 1.00 (t, 6H, J = 7.0 Hz, CH_2CH_3), 2.64 (s, 3H, CH_3), 3.18-3.23 (m, 4H, NCH_2).

δ_C (126 MHz, DMSO) 8.93, 12.20, 44.59, 113.80, 114.21, 116.22, 128.62, 132.70, 149.74, 154.30.

m/z (ESI) 306 $[M+Na]^+$, 284 $[M+H]^+$, 256 $[M-N_2+H]^+$.

*5-(diethylamino)-6-(5-undecyl-1H-tetrazol-1-yl)pyrazine-2,3-dicarbonitrile (**5b**)*

Mobile phase: hexane/Et_2O, 3:1. Yield: 27 % isolated as yellow oil

ν_{max}/cm^{-1} 2926, 2855, 2231, 1567, 1508, 1440, 1396, 1357, 1287, 1188, 1157, 1128, 1080, 1035, 989, 876, 792, 721 and 662

δ_H (500 MHz, DMSO) 0.84 (t, 3H, *J* = 6.8 Hz, CH_3), 0.99 (t, 6H, *J* = 7.0 Hz, NCH_2CH_3), 1.20-1.36 (m, 16H, CH_2), 1.73 (p, 2H, *J* = 7.5 Hz, CH_2), 2.94 (t, 2H, *J* = 7.5 Hz, CH_2), 3.19 (q, 4H, *J* = 7.0 Hz, NCH_2).

δ_C (126 MHz, DMSO) 12.24, 14.11, 22.26, 22.48, 26.50, 28.42, 28.60, 28.86, 28.98, 29.12, 29.13, 31.45, 44.57, 113.79, 114.15, 116.23, 128.50, 132.74, 149.83, 157.48.

m/z (ESI) 446 $[M+Na]^+$, 424 $[M+H]^+$, 396 $[M-N_2+H]^+$.

*5-(diethylamino)-6-(5-(pentan-3-yl)-1H-tetrazol-1-yl)pyrazine-2,3-dicarbonitrile (**5c**)*

Mobile phase: hexane/ethyl acetate, 6:1. Yield: 13 %; isolated as yellow solid

m.p. 140.5-142.3 °C

Found: C, 56.81; H, 6.63; N, 36.88 %. Calc. for $C_{16}H_{21}N_9$: C, 56.62; H, 6.24; N, 37.14 %

ν_{max}/cm^{-1} 2965, 2937, 2876, 2230, 1570, 1520, 1499, 1444, 1408, 1384, 1357, 1292, 1276, 1251, 1190, 1160, 1130, 1093, 1036, 991, 913, 875, 859, 822, 794, 774 and 756

δ_H (500 MHz, DMSO) 0.74-0.83 (m, 6H, CH_3), 0.94-1.06 (m, 6H, NCH_2CH_3), 1.65-1.81 (m, 4H, CH_2), 3.01-3.09 (m, 1H, CH), 3.13-3.23 (m, 4H, NCH_2).

δ_C (126 MHz, DMSO) 11.20, 12.30, 25.80, 36.34, 44.44, 113.82, 114.20, 116.20, 128.57, 132.71, 150.03, 160.22.

m/z (ESI) 362 $[M+Na]^+$, 340 $[M+H]^+$, 312 $[M-N_2+H]^+$.

*8-(diethylamino)-3-methyl-[1,2,4]triazolo[4,3-a]pyrazine-5,6-dicarbonitrile (**6a**)*

Mobile phase: hexane/ethyl acetate/triethylamine, 20:10:1. Yield: 49 % isolated as white crystals.

m.p. 144.4-144.9 °C

Found: C, 56.61; H, 5.15; N, 37.74 %. Calc. for $C_{12}H_{13}N_7$: C, 56.46; H, 5.13; N, 38.41 %

ν_{max}/cm^{-1} 2985, 2942, 2238, 2216, 1578, 1556, 1509, 1461, 1425, 1418, 1380, 1365, 1354, 1321, 1287, 1261, 1197, 1166, 1139, 1094, 1071, 1040, 996, 922, 850, 787, 756, 728 and 656.

δ_H (500 MHz, DMSO) 1.23 (t, 3H, *J* = 7.0 Hz, NCH_2CH_3), 1.29 (t, 3H, *J* = 6.9 Hz, NCH_2CH_3), 2.82 (s, 3H, CH_3), 3.78 (q, *J* = 7.0 Hz, 2H, NCH_2), 4.41 (q, 2H, *J* = 6.9 Hz, NCH_2).

δ_C (126 MHz, DMSO) 11.67, 11.96, 14.43, 44.51, 45.91, 99.52, 111.97, 115.01, 125.23, 138.84, 147.64, 148.21.

m/z (ESI) 278 $[M+Na]^+$, 256 $[M+H]^+$.

*8-(diethylamino)-3-undecyl-[1,2,4]triazolo[4,3-a]pyrazine-5,6-dicarbonitrile (**6b**)*

Mobile phase: hexane/Et_2O, 3:1. Yield: 69 %; isolated as slightly yellow solid.

m.p. 58.4-60.6 °C

Found: C, 66.83; H, 8.77; N, 24.89 %. Calc. for $C_{22}H_{33}N_7$: C, 66.80; H, 8.41; N, 24.79 %

ν_{max}/cm^{-1} 2949, 2916, 2850, 2216, 1570, 1548, 1493, 1471, 1456, 1422, 1383, 1357, 1322, 1258, 1251, 1156, 1132, 1085, 1022, 997, 930, 848, 790, 753, 717 and 681.

δ_H (500 MHz, DMSO) 0.84 (t, 3H, *J* = 6.3 Hz, CH_3), 1.06-1.47 (m, 22H, CH_2 and NCH_2CH_3), 1.79 (p, 2H, *J* = 7.5 Hz, CH_2), 3.19 (t, 2H, *J* = 7.7 Hz, CH_2), 3.78 (q, 2H, *J* = 7.0 Hz, NCH_2), 4.41 (q, 2H, *J* = 6.9 Hz, NCH_2).

δ_C (126 MHz, DMSO) 11.95, 14.14, 14.43, 22.28, 25.00, 26.96, 28.50, 28.79, 28.89, 29.05, 29.17, 31.48, 44.52, 45.92, 99.15, 112.16, 115.07, 125.69, 138.88, 148.36, 150.59.

m/z (ESI) 418 $[M+Na]^+$, 396 $[M+H]^+$.

*8-(diethylamino)-3-(pentan-3-yl)-[1,2,4]triazolo[4,3-a]pyrazine-5,6-dicarbonitrile (**6c**)*

Mobile phase: hexane/ethyl acetate, 6:1. Yield: 83 %; isolated as white crystals

m.p. 130.3-131.4 °C

Found: C, 61.95; H, 7.21; N, 31.30 %. Calc. for $C_{16}H_{21}N_7$: C, 61.72; H, 6.80; N, 31.49 %

ν_{max}/cm^{-1} 2972, 2937, 2875, 2209, 1577, 1559, 1485, 1461, 1427, 1378, 1362, 1257, 1190, 1148, 1124, 1089, 992, 927, 877, 852, 828, 791 and 729.

δ_H (500 MHz, DMSO) 0.89-0.82 (m, 6H, CH_3), 1.24 (t, 3H, J = 7.2 Hz, NCH_2CH_3), 1.32 (t, 3H, J = 7.0 Hz, NCH_2CH_3), 1.74-1.84 (m, 2H, CH_2), 1.86-1.98 (m, 2H, CH_2), 3.34-3.47 (m, 1H, CH), 3.79 (q, 2H, J = 7.2 Hz, NCH_2), 4.43 (q, 2H, J = 7.0 Hz, NCH_2).

δ_C (126 MHz, DMSO) 11.51, 12.19, 14.68, 25.99, 38.63, 44.79, 46.23, 98.86, 112.71, 115.40, 126.74, 139.19, 148.89, 153.31.

m/z (ESI) 334 $[M+Na]^+$, 312 $[M+H]^+$.

