En Route Towards Panchromatic Light Harvesting: Photophysical and Electrochemical Properties of Porphyrazine-Bodipy Conjugates

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Supporting Information

Synthesis and Characterization

General

The preparation and characterization of Bodipys 6 and 7 as well as the Magnesium- and Zinc-porphyrazines (3-Mg, 4-Mg, 3-Zn, 4-Zn, 1-Zn and 2-Zn) have recently been reported.[1] Reagents were purchased from commercial suppliers and used, unless otherwise noted, without further purification. Anhydrous THF, toluene and 1,4-dioxane were freshly distilled from sodium benzophenone ketyl; anhydrous diisopropylamine was distilled from CaH₂. All reactions, except of the transmetalation reactions, were carried out under an atmosphere of dry argon with oven-dried glassware and all reactions containing or yielding porphyrazines were conducted under exclusion of light. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates. Flash chromatography was executed on Merck silica gel (230–400 mesh). Gel permeation chromatography was performed with a polystyrene resin cross-linked with divinylbenzene (Bio-beads® 1-SX, Bio-Rad, Munich), swollen in THF and by using THF as the eluent. NMR spectra were recorded on Varian MR-400 or Varian 500 VNMRS instruments operating at frequencies of 400 or 500 MHz (for 1H), 101 or 126 MHz (for 13C) and 376 or 470 MHz (for 19F) respectively. Multiplicity is described by the abbreviations s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Chemical shifts are given in ppm. 1H NMR spectra were referenced to the residual solvent peaks at δ = 7.26 (CDCl₃), 5.32 (CD₂Cl₂) and 1.72 ppm (THF-d₈). 13C NMR spectra were referenced to the solvent peaks at δ = 77.16 (CDCl₃), 53.84 (CD₂Cl₂), and 67.57 ppm (THF-d₈). 19F NMR: All chemical shifts are relative to the chemical shift of CFCl₃ = 0 ppm. Infrared spectra were obtained on a Bruker ALPHA-T instrument and are reported in wavenumbers (cm⁻¹). UV/Vis spectra were obtained on a Perkin-Elmer Lambda 40 instrument and are reported in wavelengths (nm). Melting points were determined with a BÜCHI melting point M-565 hot stage and are uncorrected. Mass spectra were recorded with a Finnigan LCQ Deca (ESI and APCI ionisation). MALDI-TOF mass spectrometry was carried out on a Bruker Biflex IV MALDI-TOF mass spectrometer with a N₂-Laser (337 nm and 3 ns pulslength). DCTB (2-[(2E)-3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile) was used as matrix
unless otherwise noted. High-resolution mass spectrometry was carried out on a Bruker microTOF equipped with an ApolloTM ion funnel.

Experimental Details

[Tetrakis-(7,10-dibromo-6,11-bis(3,3,3-trip-tyl)prop-1-ynyl)dibenzo[f,h]quinoxalino-porphyrazinato]copper(II) (3-Cu)

To a stirred solution of 3-Mg (384 mg, 0.089 mmol) in THF (80 mL) was added p-TsOHxH₂O (10 eq). Stirring was continued at r.t. for 1-2 hours. Cu(OAc)₂ (242 mg, 1.34 mmol) was added and the mixture was stirred for additional 12 h. After removing the solvent on a rotary evaporator, the residue was taken up in DCM (30 mL) and the solution was washed sequentially with water (30 mL) and brine (30 mL). The organic layer was dried over MgSO₄, filtered and the solvent removed in vacuo. The crude product was filtered through a pad of silica (THF). Removal of the solvent left a dark green amorphous solid. Crystallization from DCM:EtOH (approx. 10:1) yielded 3-Cu (376 mg, 88 µmol) as a dark green solid (98%).

m.p. > 300 °C; UV/Vis λ_max(DCM)/nm 318 (ε/dm³ mol⁻¹ cm⁻¹ 3280 000), 380sh (117 000), 439 (83 000), 622 (45 000), 661 (42 000), 694 (310 000); IR (neat, diamond ATR) ν_max/cm⁻¹ 3021 (w), 2919 (w), 2864 (w), 2218 (w) (C≡C), 1909 (w), 1755 (w), 1507 (m), 1454 (m), 1377 (m), 1266 (m), 1186 (m), 1033 (m-s), 807 (s); ¹H NMR δ (400 MHz, CDCl₃, TMS) 10.59 (br s, 8H; Hphenanthrene), 8.98 (s, 8H; Hphenanthrene), 7.29 (s, 48H; Harm.), 7.05 (s, 48H; Harm.), 2.16 ppm (s, 72H; Hmethyl); ¹³C NMR δ (101 MHz, CDCl₃, TMS) 142.3, 136.4, 136.4, 132.9, 129.4, 128.8, 104.4 (Cethynyl), 82.8 (Cethynyl), 55.9 (Cquat), 21.0 ppm (Cmethyl), resonances not fully resolved*; MALDI-TOF MS (DCTB, +) m/z [M]⁺ calc. for [C₂₆₄H₁₈₄Br₆CuN₁₆]⁺ = 4283 average mass; found 4283.

