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Catalytic amination in the synthesis of hybrid polymacrocycles comprising porphyrin and azacrown ether moieties

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Conjugate 6. A two-necked flask flushed with dry argon, equipped with a magnetic stirrer and reflux condenser was charged with Zn porphyrinate **5** (0.15 mmol, 113 mg), azacrown derivative **4** (0.15 mmol, 64 mg), $Pd(dba)_2$ (7 mg, 8 mol%), BINAP (8.5 mg, 9 mol%), absolute dioxane (2 ml) and *t*BuONa (0.23 mmol, 22 mg). The reaction mixture was refluxed for 24 h, cooled to ambient temperature, diluted with CH_2Cl_2 (5 ml), the residue was filtered off, washed with CH_2Cl_2 (5 ml), combined organic fractions were evaporated *in vacuo*, dissolved in CH_2Cl_2, washed with water (5 ml) and dried over molecular sieves. Solvent was again evaporated *in vacuo* and the residue was chromatographed on silica gel using a gradient of eluents: CH_2Cl_2 – CH_2Cl_2/MeOH 3:1. The target compound was eluted with CH_2Cl_2/MeOH 10:1 Yield 24 mg (15%), deep-red solid. UV-vis (CH_3CN): λ_{max} = 409 nm (lgε 5.55), 539 (4.32), 574 (4.13); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (t, J = 7.3 Hz, 6H, CH_3), 1.51 (sextet, J = 7.3 Hz, 4H, CH_2), 1.69 (quintet, J = 7.4 Hz, 4H, CH_2), 2.12 (quintet, J = 7.4 Hz, 4H, CH_2), 2.25 (br.s, 2H, CH_2), 2.51 (s, 6H, CH_3), 2.70-3.50 (br.m, 26H, CH_2N, CH_2O), 3.11 (br.s, 2H, CH_2N), 3.34 (t, J = 6.2 Hz, 2H, CH_2N), 3.41 (s, 6H, CH_3), 3.43 (s, 6H, CH_3), 3.71 (t, J = 7.4 Hz, 4H), 6.06 (br.s, 1H, Ph), 6.27 (br.s, 2H, Ph), 6.80 (t, J_{obs} = 6.9 Hz, 1H Ph), 6.92 (d, J_{obs} = 6.8 Hz, 1H, Ph), 7.14 (s, 1H, Ph), 7.32 (d, J_{obs} = 6.2 Hz, 1H, Ph), 7.44 (t, J = 7.6 Hz, 1H, Ph), 9.42 (s, 1H, H_{meso}), 9.82 (s, 2H, H_{meso}) (two NH protons were not assigned); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 11.5 (2C), 12.1 (2C), 14.1 (2C), 15.1 (2C), 22.7 (2C), 26.3 (2C), 28.5 (1C), 32.4 (2C), 33.0 (2C), 41.6 (1C), 41.7 (1C), 51.9 (2C), 57.3 (1C), 68.8 (2C), 69.4 (4C), 69.6 (4C), 95.8 (1C), 96.7 (2C), 102.6 (1C), 112.5 (1C), 118.8 (1C), 123.0 (2C), 128.0 (1C), 135.6 (2C), 137.8 (2C), 138.4 (2C), 140.9 (2C), 144.4 (1C), 146.8 (2C), 146.9 (2C), 147.5 (2C), 147.7 (2C), 149.1 (1C), 149.2 (1C) (four quaternary carbon atoms were not assigned); MALDI-TOF: $[M+H]^+$ 1096.6054; calcd for $C_{64}H_{86}N_7O_5Zn$: 1096.5982.