*8-(diethylamino)-3-phenyl-[1,2,4]triazolo[4,3-a]pyrazine-5,6-dicarbonitrile (**6d**)*

Mobile phase: hexane/ethyl acetate, 5:1.Yield: 95 %; isolated as yellowish solid.

m.p. 161.9-162.7 °C

Found: C, 64.25; H, 5.03; N, 31.07 %. Calc. for $C_{17}H_{15}N_7$: C, 64.34; H, 4.76; N, 30.90 %

ν_{max}/cm^{-1} 2979, 2938, 2863, 2240, 2213, 1578, 1523, 1466, 1447, 1419, 1382, 1361, 1327, 1258, 1211, 1149, 1080, 1010, 923, 848, 780, 771 and 703.

δ_H (500 MHz, DMSO) 1.26 (t, 3H, J = 7.0 Hz, NCH_2CH_3), 1.36 (t, 3H, J = 6.9 Hz, NCH_2CH_3), 3.82 (q, 2H, J = 7.0 Hz, NCH_2), 4.48 (q, 2H, J = 6.9 Hz, NCH_2), 7.55-7.76 (m, 5H, ArH).

δ_C (126 MHz, DMSO) 11.97, 14.48, 44.64, 46.01, 99.42, 110.62, 115.04, 124.74, 126.47, 128.47, 130.96, 131.68, 138.82, 139.15, 148.40, 149.61.

m/z (ESI) 340 $[M+Na]^+$, 318 $[M+H]^+$.

*3-(adamantan-1-yl)-8-(diethylamino)-[1,2,4]triazolo[4,3-a]pyrazine-5,6-dicarbonitrile (**6e**)*

Yield: 97 %; isolated as yellowish solid.

m.p. 192.6-195.3 °C

ν_{max}/cm^{-1} 2988, 2968, 2905, 2852, 2210, 1569, 1547, 1474, 1481, 1424, 1403, 1385, 1363, 1338, 1316, 1281, 1246, 1141, 1097, 1077, 1018, 988, 939, 918, 857, 814, 785, 769, 728 and 684.

δ_H (300 MHz, DMSO) 1.23 (t, 3H, *J* = 6.9 Hz, NCH_2CH_3), 1.30 (t, 3H, *J* = 6.8 Hz, NCH_2CH_3), 1.69-1.90 (m, 6H, CH_2), 2.08-2.17 (m, 3H, CH), 2.30 (d, 6H, *J* = 3.0 Hz, CH_2), 3.78 (q, 2H, *J* = 6.9 Hz, NCH_2), 4.41 (q, 2H, *J* = 6.8 Hz, NCH_2).

δ_C (75 MHz, DMSO) 11.92, 14.40, 27.81, 35.31, 35.67, 39.51, 44.83, 46.18, 99.13, 115.57, 116.11, 128.46, 140.1, 149.20, 156.37.

m/z (ESI) 398 $[M+Na]^+$, 376 $[M+H]^+$.

*3-(3,5-di(tert-butyl)-4-methoxyphenyl)-8-(diethylamino)-[1,2,4]triazolo[4,3-a]pyrazine-5,6-dicarbonitrile (**6f**)*

Mobile phase: hexane/ethyl acetate 7:1, Yield: 94 %; isolated as yellow oil.

δ_H (500 MHz, DMSO) 1.26 (t, 3H, *J* = 6.9 Hz, NCH_2CH_3), 1.35 (t, 3H, *J* = 6.9 Hz, NCH_2CH_3), 1.41 (s, 18H, CH_3), 3.69 (s, 3H, OCH_3), 3.82 (q, 2H, *J* = 6.9 Hz, NCH_2), 4.47 (q, 2H, *J* = 6.9 Hz, NCH_2), 7.54 (s, 2H, ArH),

δ_C (126 MHz, DMSO) 11.98, 14.48, 31.77, 35.75, 44.59, 45.94, 64.82, 99.65, 110.48, 115.12, 119.07, 126.30, 129.39, 138.94, 143.40, 148.29, 150.00, 161.97.

m/z (APCI) 460.4 $[M+H]^+$.

Synthesis of azaphthalocyanines 1a-f

Synthesis was performed using general procedure mentioned in article.

*Magnesium azaphthalocyanine **1a***

Compound **6a** (280 mg, 1.18 mmol), Mg turnings (200 mg, 8.23 mmol), reflux for 6 h, mobile phase for column chromatography chloroform/toluene/MeOH/pyridine 50:50:10:3. Column chromatography was performed three times. Washed with MeOH. Yield: violet solid (95 mg, 33 %) – mixture of constitutional isomers.

λ_{max} (THF)/nm 377 (ε/dm^{3}mol^{-1}cm^{-1} 110 800), 496sh, 656 (44 600), 717 (87 400);

ν_{max}/cm^{-1} 2974, 2935, 1572, 1537, 1493, 1457, 1431, 1387, 1361, 1320, 1294, 1248, 1215, 1193, 1154, 1132, 1081, 1024, 959, 928, 868, 825, 767, 752, 743, 711 and 678;

δ_H (300 MHz, $CDCl_3/C_5D_5N$ 3:1) 1.14-1.61 (m, 24H, CH_2CH_3), 3.77 (bs, 6H, CH_3), 4.24 (bs, 6 H, CH_3), 4.41 (bs, 8H, CH_2, overlapped with signal of water), 4.64 (bs, 8H, CH_2);

δ_C (75 MHz, $CDCl_3/C_5D_5N$ 3:1) 12.80, 14.30, 14.76, 15.31, 16.57, 17.17, 44.37, 46,11, 116.05, 117.42, 118.03, 140.10, 140.58, 140.69, 140.72, 142.46, 143.19, 143.45, 144.42, 145.06, 145.73, 147.37, 147.72, 147.89 and 148.00;

m/z (HR MALDI TOF) 1044.4760 (calcd. for $[M]^+$ 1044.4780).

*Magnesium azaphthalocyanine **1b***

Compound **6b** (100 mg, 0.25 mmol), Mg turnings (43 mg, 1.77 mmol), reflux for 6 h, mobile phase for column chromatography toluene/chlotoform/pyridine 100:50:5. Column chromatography was performed twice. Yield: violet solid (34 mg, 33 %) – mixture of constitutional isomers.

λ_{max} (THF)/nm 378 (ε/dm^{3}mol^{-1}cm^{-1} 75 300), 488 (14 600), 642 (23 300), 680sh, 710 (80 100);

ν_{max}/cm^{-1} 2924, 2853, 1662, 1573, 1539, 1494, 1456, 1431, 1388, 1357, 1301, 1250, 1199, 1156, 1133, 1077, 1023, 990, 963, 931, 833, 784, 753, 732 and 679;

δ_H (300 MHz, $CDCl_3/C_5D_5N$ 3:1) 0.53-1.12 (several m, 92H, CH_2 and CH_3), 1.29-1.38 (m, 8H, CH_2), 1.98-2.14 (m, 8H, CH_2), 4.39 (bs, 16H, NCH_2), 5.14-5.25 (m, 8H, CH_2);

δ_C (75 MHz, $CDCl_3/C_5D_5N$ 3:1) 13.32, 13.43, 21.84, 21.98, 27.51, 28.05, 28.47, 28.66, 28.75, 28.80, 28.97, 29.00, 31.05, 31.19, 44.26, 118.50, 140.91, 145.02, 146.34, 149.87 and 151.87;

m/z (HR MALDI TOF) 1605.1005 (calcd. for $[M]^+$ 1605.1040).