* Due to the paramagnetic copper ion most NMR signals of the compound are broad and difficult to resolve.
[Tetrakis-(6,7,10,11-tetrakis(3,3,3-tri(p-tolyl)prop-1-ynyl)dibenzo[f,h]quinoxalino)-porphyrazine (4-H₂]

To a stirred solution of 4-Mg (63 mg, 10.4 µmol) in THF (20 mL) was added p-TsOH·H₂O (10 eq). Stirring was continued at r.t. for 2 hours. After removing the solvent on a rotary evaporator, the residue was taken up in DCM (30 mL) and the solution washed sequentially with water (2 x 20 mL), 10% aqueous NH₃ solution (20 mL) and water (20 mL) again. The solvent of the organic layer was removed in vacuo. The crude product was filtered through a pad of silica (THF). Removal of the solvent left 4-H₂ (57 mg, 9.7 µmol) as a brown amorphous solid (93% yield).

m.p. > 300 °C, UV/Vis λmax(DCM)/nm 313 (ε/dm³ mol⁻¹ cm⁻¹ 366 000), 370 (128 000), 396sh (122 000), 459sh (48 000), 643 (22 000), 710 (132 000); UV/Vis λmax(Toluol)/nm 314 (ε/dm³ mol⁻¹ cm⁻¹ 370 000), 360sh (136 000), 398 (125 000), 465sh (55 000), 677sh (22 000), 713 (73 000), 738 (73000); IR (neat, diamond ATR) νmax/cm⁻¹ 3021 (w), 2917 (w), 2860 (w), 2213 (w) (C≡C), 1905 (w), 1749 (m), 1597 (w), 1501 (s), 1441 (m), 1354 (m), 1260 (m), 1118 (m), 808 (s); ¹H NMR δ (500 MHz, THF-d₈, TMS) 10.22 (s, 8H; Hphenanthrene), 9.09 (s, 8H; Hphenanthrene), 7.23 (d, 3J(H,H) = 8.0 Hz, 48H; H arom.), 7.10 (d, 3J(H,H) = 8.1 Hz, 48H; H arom.), 6.90 (d, 3J(H,H) = 8.0 Hz, 48H; H arom.), 6.84 (d, 3J(H,H) = 8.2 Hz, 48H; H arom.), 2.23 (s, 72H; H methyl), 2.08 ppm (s, 72H; H methyl); ¹³C NMR δ (126 MHz, THF-d₈, TMS) 143.6, 143.5, 137.1, 136.8, 131.6, 131.44, 131.36, 130.2, 130.0, 129.8, 129.71, 129.66, 129.6, 129.1, 103.9 (C ethynyl), 103.2 (C ethynyl), 85.2 (C ethynyl), 84.4 (C ethynyl), 57.0 (C quat), 56.8 (C quat), 21.3 (C methyl), 21.2 (C methyl), arom. resonances not fully resolved; MALDI-TOF MS (DCTB, +) m/z [M]+ calcd. for [C₄₅₅H₃₅₄N₁₂]⁺ = 6058 average mass; found 6056.
[Tetrakis-(6,7,10,11-tetrakis(3,3,3-tri(p-tolyl)prop-1-ynyl)dibenzo[f,h]quinoxalino)-porphyrazinato]copper(II) (4-Cu)

To a stirred solution of 4-Mg (50 mg, 8.2 µmol) in THF (20 mL) was added p-TsOH·H₂O (10 eq). Stirring was continued at r.t. for 1-2 hours. Cu(OAc)₂ (22 mg, 123 µmol) was added and the mixture was stirred for additional 12 h. After removing the solvent on a rotary evaporator, the residue was taken up in DCM (30 mL) and the solution washed sequentially with water (20 mL) and brine (20 mL). The organic layer was dried over MgSO₄, filtered and the solvent removed in vacuo. The crude product was filtered through a pad of silica (THF). Removal of the solvent left a dark green amorphous solid. Crystallization from DCM:EtOH (approx. 10:1) yielded 4-Cu (49 mg, 8 µmol) as a dark green solid (95%).