Conjugate 9. Yield 28 mg (15%), deep-red solid. UV-vis (CH_3CN): λ_{max} = 417 nm (lgε 4.80), 546 (3.45), 578 (3.17); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, J = 7.3 Hz, 12H, CH_3), 1.53 (sextet, J = 7.0 Hz, 8H, CH_2), 1.73 (quintet, J = 6.8 Hz, 8H, CH_2), 2.01 (br.s, 4H, CH_2), 2.18 (quintet, J = 6.4 Hz, 8H, CH_2), 2.56 (s, 12H, CH_3), 2.70 (br.s, 8H, CH_2N), 3.21 (br.s, 4H, CH_2N), 3.35-3.68 (m, 48H, CH_2N, CH_2O), 3.94 (t, J = 7.1 Hz, 8H, CH_2N), 6.44 (d, J_{obs} = 5.4 Hz, 2H, Ph), 6.63 (d, J_{obs} = 7.0 Hz, 4H, Ph), 6.93 (d, J_{obs} = 7.8 Hz, 4H, Ph), 7.10 (t, J = 7.8 Hz, 2H, Ph), 7.77 (d, J_{obs} = 7.8 Hz, 4H), 10.10 (s, 2H, H_{meso}) (four NH protons were not assigned); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.2 (4C), 15.5 (4C), 22.8 (4C), 26.7 (4C), 29.6 (2C), 32.5 (4C), 33.1 (4C), 42.0 (2C), 42.2 (2C), 53.6 (4C), 59.3 (2C), 69.7-70.6 (m, 20C), 97.0 (2C), 111.7 (2C), 112.0 (4C), 114.3 (2C), 118.4 (2C), 128.7 (2C), 129.0 (4C), 133.7 (4C), 138.2 (4C), 142.8 (4C), 146.2 (4C), 148.2 (2C), 148.4 (4C) (four quaternary carbon atoms were not assigned); MALDI-TOF: $[M+H]^+$ 1708.0395; calcd for $C_{100}H_{143}N_{10}O_{10}Zn$: 1708.0280.

Conjugate 10. A two-necked flask flushed with dry argon, equipped with a magnetic stirrer and reflux condenser was charged with porphyrin **8** (0.1 mmol, 96 mg), azacrown derivative **3** (0.2 mmol, 76 mg), $Pd(dba)_2$ (9 mg, 16 mol%), BINAP (11 mg, 18 mol%), absolute dioxane (1 ml) and *t*BuONa (0.3 mmol, 29 mg). The reaction mixture was refluxed for 24 h and then worked up in a similar manner as described for compound **6**. The target compound was eluted with CH_2Cl_2/MeOH/NH_3aq 100:20:3. Yield 32 mg (20%), deep-red solid. UV-vis (CH_3CN): λ_{max} = 409 nm (lgε 5.02); ^{1}H NMR (400 MHz, $CDCl_3$): δ = -2.40 (br.s, 2H, NH_{porph}), 0.95 (t, J = 7.2 Hz, 12H, CH_3), 1.51 (sextet, J = 7.3 Hz, 8H, CH_2), 1.71 (quintet, J = 7.4 Hz, 8H, CH_2), 2.15 (quintet, J = 5.8 Hz, 4H, CH_2), 2.19 (quintet, J = 7.1 Hz, 8H, CH_2), 2.61 (s, 12H, CH_3), 2.84 (br., 8H, CH_2N), 3.42 (t, J = 6.3 Hz, 4H, CH_2N), 3.53 (t, J = 6.1 Hz, 4H, CH_2N), 3.64 (br.s, 36H, CH_2N, CH_2O), 3.98 (t, J = 7.0 Hz, 8H, CH_2), 6.60 (d, J = 7.6 Hz, 2H, Ph), 6.69 (d, J_{obs} = 7.1 Hz, 2H, Ph), 6.86 (br.s, 2H, Ph), 6.98 (d, J_{obs} = 8.1 Hz, 4H, Ph), 7.17 (t, J = 7.7 Hz, 2H, Ph), 7.79 (d, J_{obs} = 8.1 Hz, 4H, Ph), 10.20 (s, 2H, H_{meso}) (four NH protons were not assigned); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.2 (4C), 14.9 (4C), 22.8 (4C), 26.7 (4C), 29.5 (2C), 32.5 (4C), 33.0 (4C), 42.2 (2C), 42.4 (2C), 54.4 (4C), 60.7 (2C), 69.9 (4C), 70.2 (4C), 70.5 (4C), 70.9 (4C), 96.6 (2C), 111.1 (2C), 112.0 (4C), 113.7 (2C), 118.1 (4C), 122.5 (2C), 129.1 (2C), 133.5 (4C), 136.5 (4C), 141.3 (4C), 142.8 (4C), 145.8 (2C), 148.3 (2C), 148.4 (2C) (four quaternary carbon atoms were not assigned); MALDI-TOF: $[M+H]^+$ 1558.0527; calcd for $C_{96}H_{137}N_{10}O_8$: 1558.0621.