Magnesium azaphthalocyanine ***1c***

Compound **6c** (380 mg, 1.22 mmol), Mg turnings (208 mg, 8.54 mmol), reflux for 6 h, mobile phase for column chromatography chloroform/toluene/pyridine 50:150:5, isomers eluted in the order $\boldsymbol{C_{4h}}$ (first), $\boldsymbol{C_{2v}}$, $\boldsymbol{C_s}$ (last). Positional isomers were further purified twice by column chromatography with toluene/chloroform/MeOH/pyridine 150:50:5:5. Washed with hexane. Yield: blue-green solids $\boldsymbol{C_{4h}}$ (130 mg, 34 %), $\boldsymbol{C_{2v}}$ (20 mg, 4 %) and $\boldsymbol{C_s}$ (32 mg, 5 %).

***1c**, isomer* $\boldsymbol{C_{4h}}$

λ_{max} (THF)/nm 380 (ε/dm^{3}mol^{-1}cm^{-1} 95 500), 491 (17 700), 646 (30 900), 684sh, 715 (112 400);

ν_{max}/cm^{-1} 2964, 2933, 2873, 1732, 1567, 1534, 1488, 1429, 1404, 1375, 1359, 1306, 1250, 1231, 1195, 1158, 1145, 1124, 1076, 1019, 987, 960, 931, 871, 837, 786, 769, 754, 734 and 687;

δ_H (500 MHz, $CDCl_3/C_5D_5N$ 3:1) 0.94 (t, 24H, *J*=7.0 Hz, CH_3), 1.37 (t, 24H, *J*=6.7 Hz, CH_3), 1.99-2.09 (m, 8H, CHCH_2), 2.98-2.42 (m, 8H, CHCH_2), 4.42-4.55 (br m, 16H, NCH_2), 6.89-6.97 (m, 4H, CH, overlapped with signal of solvent);

δ_C (75 MHz, $CDCl_3/C_5D_5N$ 3:1) 11.26, 13.65, 27.01, 39.30, 43.26, 118.77, 140.60, 145.43, 146.28, 148.95, 149.80 and 154.29;

m/z (HR MALDI TOF) 1268.7320 (calcd. for $[M]^+$ 1268.7284).

***1c**, isomer* $\boldsymbol{C_{2v}}$

λ_{max} (THF)/nm 383 (ε/dm^{3}mol^{-1}cm^{-1} 41 700), 540sh, 656 (12 300), 694sh, 726 (36 500);

ν_{max}/cm^{-1} 2965, 2934, 2874, 1652, 1558, 1506, 1488, 1472, 1456, 1443, 1398, 1378, 1356, 1309, 1253, 1205, 1193, 1156, 1124, 1076, 1019, 987, 961, 931, 872, 785, 753, 733 and 700;

δ_H (300 MHz, $CDCl_3/C_5D_5N$ 3:1) -0.42 (t, 6H, *J*=7.4 Hz, CH_3), 0.48-1.80 (m, 46H, 14×CH_3 and 2×CH_2), 1.89-2.57 (m, 12H, CHC*H*$_2$), 3.14-4.87 (m, 16H, NCH_2), 5.62-5.72 (m, 2H, CH), 6.87-6.96 (m, 2H, CH, overlapped with signal of solvent);

δ_C (75 MHz, $CDCl_3/C_5D_5N$ 3:1) 7.84, 11.21, 11.57, 11.79, 11.96, 22.12, 22.51, 26.91, 27.62, 28.30, 29.41, 38.18, 38.38, 39.63, 44.08, 45.26, 45.55, 116.35, 118.64, 138.82, 140.13, 140.91, 141.55, 144.80, 146.91, 147.06, 149.91, 150.28, 150.46, 150.68, 152.67 and 154.62;

m/z (HR MALDI TOF) 1268.7284 (calcd. for $[M]^+$ 1268.7284).

***1c**, isomer* $\boldsymbol{C_s}$

λ_{max} (THF)/nm 381 (ε/dm^{3}mol^{-1}cm^{-1} 30 600), 509sh, 655 (7 300), 729 (15 600);

ν_{max}/cm^{-1} 2965, 2933, 2874, 1652, 1568, 1538, 1455, 1428, 1401, 1376, 1357, 1303, 1252, 1205, 1192, 1156, 1146, 1123, 1076, 1019, 985, 958, 930, 872, 832, 767, 753, 733 and 710;

δ_H (300 MHz, $CDCl_3/C_5D_5N$ 3:1)) -0.47-(-0.39) (m, 6H, CH_3), 0.47-1.08 (m, 22H, 6×CH_3 and 2×CHC*H*$_2$), 1.30-1.53 (m, 24H, NCH_2CH_3), 1.89-2.04 (m, 2H, CHC*H*$_2$), 2.08-2.22 (m, 4H, CHC*H*$_2$), 2.22-2.38 (m, 4H, CHC*H*$_2$), 2.40-2.55 (m, 2H, CHC*H*$_2$), 4.10-4.77 (m, 16H, NCH_2), 6.78-6.87 (m, 1H, CH), 6.94-7.04 (m, 1H, CH), 5.56-5.71 (m, 2H, CH);

δ_C (75 MHz, $CDCl_3/C_5D_5N$ 3:1) 7.90, 7.93, 11.19, 11.21, 11.39, 11.56, 11.82, 11.93, 11.96, 14.00, 21.95, 22.30, 22.93, 26.89, 27.26, 27.51, 27.99, 28.12, 38.15, 39.58, 39.74, 43.72, 45.22, 116.41, 116.48, 118.69, 118.94, 140.89, 140.95, 141.55, 141.66, 144.92, 144.95,

145.56, 146.10, 146.35, 146.64, 146.79, 146.87, 149.68, 149.81, 149.90, 150.66, 151.23, 151.46, 154.58 and 154.66;

m/z (HR MALDI TOF) 1268.7222 (calcd. for $[M]^+$ 1268.7284).

Magnesium azaphthalocyanine ***1d***

Compound **6d** (430 mg, 1.35 mmol), Mg turnings (231 mg, 9.48 mmol), reflux for 8 h, mobile phase for column chromatography chloroform/THF 5:1, isomers eluted in the order $\boldsymbol{C_{4h}}$ (first), $\boldsymbol{C_s}$ (second). Column chromatography was performed three times. Yield green solid $\boldsymbol{C_{4h}}$ (washed with MeOH, 160 mg, 37 %) and violet solid $\boldsymbol{C_s}$ (washed with hexane, 155 mg, 35 %).

1d, *isomer* $\boldsymbol{C_{4h}}$

λ_{max} (THF)/nm 380 (ε/$dm^3mol^{-1}cm^{-1}$ 121 000), 485 (24 100), 645 (42 200), 682sh, 713 (170 800);

ν_{max}/cm^{-1} 2977, 2932, 2865, 1538, 1453, 1374, 1361, 1305, 1294, 1245, 1201, 1168, 1146, 1113, 1075, 1012, 956, 930, 865, 830, 765, 752, 733 and 696;

δ_H (500 MHz, $CDCl_3/C_5D_5N$ 3:1) 1.16 (t, 24H, *J*=6.4 Hz, CH_3), 4.05 (bs, 16H, CH_2, overlapped with the signal of water), 7.14 (t, 8H, *J*=7.6 Hz, ArH), 7.25-7.30 (m, 4H, ArH, overlapped with solvent signal), 8.06 (d, 8H, J=7.6 Hz, ArH);

δ_C (75 MHz, $CDCl_3/C_5D_5N$ 3:1) 13.21, 43.42, 118.29, 127.22, 128.32, 128.97, 129.01, 140.90, 144.60, 147.80, 148.37, 149.34, 149.89;

m/z (HR MALDI TOF) 1292.5349 (calcd. for $[M]^+$ 1292.5406).