m.p. > 300 °C; UV/Vis λ<sub>max</sub>(DCM)/nm 312 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 386 000), 363sh (148 000), 395 (138 000), 455sh (81 000), 630 (43 000), 702 (293 000); IR (neat, diamond ATR) ν<sub>max</sub>/cm<sup>-1</sup> 3021 (w), 2918 (w), 2857 (w), 2208 (w) (C≡C), 1901 (w), 1752 (m), 1597 (w), 1506 (s), 1438 (m), 1354 (m), 1260 (m), 1112 (m), 807 (s); <sup>1</sup>H NMR δ (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, TMS) 10.44 (br s, 8H; H<sub>phenanthrene</sub>), 8.88 (s, 8H; H<sub>phenanthrene</sub>), 7.24 (d, J(H,H) = 7.7 Hz, 48H; H<sub>arom</sub>), 7.14 (s, 48H; H<sub>arom</sub>), 6.92 (d, J(H,H) = 7.8 Hz, 48H; H<sub>arom</sub>), 6.78 (s, 48H; H<sub>arom</sub>), 2.24 (s, 72H; H<sub>methyl</sub>), 2.01 ppm (s, 72H; H<sub>methyl</sub>); <sup>13</sup>C NMR δ (101 MHz, CDCl<sub>3</sub>, TMS) 142.9, 142.4, 137.0, 136.6, 129.5, 129.3, 129.1, 102.7 (C<sub>ethynyl</sub>), 83.4 (C<sub>ethynyl</sub>), 56.8 (C<sub>quart</sub>), 56.1 (C<sub>quart</sub>), 21.2 (C<sub>methyl</sub>), 21.0 (C<sub>methyl</sub>), resonances not fully resolved; MALDI-TOF MS (DCTB, +) m/z [M]+ calc. for [C<sub>456</sub>H<sub>352</sub>CuN<sub>16</sub>]<sup>+</sup> = 6119 average mass; found 6119.

* Due to the paramagnetic copper ion most NMR signals of the compound are broad and difficult to resolve.
In a high pressure Schlenk tube 3-Cu (50 mg, 12 µmol), tetrakis(triphenylphosphine)-palladium(0) (3 mg, 3 µmol, 24 mol%), Cul (1 mg, 6 µmol, 48 mol%) and Bodipy 5[1] (76 mg, 186 µmol) were dissolved in dioxane (2 mL) and diisopropylamine (1 mL) and the sealed tube was placed in an oilbath. The reaction mixture was stirred at 80°C for 21 h. After cooling the mixture to room temperature DCM (20 mL) was added and the organic phase was washed sequentially with water (3 x 20 mL) and brine (20 mL). The organic layer was dried over MgSO₄, filtered and the solvent was removed in vacuo. The crude product was filtered through a pad of silica (THF) and purified by gel permeation chromatography (THF). After another filtration through silica (THF) 1-Cu (50 mg, 7.3 µmol) was obtained as almost black platelets with a metallic luster (yield 63%).

**m.p. > 300 °C; UV/Vis** λ_{max}(DCM)/nm 320 (ε/dm³ mol⁻¹ cm⁻¹ 447 000), 369sh (267 000), 400sh (238 000), 494sh (145 000), 526 (547 000), 633sh (42 000), 668sh (40 000), 706 nm (273 000);
**IR** (neat, diamond ATR) ν_{max}/cm⁻¹ 2961 (m), 2923 (m), 2865 (m), 2207 (w) (C≡C), 2158 (w) (C≡C), 1773 (w), 1535 (m), 1473 (m), 1316 (m), 1183 (s), 975 (s);
**¹H NMR** δ (500 MHz, CDCl₃, TMS) 10.67 (br s, 8H; Hphenanthrene), 9.05 (s, 8H; Hphenanthrene), 7.33-6.94 (m, 128H; H_aram.), 2.55 (s, 48H; H_methyl), 2.32 (m, 32H; H_{CH2-ethyl}), 2.10 (br s, 72H; H_methyl), 1.30 (s, 48H; H_methyl), 1.01 ppm (m, 48H; H_{CH3-ethyl});
**¹³C NMR** δ (126 MHz, THF-d₈, TMS) 154.9, 143.6, 140.8, 138.7, 137.4, 137.0, 133.7, 133.2, 131.4, 130.3, 129.9, 129.7, 129.6, 129.5, 94.7 (C_{ethyl}), 83.9(C_{ethyl}), 56.8 (C_{quas})


21.2, 17.9, 15.2, 12.8, 12.6 ppm, resonances not fully resolved; $^{19}$F NMR $\delta$ (470 MHz, CDCl$_3$, CFCl$_3$) -145.8 ppm; MALDI-TOF MS (DCTB, +) $m/z$ [M]$^+$ calc. for [C$_{464}$H$_{392}$B$_8$CuF$_{16}$N$_{32}$]$^+$ = 6870 average mass, 6866 monoisotopic mass; found 6867.