Porphyrin 11. A two-necked flask flushed with dry argon, equipped with a magnetic stirrer and reflux condenser was charged with porphyrin **8** (0.1 mmol, 96 mg), propane-1,3-diamine (0.3 mmol, 22 mg), $Pd(dba)_2$ (2.5 mg, 4 mol%), BINAP (3 mg, 4.5 mol%), absolute dioxane (1 ml)

and *t*BuONa (0.3 mmol, 29 mg). The reaction mixture was refluxed for 24 h, cooled to ambient temperature, diluted with CH_2Cl_2 (5 ml), the residue was filtered off, washed with CH_2Cl_2 (5 ml), combined organic fractions were evaporated *in vacuo*, and chromatographed on silica gel using a gradient of eluents: CH_2Cl_2 – CH_2Cl_2/MeOH 3:1 – CH_2Cl_2/MeOH/NH_3aq 100:20:1-10:14:1. The target compound was eluted with CH_2Cl_2/MeOH/NH_3aq 100:20:3. Yield 46 mg (49%), deep-red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = -2.30 (br.s, 2H, NH_{porph}), 1.00 (t, J = 7.3 Hz, 12H, CH_3), 1.57 (sextet, J = 7.3 Hz, 8H, CH_2), 1.77 (quintet, J = 7.3 Hz, 8H, CH_2), 1.88 (quintet, J = 6.4 Hz, 4H, CH_2), 2.25 (quintet, J_{obs} = 5.8 Hz, 8H, CH_2), 2.65 (s, 12H, CH_3), 2.93 (t, J = 6.4 Hz, 4H, CH_2N), 3.37 (t, J = 6.4 Hz, 4H, CH_2N), 4.03 (t, J_{obs} = 5.8 Hz, 8H, CH_2), 6.92 (d, J_{obs} = 8.1 Hz, 4H, Ph), 7.80 (d, J_{obs} = 8.1 Hz, 4H, Ph), 10.26 (s, 2H, H_{meso}) (six NH protons were not assigned); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.2 (4C), 14.9 (4C), 22.8 (4C), 26.7 (4C), 32.5 (6C), 33.0 (4C), 40.2 (2C), 42.4 (2C), 96.6 (2C), 111.9 (4C), 118.4 (2C), 131.1 (2C), 133.5 (4C), 136.5 (4C), 141.3 (4C), 142.8 (4C), 145.9 (4C), 148.5 (2C); MALDI-TOF: $[M+H]^+$ 943.7136; calcd for $C_{62}H_{87}N_8$: 943.7054.