1d, *isomer* $\boldsymbol{C_s}$

λ_{max} (THF)/nm 385 (ε/$dm^3mol^{-1}cm^{-1}$ 95 100), 532 (20 200), 655 (36 800); 724 (110 500);

ν_{max}/cm^{-1} 2976, 2933, 2859, 1652, 1539, 1489, 1454, 1439, 1373, 1360, 1307, 1247, 1221, 1197, 1146, 1115, 1075, 1012, 967, 954, 929, 867, 824, 766, 750, 732 and 697;

δ_H (300 MHz, $CDCl_3/C_5D_5N$ 3:1) 1.18 (t, 6H, *J*=7.0 Hz, CH_3), 1.22-1.30 (m, 6H, CH_3), 1.36-1.51 (m, 12H, CH_3), 4.30-4.57 (m, 16H, CH_2), 6.31-6.45 (m, 4H, ArH), 6.45-6.59 (m, 2H, ArH), 6.93-7.00 (m, 2H, ArH), 7.05-7.22 (m, 6H, ArH), 7.24-7.34 (m, 2H, ArH, overlapped with the signal of solvent), 8.05-8.18 (m, 4H, ArH);

δ_C (75 MHz, $CDCl_3/C_5D_5N$ 3:1) 13.37, 43.50, 43.84, 44.78, 114.32, 114.35, 114.99, 117.61, 117.83, 125.53, 125.61, 126.85, 126.93, 127.25, 127.29, 127.65, 127.89, 127.99, 128.17, 128.34, 128.42, 128.50, 128.63, 128.71, 128.78, 129.08, 129.13, 129.22, 140.59, 140.61, 140.86, 141.00, 141.23, 141.27, 143.57, 144.09, 144.65, 144.90, 145.14, 145.52, 145.98, 146.03, 146.16, 146.23, 146.72, 147.80, 147.93, 148.89, 149.91, 150.03, 150.14, 150.23, 150.30, 150.61, 150.68 and 151.32;

m/z (HR MALDI TOF) 1292.5408 (calcd. for $[M]^+$ 1292.5406).

Magnesium azaphthalocyanine ***1e***

Compound **6e** (100 mg, 0.27 mmol), Mg turnings (46 mg, 1.86 mmol), reflux for 24 h, mobile phase for column chromatography chloroform/THF 20:1. Column chromatography was performed three times. Washed with MeOH. Yield: violet solid (16 mg, 16 %).

λ_{max} (THF)/nm 374 (ε/dm^{3}mol^{-1}cm^{-1} 39 300), 483 (7 800), 650 (12 000), 688sh, 720 (50 600);

ν_{max}/cm^{-1} 2910, 2850, 1652, 1558, 1541, 1434, 1375, 1359, 1303, 1257, 1235, 1197, 1152, 1138, 1097, 1076, 1035, 1015, 982, 957, 929, 870, 828, 785, 750, 734, 709 and 684;

δ_H (300 MHz, $CDCl_3/C_5D_5N$ 3:1,) 0.99-1.26 (m, 24H, CH_3), 1.43-1.58 (m, 16H), 1.74-1.92 (m, 20H), 2.72 (d, 12H, *J*=11.8 Hz), 3.52 (d, 12H, *J*=11.7 Hz), 4.00 (bs, 16H, NCH_2);

δ_C (75 MHz, $CDCl_3/C_5D_5N$ 3:1) 28.18, 36.16, 37.43, 39.79, 120.47, 142.17, 144.54, 149.43, 150.66 and 159.80;

m/z (HR MALDI TOF) 1524.8568 (calcd. for $[M]^+$ 1524.8536).

Magnesium azaphthalocyanine ***1f***

Compound **6f** (150 mg, 0.33 mmol), Mg turnings (55 mg, 2.29 mmol), reflux for 21 h, mobile phase for column chromatography chloroform/toluene/THF 100:50:5. Column chromatography was performed twice. Washed with MeOH. Yield: violet-blue solid (48 mg, 32 %).

λ_{max} (THF)/nm 385 (ε/$dm^3mol^{-1}cm^{-1}$ 113 300), 495 (19 700), 654 (42 500), 698sh, 724 (161 800);

ν_{max}/cm^{-1} 2964, 2856, 1636, 1542, 1441, 1426, 1391, 1359, 1311, 1244, 1203, 1171, 1149, 1118, 1077, 1018, 962, 932, 888, 877, 830, 789, 767, 734, 711 and 694;

δ_H (300 MHz, $CDCl_3/C_5D_5N$ 3:1) 0.88 (bs, 72H, CCH_3), 1.11-1.22 (m, 24H, CH_2CH_3), 3.42 (s, 12H, OCH_3), 4.41-5.09 (br m, 16H, NCH_2, overlapped with the signal of water), 8.34 (s, 8H, ArH);

δ_C (75 MHz, $CDCl_3/C_5D_5N$ 3:1) 11.52, 13.88, 31.04, 35.07, 44.64, 63.69, 117.93, 126.52, 140.82, 141.50, 145.14, 147.78, 147.90, 149.36, 150.67 and 160.91;

m/z (HR MALDI TOF) 1861.0820 (calcd. for $[M]^+$ 1861.0837).

3. PHOTOPHYSICAL AND PHOTOCHEMICAL MEASUREMENTS

General

The UV/vis spectra were recorded using a Shimadzu UV-2401PC spectrophotometer. The fluorescence spectra were obtained by an AMINCO-Bowman Series 2 luminescence spectrometer. Zinc phthalocyanine (ZnPc) was purchased from Aldrich.

Singlet oxygen quantum yields

Quantum yields of singlet oxygen formation (Φ_Δ) were determined according to a previously published procedure in pyridine using the decomposition of chemical trap 1,3-diphenylisobenzofuran (DPBF).[7] Unsubstituted zinc phthalocyanine (ZnPc) was used as a reference (Φ_Δ = 0.61 in pyridine[8]). The procedure was as follows: 2.5 mL of a stock solution of DPBF in pyridine (5×10^{-5} M) was transferred into a 10 × 10 mm quartz optical cell and bubbled with oxygen for 1 min. Defined amount of concentrated stock solution of the tested compound in pyridine (usually 30 μL) was then added. Absorbance of the final solution in a Q-band maximum was always about 0.1. The solution was stirred and irradiated for defined times using a halogen lamp (Tip, 300 W). Incident light was filtered through a water filter (6 cm) and an orange HOYA G filter to remove heat and light under 506 nm, respectively. The decrease of DPBF absorbance with irradiation time was monitored at 418 nm. All calculations were performed according to the previously published procedure.[7] All experiments were performed three times and data presented in the paper represent a mean of these three experiments. The estimated error is 15 %.

Fluorescence quantum yields

Fluorescence quantum yields (Φ_F) were determined in pyridine by the comparative method[9] using ZnPc as a reference (Φ_F = 0.30 in chloronaphthalene[10]). Both reference and sample were excited at 608 nm. Absorbance of the solution in a Q-band maximum was always below

0.1, absorbance at excitation wavelength was always below 0.03. The Φ_F values were calculated using Equation 1:

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

where F is the integrated area under the emission spectrum, A is absorbance at excitation wavelength, n is the refractive index of the solvent. Superscripts R and S correspond to the reference and sample, respectively. All experiments were performed three times and data represent a mean of these three experiments. The estimated error is 15 %.