[Tetrakis-(7,10-bis(4,4-difluoro-2,6-(4'-ethynylbenzoic acid-t-butylester)-8-(4'-ethynylphenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene)-6,11-bis(3,3,3-tri(p-tolyl)prop-1-ynyl)dibenzo[f,h]quinoxalino]porphyrazinato)copper(II) (2-Cu)

In a high pressure Schlenk tube 3-Cu (25 mg, 5.8 µmol), tetrakis(triphenylphosphine)-palladium(0) (2 mg, 1.4 µmol, 24 mol%) and CuI (0.5 mg, 2.7 µmol, 48 mol%) were dissolved in toluene (3 mL) and diisopropylamine (1.5 mL) and the sealed tube was placed in an oilbath. After the oilbath had reached 45 °C, Bodipy 7 (174 mg, 232 µmol) was added. The reaction mixture was stirred at 110°C for 2 h. After cooling the mixture to room temperature DCM (20 mL) was added and the organic phase was washed sequentially with water (3 x 20 mL) and brine (20 mL). The organic layer was dried over MgSO$_4$, filtered and the solvent removed in vacuo. The crude product was filtered through a pad of silica (THF) and purified by gel permeation chromatography (THF). After another filtration through silica (THF) 2-Cu (40 mg, 4.2 µmol) was obtained as almost black platelets with a metallic luster (yield 72%).

m.p. > 300 °C; UV/Vis $\lambda_{\text{max}}$(DCM)/nm 320 (ε/dm$^3$ mol$^{-1}$ cm$^{-1}$ 571 000), 367sh (249 000), 402 (274 000), 575 (553 000), 632sh (40 000), 669sh (36 000), 707 nm (254 000); IR (neat, diamond ATR) $\tilde{\nu}_{\text{max}}$/cm$^{-1}$ 2967 (w), 2920 (w), 2204 (w) (C≡C), 1711 (s) (C=O), 1604 (m), 1526 (s), 1178 (s), 1160 (s), 1004 (s); $^1$H NMR $\delta$ (500 MHz, CDCl$_3$, TMS) 10.69 (br s, 8H; H$_{\text{phenanthrene}}$), 9.07 (s, 8H; H$_{\text{phenanthrene}}$), 7.93 (d, 3J(H,H) = 7.7 Hz, 32H; H$_{\text{arom}}$), 7.47 (d, 3J(H,H) = 7.7 Hz, 32H;

* Due to the paramagnetic copper ion most NMR signals of the compound are broad and difficult to resolve.
H_{arom.}) 7.22-6.95 (m, 128H; H_{arom.}), 2.75 (s, 48H; H_methyl), 2.12 (br, 72H; H_methyl), 1.57 ppm (s, 192H; H_{-butyl + H_methyl}); \textsuperscript{13}C NMR δ (101 MHz, CDCl\textsubscript{3}, TMS) 165.2 (C_{ester}), 159.2, 144.3, 142.6, 142.0, 137.1, 136.1, 134.5, 133.0, 132.6, 131.4, 131.2, 131.1, 129.5, 129.3, 129.0, 128.8, 128.2, 127.5, 124.8, 116.2, 110.1, 104.3, 96.5 (C_{ethynyl}), 93.5 (C_{ethynyl}), 84.3 (C_{ethynyl}), 82.8 (C_{ethynyl}), 81.5 (C_{-butyl, c}), 55.8 (C_{quas}), 28.3 (C_{-butyl, cit3}), 21.0 (C_{methyl}), 13.9 (C_{methyl}) ppm, resonances not fully resolved; \textsuperscript{19}F NMR δ (470 MHz, CDCl\textsubscript{3}, CFCI\textsubscript{3}) -146.2 ppm; MALDI-TOF MS (DCTB, +) m/z [M]+ calc. for [C\textsubscript{64}H\textsubscript{520}B\textsubscript{6}CuF\textsubscript{16}N\textsubscript{32}O\textsubscript{32}]\textsuperscript{+} = 9625 average mass, 9618 monoisotopic mass; found 9619 [M]+.

[Tetrakis-(7,10-bis(4,4-difluoro-8-(4′-ethynylphenyl)-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene)-6,11-bis(3,3,3-tri(p-tolyl)prop-1-ynyl)dibenzo[f,h]quinalino)porphyrazinato]magnesium(II) (1-Mg)

In a high pressure Schlenk tube 3-Mg (10 mg, 2.4 μmol), tetrakis(triphenylphosphine)-palladium(0) (1 mg, 0.6 μmol, 24 mol%) and Bodipy 5\textsuperscript{[2]} (24 mg, 58 μmol) were dissolved in dioxane (2 mL) and diisopropylamine (1 mL) and the sealed tube was placed in an oilbath. The reaction mixture was stirred at 80° C for 16 h. After cooling the mixture to room temperature DCM (20 mL) was added and the organic phase was washed sequentially with water (3 x 20 mL) and brine (20 mL). The organic layer was dried over MgSO\textsubscript{4}, filtered and the solvent removed in vacuo. The crude product was filtered through a pad of silica (THF) and purified by gel permeation chromatography (THF). After another filtration through silica (THF) 1-Mg (9.5 mg, 1.4 μmol) was obtained as almost black platelets with a metallic luster (yield 58 %).