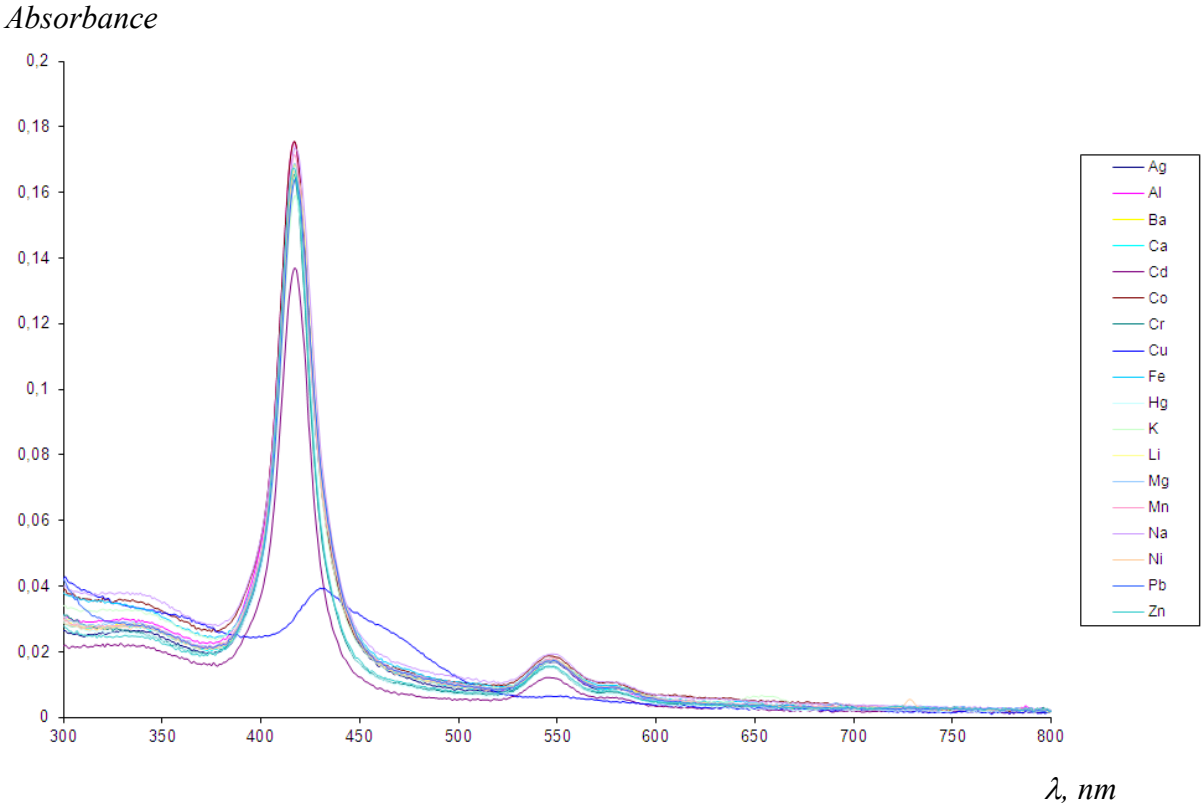

Figure S1 Evolution of UV-vis spectrum of trismacrocycle **9** after addition of 2.5 equiv. metal perchlorates (MeCN, C = $3.33*10^{-6}$ M).