4. ADVANCED NMR EXPERIMENTS OF CONSTITUTIONAL ISOMERS OF 1c IN $CDCl_3$/PYRIDINE-D_5 (3:1)

COSY spectra of 1c

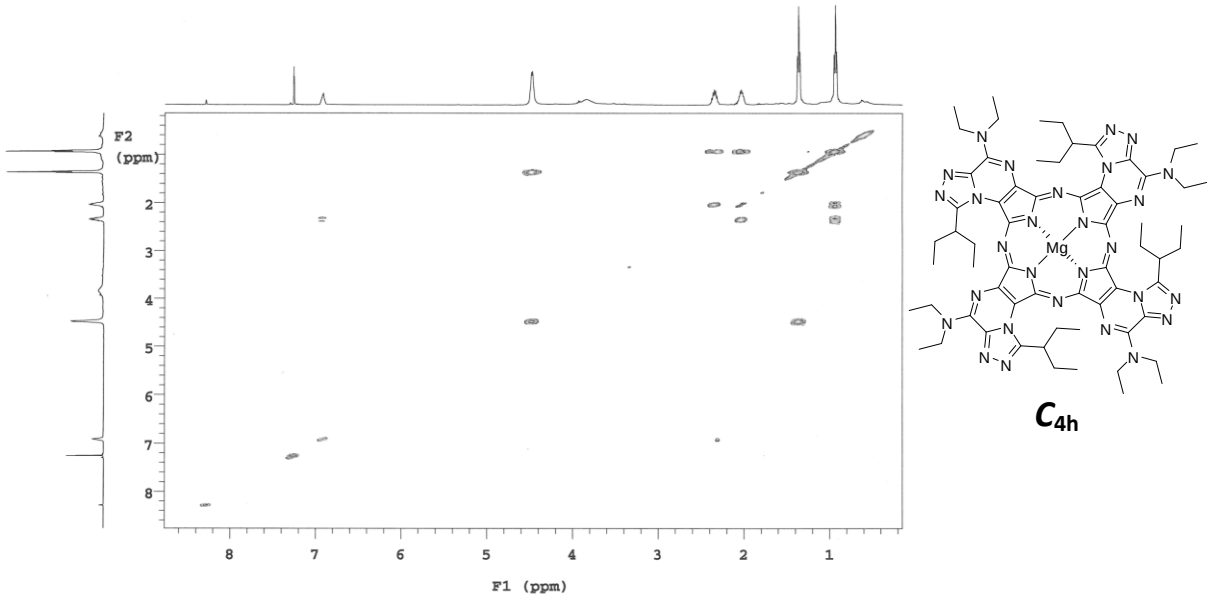


Figure S3:

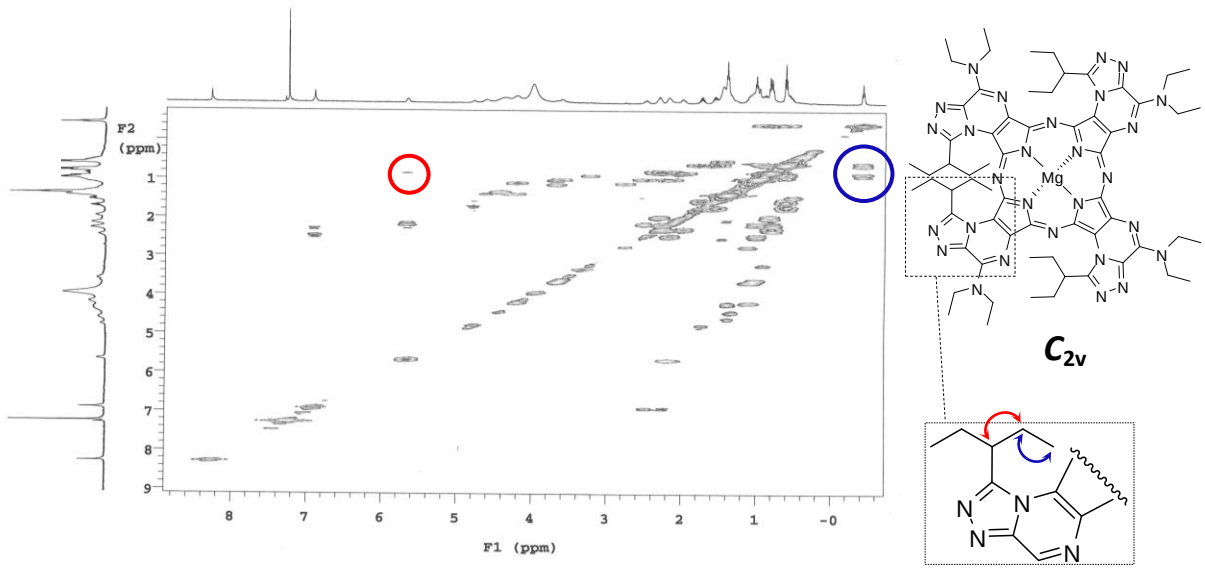


Figure S4: Two ethyls of pentan-3-yl substituents of C_{2v} isomer are strongly shielded because they are oriented over macrocyclic aromatic system. For this reason methyls are located at -0.41 ppm and correlate (COSY) with two methylenes at 0.88 and 0.62 ppm (blue) that are overlapped with the signals of the rest of methyls. The methylenes also weakly correlate with CH of pentan-3-yl at 5.65 ppm (red).

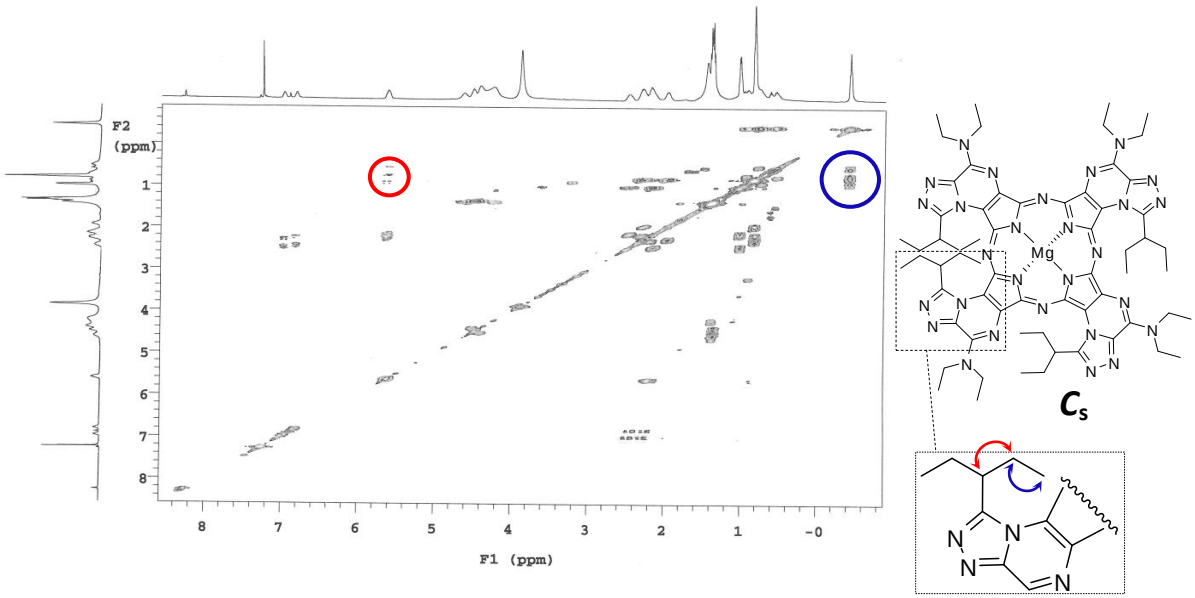


Figure S5: Two ethyls of pentan-3-yl substituents of C_s isomer are strongly shielded because they are oriented over macrocyclic aromatic system. For this reason methyls are located at -0.47-(-0.39) ppm as multiplet and correlate (COSY) with two methylenes in the multiplet located at 0.47-1.08 (blue). The methylenes also correlate with CH of pentan-3-yl in multiplet located at 5.56-5.71 ppm (red).