* Due to the paramagnetic copper ion most NMR signals of the compound are broad and difficult to resolve.
m.p. > 300 °C; UV/Vis $\lambda_{\text{max}}$(DCM)/nm 318 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 278 000), 379 (184 000), 401sh (176 000), 527 (326 000), 648sh (18 000), 678sh (sh, 20 000), 710 nm (120 000); IR (neat, diamond ATR) $\tilde{\nu}_{\text{max}}$/cm$^{-1}$ 2960 (m), 2924 (m), 2867 (m), 2219 (w) (C≡C), 2189 (w) (C≡C), 1773 (w), 1538 (m), 1475 (m), 1319 (m), 1188 (s), 978 (s); $^1$H NMR $\delta$ (400 MHz, CD$_2$Cl$_2$, TMS) 10.36 (s, 8H; $\text{H}_{\text{phenanthrene}}$), 9.21 (s, 8H; $\text{H}_{\text{phenanthrene}}$), 7.30-7.20 and 6.99-6.96 (m, 128H; $\text{H}_{\text{arom.}}$), 2.51 (s, 48H; $\text{H}_{\text{methyl}}$), 2.34 (m, 32H; $\text{H}_{\text{CH2-ethyly}}$), 2.13 (br s, 72H; $\text{H}_{\text{methyl}}$), 1.36 (s, 48H; $\text{H}_{\text{methyl}}$), 1.01 ppm (m, 48H; $\text{H}_{\text{CH3-ethyly}}$); $^{19}$F NMR $\delta$(376 MHz, CD$_2$Cl$_2$, CFC$_3$) -145.7 ppm; MALDI-TOF MS (DCTB, -) m/z [M]·calc. for [C$_{466}$H$_{392}$Br$_8$MgF$_{18}$N$_{32}$]$^+$ = 6831 average mass, 6827 monoisotopic mass; found 6834.

[Tetrakis-[7,10-bis(4,4-difluoro-2,6-(4'-ethynylbenzoic acid-t-butylester)-8-(4'-ethynylphenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene)-6,11-bis(3,3,3-tri(p-tolyl)-prop-1-ynyl)dibenzo[6,12]quinoxalino]porphyrazinato]magnesium(II) (2-Mg)

In a high pressure Schlenk tube 3-Mg (10 mg, 2.4 μmol) and tetrakis(triphenylphosphine)palladium(0) (1 mg, 0.6 μmol, 24 mol%) were dissolved in in toluene (2 mL) and diisopropylamine (1 mL) and the sealed was placed in an oil bath. After the oilbath had reached 45 °C, Bodipy 7 (70 mg, 94 μmol) was added. The reaction mixture was stirred at 110 °C for 2 h. After cooling the mixture to room temperature DCM (20 mL) was added and the organic phase was washed sequentially with water (3 x 20 mL) and brine (20 mL). The organic layer was dried over MgSO$_4$ filtered and the solvent removed in vacuo. The crude product was filtered through a pad of silica (THF) and purified by gel permeation chromatography (THF). After another filtration through silica (THF) 2-Mg (12 mg, 1.3 μmol) was obtained as almost black platelets with a metallic luster (yield 54%).

m.p. > 300 °C; UV/Vis $\lambda_{\text{max}}$(DCM)/nm 323 ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 456 000), 398 (282 000), 575 (470 000), 632 (sh, 230 000), 669(sh, 23 000), 711 nm (214 000); IR (neat, diamond ATR) $\tilde{\nu}_{\text{max}}$/cm$^{-1}$
2970 (w), 2922 (w), 2861 (w), 2206 (w) (C≡C), 1709 (s) (C=O), 1604 (m), 1525 (s), 1256 (m), 1178 (s), 1160 (s), 1004 (s); $^1$H NMR $\delta$ (400 MHz, CD$_2$Cl$_2$, TMS) 10.40 (s, 8H; H$_{\text{phenanthrene}}$), 9.22 (s, 8H; H$_{\text{phenanthrene}}$), 7.93 (m, 32H; H$_{\text{arom}}$), 7.51 (m, 32H; H$_{\text{arom}}$) 7.32-6.99 (m, 128H; H$_{\text{arom}}$), 2.73 (s, 48H; H$_{\text{methyl}}$), 2.16 (br s, 72H; H$_{\text{methyl}}$), 1.56 ppm (s, 192H; H$_{\text{tert-butyl} + \text{H}_{\text{methyl}}}$); $^{13}$C NMR $\delta$ (101 MHz, CD$_2$Cl$_2$, TMS) 165.4 (C$_{\text{Ester}}$), 159.4, 145.0, 143.0, 136.6, 135.1, 133.4, 132.0, 131.7, 131.4, 129.8, 129.6, 129.4, 129.2, 128.6, 127.9, 124.7, 116.5, 110.6, 96.7, 84.7, 81.7, 28.4 (C$_{\text{tert-butyl,CH3}}$), 21.2 (C$_{\text{methyl}}$), 14.2 (C$_{\text{methyl}}$), 14.2 (C$_{\text{methyl}}$), resonances not fully resolved; $^{19}$F NMR $\delta$ (470 MHz, CD$_2$Cl$_2$, CFCl$_3$) -146.2 ppm; MALDI-TOF MS (DCTB, ·) m/z [M-F]$^-\$ calc. for [C$_{640}$H$_{520}$R$_9$MgF$_{15}$N$_{32}$O$_{32}$]$^+ = 9567$ average mass, 9561 monoisotopic mass; found 9560.
NMR Spectra of all compounds