Emission

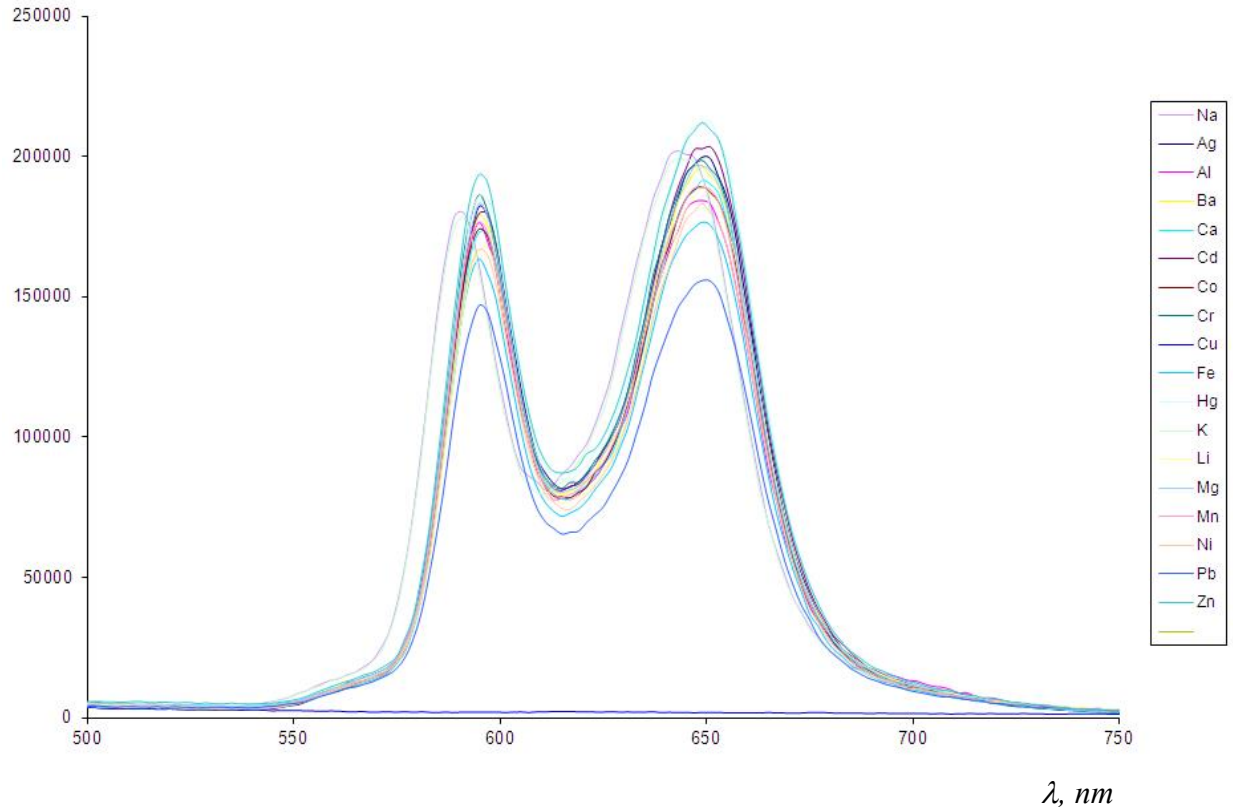

Figure S2 Evolution of the fluorescence of trismacrocycle **9** after addition of 2.5 equiv. metal perchlorates (MeCN, C = $3.33*10^{-6}$ M, λ_{ex} 418 nm).

Absorbance

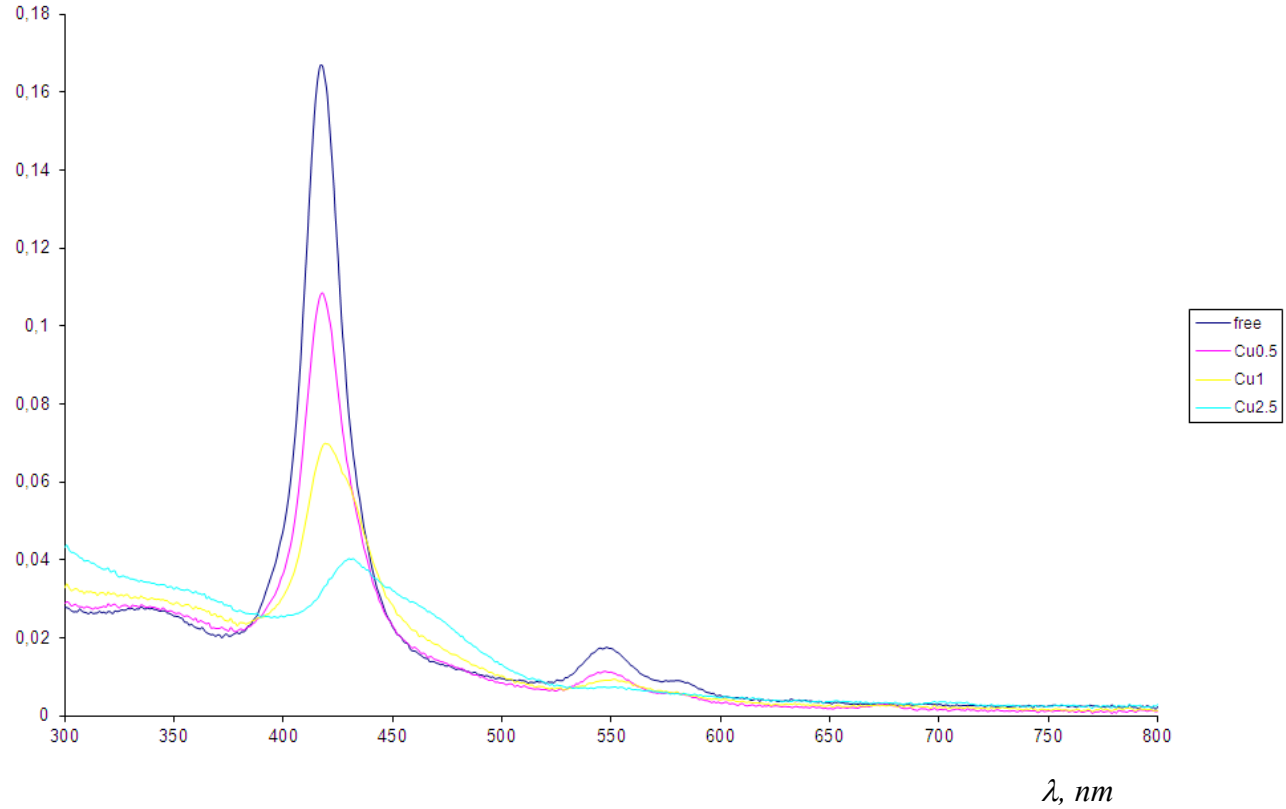

Figure S3 Evolution of UV-vis spectrum of trismacrocycle **9** after addition of 0.5, 1 and 2.5 equiv. $Cu(ClO_4)_2$ (MeCN, C = $3.33*10^{-6}$ M).