gHSQC spectra of 1c

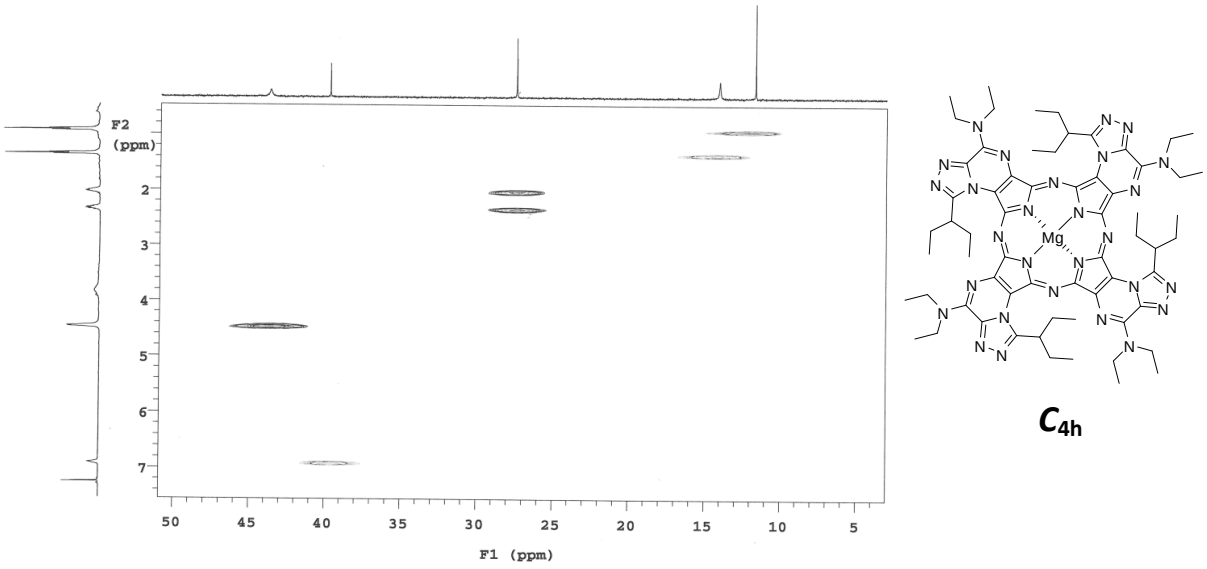


Figure S6: gHSQC spectrum of constitutional isomer C_{4h} of compound **1c** in $CDCl_3$/pyridine-d_5 3:1

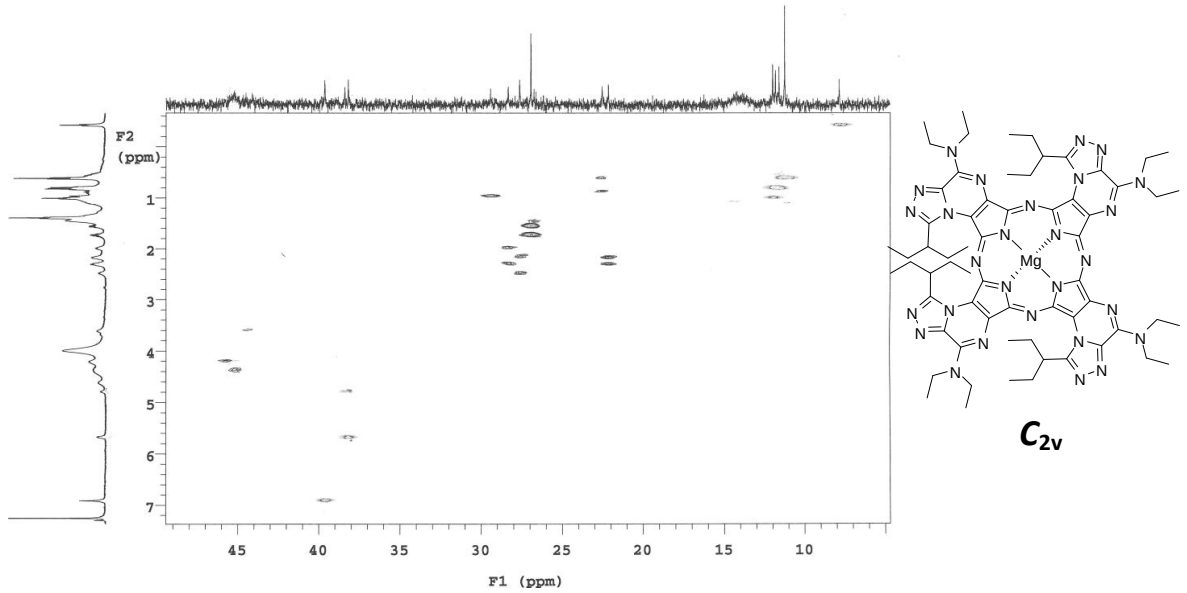


Figure S7: gHSQC spectrum of constitutional isomer C_{2v} of compound **1c** in $CDCl_3$/pyridine-d_5 3:1

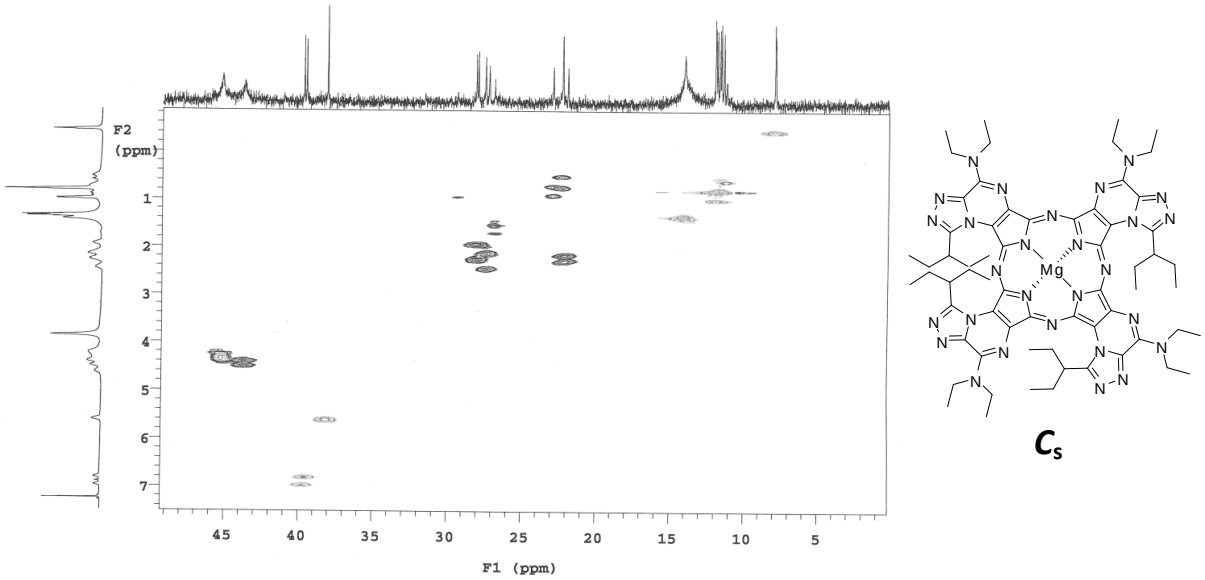


Figure S8: gHSQC spectrum of constitutional isomer C_s of compound **1c** in $CDCl_3$/pyridine-d_5 3:1

5. NMR SPECTRA OF CONSTITUTIONAL ISOMERS OF 1d IN $CDCl_3$/PYRIDINE-D_5 (3:1)

^{1}H NMR spectrum of 1d (C4h)