$^1$H NMR-Spectrum of 3-Cu in CDCl$_3$:

* Due to the paramagnetic copper ion most NMR signals of the compound are broad and difficult to resolve.
$^1$H NMR-Spectrum of 4-H$_2$ in THF-$d_8$:

$^{13}$CNMR-Spectrum of 4-H$_2$ in THF-$d_8$:
Due to the paramagnetic copper ion most NMR signals of the compound are broad and difficult to resolve.
$^1$H NMR-Spectrum of 1-Cu in CDCl₃:

$^{13}$CNMR-Spectrum of 1-Cu in CDCl₃:

* Due to the paramagnetic copper ion most NMR signals of the compound are broad and difficult to resolve.
$^1$H NMR-Spectrum of 2-Cu in CDCl$_3$:

$^{13}$C NMR-Spectrum of 2-Cu in CDCl$_3$:

* Due to the paramagnetic copper ion most NMR signals of the compound are broad and difficult to resolve.
$^1$H NMR-Spectrum of 1-Mg in CD$_2$Cl$_2$:

$^1$H NMR-Spectrum of 2-Mg in CD$_2$Cl$_2$: 
\[ ^{13}\text{CNMR-Spectrum of 2-Mg in } \text{CD}_2\text{Cl}_2: \]

![CNMR spectrum diagram](image-url)
**MALDI-TOF mass spectra**

MALDI-TOF mass spectrum of **3-Cu** (DCTB, reflector, positive):

MALDI-TOF mass spectrum of **4-Cu** (DCTB, reflector, positive):
MALDI-TOF mass spectrum of **4-H**₂ (DCTB, linear, positive):

![Mass Spectrum Image]

MALDI-TOF mass spectrum of **1-Cu** (DCTB, reflector, positive):

![Mass Spectrum Image]
MALDI-TOF mass spectrum of **2-Cu** (DCTB, linear, positive):

MALDI-TOF mass spectrum of **1-Mg** (DCTB, reflector, negative):
MALDI-TOF mass spectrum of 2-Mg (DCTB, linear, negative):

2-Mg exhibits an unexpected ionization behaviour in the MALDI experiment that we are currently unable to explain. Other ionization techniques (MALDI with different acquisition operation modes – linear and reflector – and polarity, GCMS/EI, ESI) and MALDI-matrices (DHB, dithranol, sinapinic acid, DHAP, HPA, TMPDA, no matrix, DCTB with Ag-addition) failed to give a distinct molecular ion.

**Photophysical Investigation**

**General**

All measurements were performed in solvents (spectroscopic rate) at room temperature.

**Steady state UV/vis absorption spectroscopy:** Steady state absorption spectra were obtained using a Perkin Elmer Lambda2 UV/vis two-beam spectrophotometer using a slit width of 2 nm and a scan rate of 480 nm/min. All spectra were recorded using a quartz glass cuvette of 10x10 mm.

**Steady state emission spectroscopy:** Steady state emission spectra were recorded using a Horiba Jobin Yvon FluoroMax-3 spectrometer using a slit width of 2 nm for excitation and emission and an integration time of 0.5 s. The studies were performed in a 10x10 mm quartz glass cuvette. Quantum yields were determined from corrected emission spectra following the standard methods\(^3\) using meso-tetraphenyl porphyrin (TPP) (Φ = 0.11 in toluene\(^4\)) or Zinc meso-tetraphenyl porphyrin (ZnTPP) (Φ = 0.03 in toluene\(^4\)) as standards.
**Time resolved emission studies:** Emission lifetimes were determined via time correlated single photon counting (TCSPC) on a Horiba Jobin Yvon FluoroLog3 emission spectrometer with a Hamamatsu MCP photomultiplier (R3809U-58). For excitation a laser diode (NanoLED-405L, 403 nm, pulse width ≤ 200 ps, maximum of repetition rate 100 kHz) was used. All measurements were performed in a 10x10 mm quartz glass cuvette.

**Electrochemistry:** Electrochemical data were obtained by cyclic voltammetry and square wave voltammetry using a conventional single-compartment three-electrode cell arrangement in combination with a potentiostat “AUTOLAB®, eco chemie”. As auxiliary and reference electrode Pt and silver wires were used; working electrode: glassy carbon. The measurements were carried out in argon saturated toluene/acetonitrile (4/1). Tetrabutylammonium hexafluorophosphate (TBAPF6 = 0.1 M) was used as supporting electrolyte at room temperature. All potentials are referenced to ferrocene/ferrocenium (E(Fc/Fc+) = 0.2 V) with a scan rate of 0.05 V/s.

**Femtosecond transient absorption spectroscopy:** Femtosecond transient absorption studies were performed with an amplified Ti/sapphire laser system (Model CPA 2101, Clark-MXR Inc. – output: 775 nm, 1 kHz and 150 fs pulse width) in the TAPPS - Transient Absorption Pump / Probe System - Helios from Ultrafast Systems. That is referred to as a two-beam setup where the pump pulse of 387, 530 and 695 nm and 200 nJ, generated out of a NOPA - noncollinear optical parametrical amplifier, Clark MRX Inc. - is used as excitation source for transient species and the delay of the probe pulse is exactly controlled by an optical delay rail of 3.3 ns. As probe beam (white light continuum), a small fraction of 775 nm pulses stemming from the CPA laser system was focused by a 50 mm lens into a 3 mm thick sapphire disc. Finally, the changes in optical density (ΔA) are measured against the wavelength in both visible and near-infrared regions. The transient spectra were recorded in a 2 mm quartz glass cuvette.
Characterization

Figure S1: Cyclovoltammetry diagram of the first reduction step of 4-Mg (red), 1-Mg (blue) and 2-Mg (dark cyan), measured at room temperature in degased toluene / acetonitrile (4:1/ v:v) with tetrabutylammonium hexafluorophosphate 0.1M as supporting electrolyte.

Figure S2: Cyclovoltammetry diagram of the first reduction step of 4-Zn (grey), 1-Zn (blue) and 2-Zn (dark cyan), measured at room temperature in degased toluene / acetonitrile (4:1/ v:v) with tetrabutylammonium hexafluorophosphate 0.1M as supporting electrolyte.
Figure S3: Cyclovoltammetry diagram of the first reduction step of 4-Cu (black), 1-Cu (blue) and 2-Cu (dark cyan), measured at room temperature in degased toluene / acetonitrile (4:1/v:v) with tetrabutylammonium hexafluorophosphate 0.1M as supporting electrolyte.

Figure S4: Absorption spectra of 4-Cu (black), 4-Mg (red) and 4-Zn (grey) measured in toluene at room temperature.
Figure S5: Absorption spectra of 4-Mg in different solvents to monitor the influence of the solvent. Tol (black), ODCB (grey), CB (blue), DMF (purple), THF (red) measured in toluene at room temperature. Note the blue shift of 10 nm at 706 nm for THF.

Figure S6: Absorption spectra of Bodipy 5 (blue) and 6 (dark cyan) measured in toluene at room temperature.
Figure S7: Absorption spectra of 5 (blue) and 6 (dark cyan), 4-Zn (black), 1-Zn (red) and 2-Zn (grey) measured in toluene at room temperature.

Figure S8: Absorption spectra of 5 (blue) und 6 (dark cyan), 4-Cu (black), 1-Cu (red) and 2-Cu (grey) measured in toluene at room temperature.
**Figure S9:** Room temperature fluorescence spectra **4-Cu (black), 4-Mg (red)** and **4-Zn (grey)** measured in toluene with solutions that exhibit the same optical absorbance of 0.01 at the 410 nm excitation wavelength.

**Figure S10:** Room temperature fluorescence spectra of **4-Cu (black), 4-Mg (red)** and **4-Zn (grey)** measured in toluene with solutions that exhibit the same optical absorbance of 0.01 at the 680 nm excitation wavelength.
Figure S11 Room temperature fluorescence spectra of 4-Mg (red), 1-Mg (blue) and 2-Mg (dark cyan) measured in toluene with solutions that exhibit the same optical absorbance of 0.01 at the 680 nm excitation wavelength.

Figure S12: Room temperature fluorescence spectra of 4-Zn (grey), 1-Zn (blue) and 2-Zn (dark cyan) measured in toluene with solutions that exhibit the same optical absorbance of 0.01 at the 680 nm excitation wavelength.
Figure S13: Room temperature fluorescence spectra of, 4-Zn (grey), 1-Zn (blue) and 2-Zn (dark cyan) measured in toluene with solutions that exhibit the same optical absorbance of 0.01 at the 410 nm excitation wavelength.