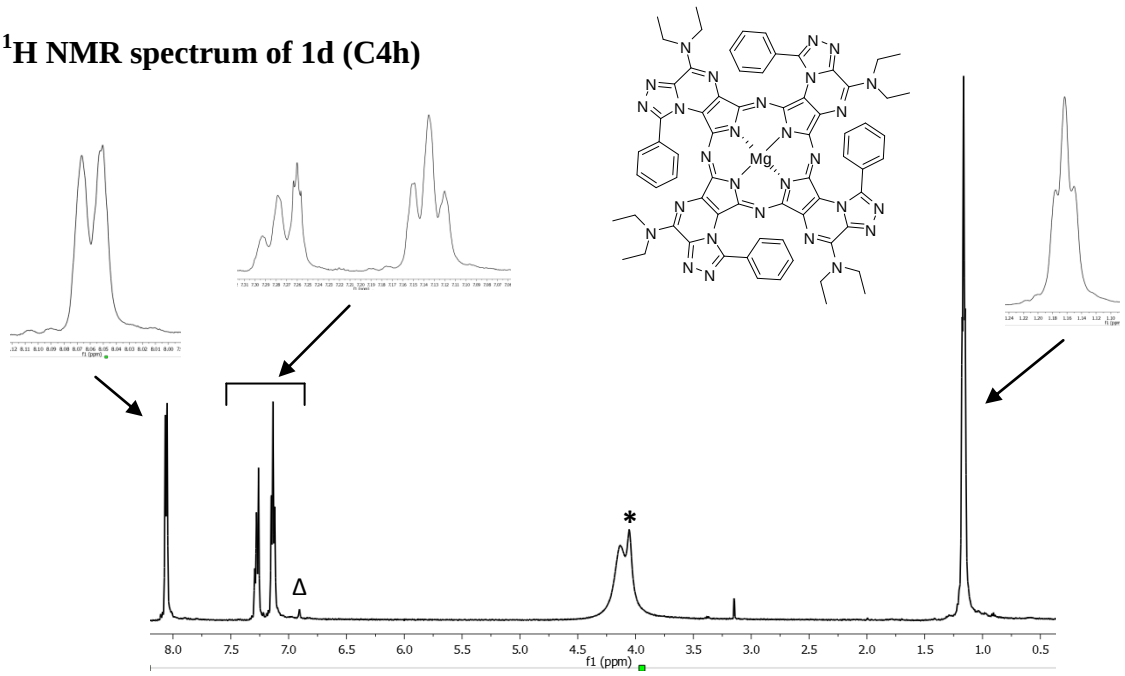


Figure S11: Asterisk indicates signal of water and triangle one of the residual signals of non-deutered pyridine. The rest of non-deutered pyridine signals and the signal of non-deutered chloroform are overlapped with the signals of **1d**.

^{13}C NMR spectrum of 1d (C4h)

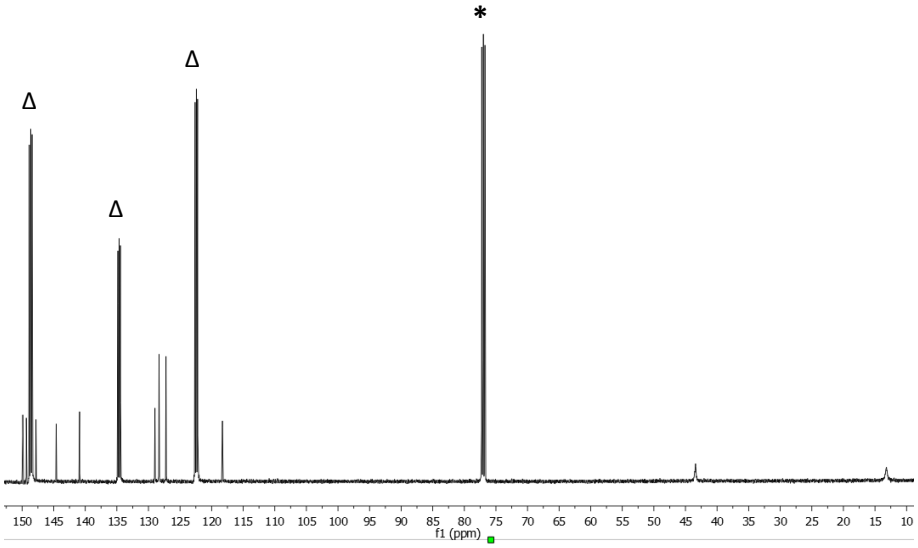


Figure S12: Asterisk indicates signal of chloroform, triangles pyridine.

^{1}H NMR spectrum of 1d (Cs)

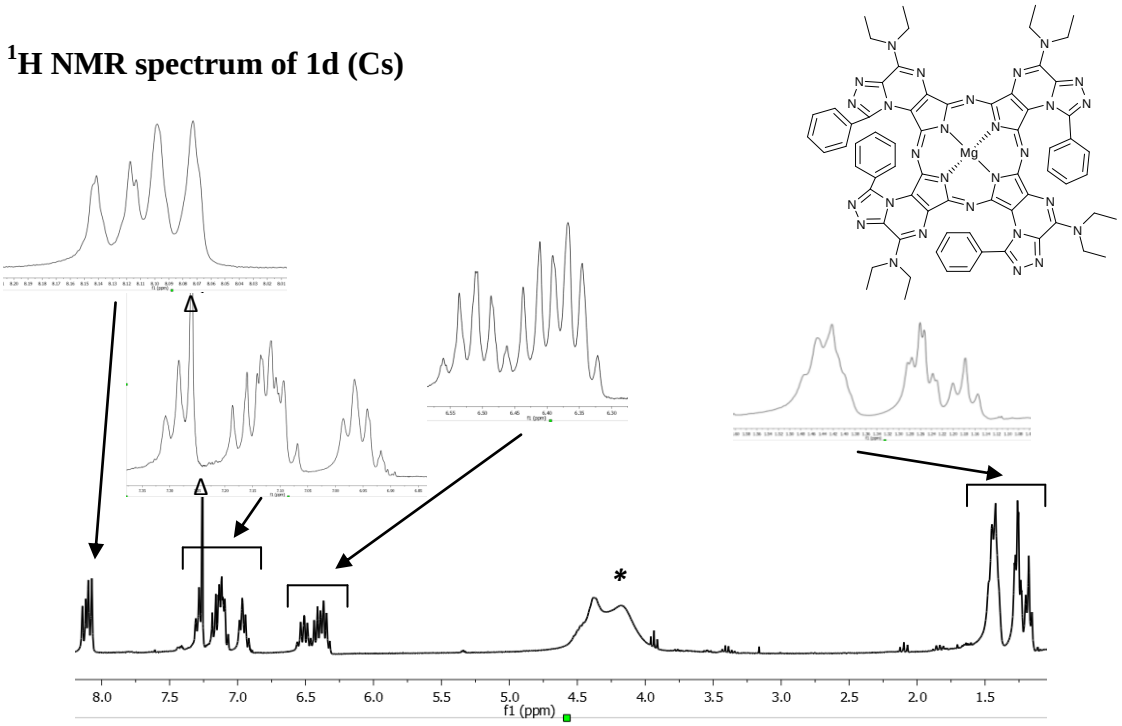


Figure S13: Asterisk indicates signal of water, triangle residual signal of non-deutered chloroform. The non-deutered pyridine signals are overlapped with the signals of **1d**.

^{13}C NMR spektrum of 1d (Cs)

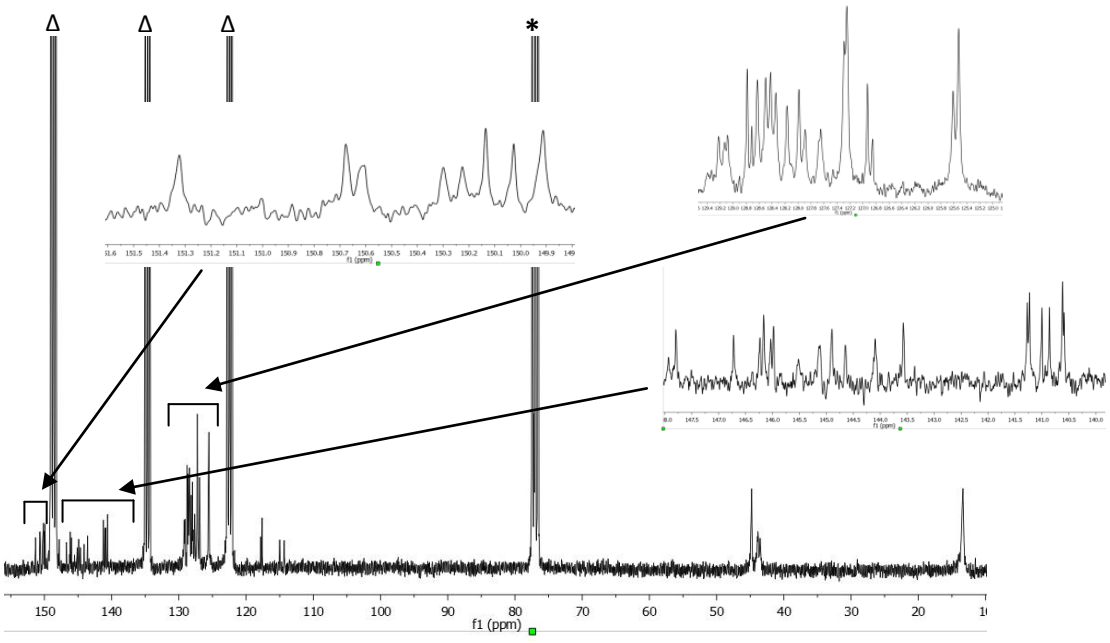


Figure S14: Asterisk indicates signal of chloroform, triangles pyridine.

6. ABSORPTION AND FLUORESCENCE SPECTRA

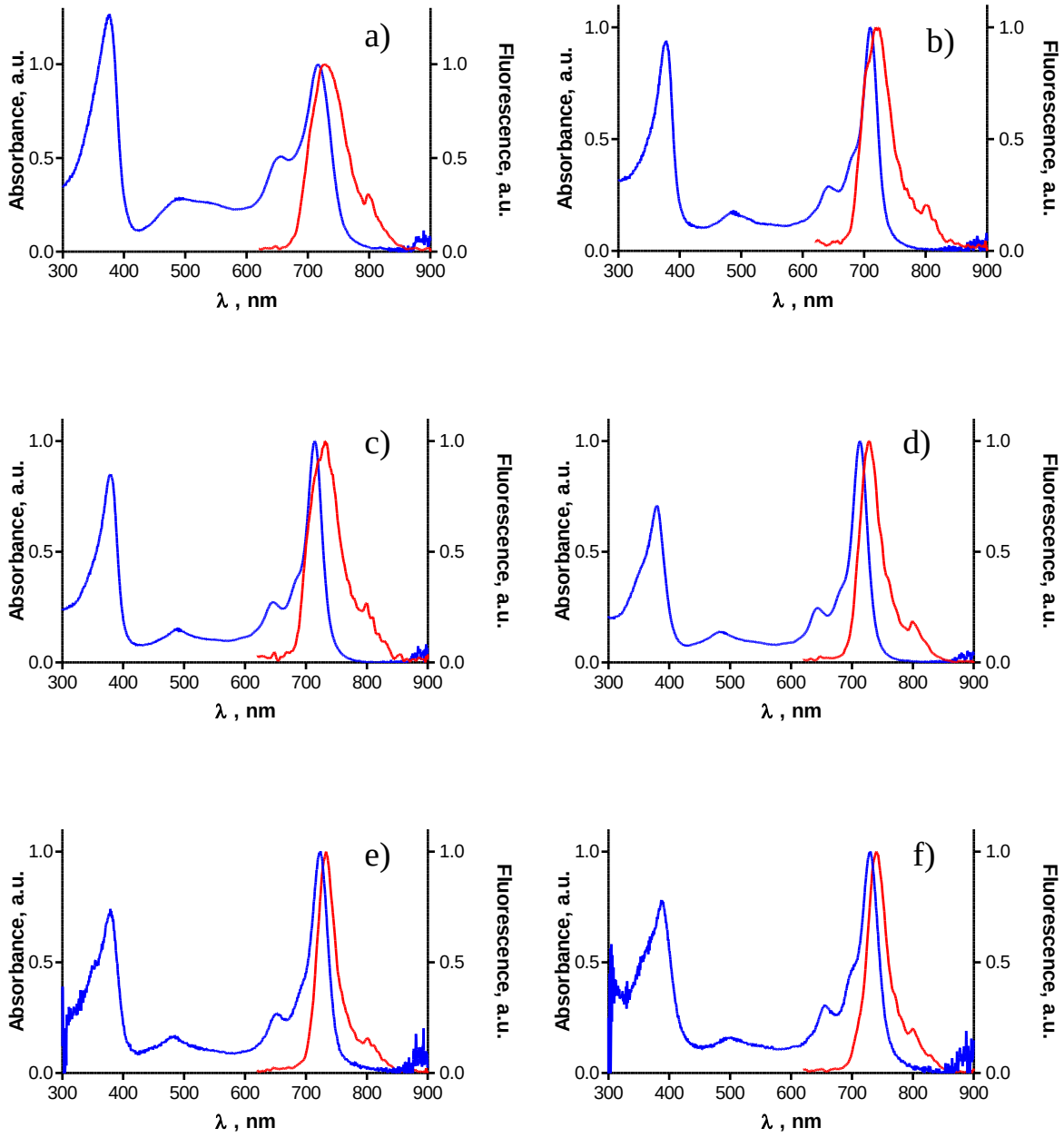


Figure S15: Normalized absorption (blue) and emission (red) spectra of compounds **1a** (a), **1b** (b), **1c**-C_{4h} isomer (c), **1d**-C_{4h} isomer (d), **1e** (e), **1f** (f) in pyridine. λ_{exc} = 608 nm.

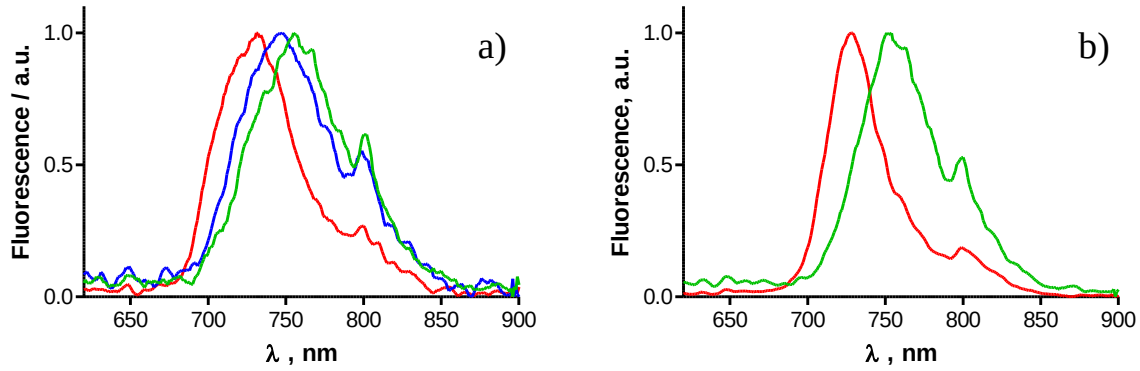
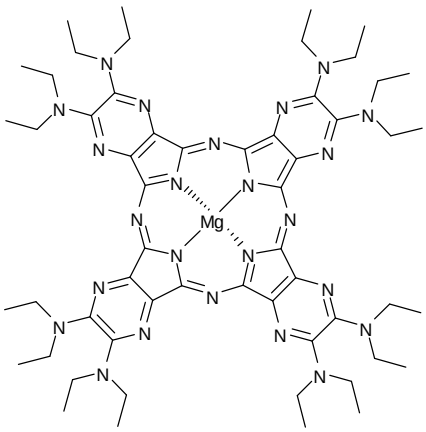


Figure S16. Normalized emission spectra of C_{4h} (red), C_s (green) and C_{2v} (blue) isomers of compound **1c** (a) and **1d** (b) in pyridine. λ_{exc} = 608 nm.

7. STRUCTURE OF COMPOUND 7



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