Figure S14: Room temperature fluorescence spectra of, 4-Cu (black), 1-Cu (blue) and 2-Cu (dark cyan) measured in toluene with solutions that exhibit the same optical absorbance of 0.01 at the 410 nm excitation wavelength.
Figure S15: Normalized room temperature excitation spectra of 1-Mg (blue) ($\lambda_{ex} = 540$ nm) and 2-Mg (dark cyan) ($\lambda_{ex} = 600$ nm) measured in toluene with solutions that exhibit the same optical absorbance of 0.01.

Figure S16: Room temperature fluorescence spectra of 5 (blue), 1-Cu (black), 1-Mg (red) and 1-Zn (grey) measured in toluene with solutions that exhibit the same optical absorbance of 0.01 at the 520 nm excitation wavelength.
Figure S17: Time resolved emission spectra ($\lambda_{ex} = 403$ nm) of 4-Mg (red) and 4-Zn (grey) recorded at 708 nm in toluene.

Figure S18: Time resolved emission spectra ($\lambda_{ex} = 403$ nm) of 5 (blue), 1-Cu (black), 1-Mg (red) and 1-Zn (grey) recorded at 550 nm in toluene.
Figure S19: Time resolved emission spectra ($\lambda_{ex} = 403$ nm) of 6 (dark cyan), 2-Cu (black), 2-Mg (red) and 2-Zn (grey) recorded at 600 nm in toluene.

Figure S20: Time resolved emission spectra ($\lambda_{ex} = 403$ nm) of 4-Mg (red), 1-Mg (blue) and 2 Mg (dark cyan) recorded at 708 nm in toluene.
Figure S21: Time resolved emission spectra ($\lambda_{ex} = 403$ nm) of 4-Zn (red), 1-Zn (blue) and 2-Zn (dark cyan) recorded at 708 nm in toluene.

Figure S22: Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (695 nm and 200 nJ) of 4-Zn in toluene with several time delays between 0 and 8000 ps at room temperature. **Insert** – Time-absorption profiles of the spectra at 710 and 900 nm, monitoring the intersystem crossing dynamics (i.e., $1.6 \pm 0.1$ ns).
**Figure S23:** Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (695 nm and 200 nJ) of 4-Cu in toluene with several time delays between 0 and 8000 ps at room temperature. **Insert** – Time-absorption profiles of the spectra at 710 and 900 nm, monitoring the intersystem crossing dynamics and the life time (i.e. 8.9 ± 0.5 ns).

**Figure S24:** Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (530 nm and 200 nJ) of Bodipy 5 in toluene with several time
delays between 0 and 8000 ps at room temperature. **Insert** – Time-absorption profiles of the spectra at 530 monitoring the intramolecular energy dynamics (i.e. $4.9 \pm 0.2$ ns).

**Figure S25:** Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (530 nm and 200 nJ) of Bodipy 6 in toluene with several time delays between 0 and 8000 ps at room temperature. **Insert** – Time-absorption profiles of the spectra at 580 monitoring the intramolecular dynamics (i.e. $0.9 \pm 0.1$ ns).
**Figure S26:** Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (530 nm and 200 nJ) of 1-Zn in toluene with several time delays between 0 and 8000 ps at room temperature. **Insert** – Time-absorption profiles of the spectra at 520 and 710 nm, monitoring the intramolecular energy transfer dynamics (i.e., 8.7 ± 1.4 ps).

![Figure S26](image)

**Figure S27:** Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (530 nm and 200 nJ) of 2-Zn in toluene with several time delays between 0 and 8000 ps at room temperature. **Insert** – Time-absorption profiles of the spectra at 590 and 710 nm, monitoring the intramolecular energy transfer dynamics (i.e., 2.5 ± 0.2 ps).

![Figure S27](image)
**Figure S28:** Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (530 nm and 200 nJ) of 1-Cu in toluene with several time delays between 0 and 8000 ps at room temperature. **Insert** – Time-absorption profiles of the spectra at 520 and 710 nm, monitoring the intramolecular energy transfer dynamics (i.e. 4.4 ± 0.5 ps).

![Differential absorption spectra](image)

**Figure S29:** Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (530 nm and 200 nJ) of 2-Cu in toluene with several time delays between 0 and 8000 ps at room temperature. **Insert** – Time-absorption profiles of the spectra at 590 and 710 nm, monitoring the intramolecular energy transfer dynamics (i.e. 5.3 ± 0.3 ps).

**Table S1:** Summary of the extinction coefficients at different solvents.

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**Table S2:** Summary of the life times in different solvents at room temperature by exciting at 403 nm.
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**Literature**