Emission

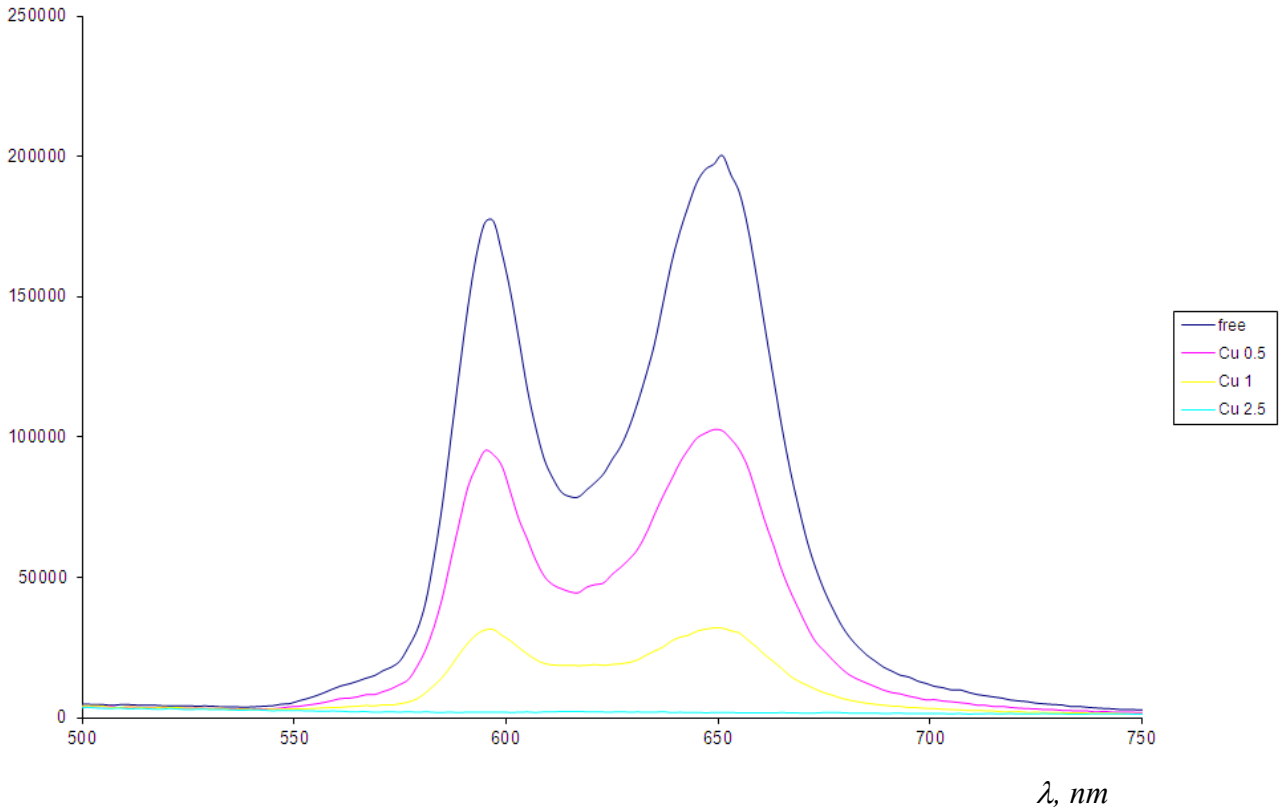

Figure S4 Evolution of the fluorescence of trismacrocycle **9** after addition of 0.5, 1 and 2.5 equiv. $Cu(ClO_4)_2$ (MeCN, C = $3.33*10^{-6}$ M, λ_{ex} 418 nm).

Absorbance

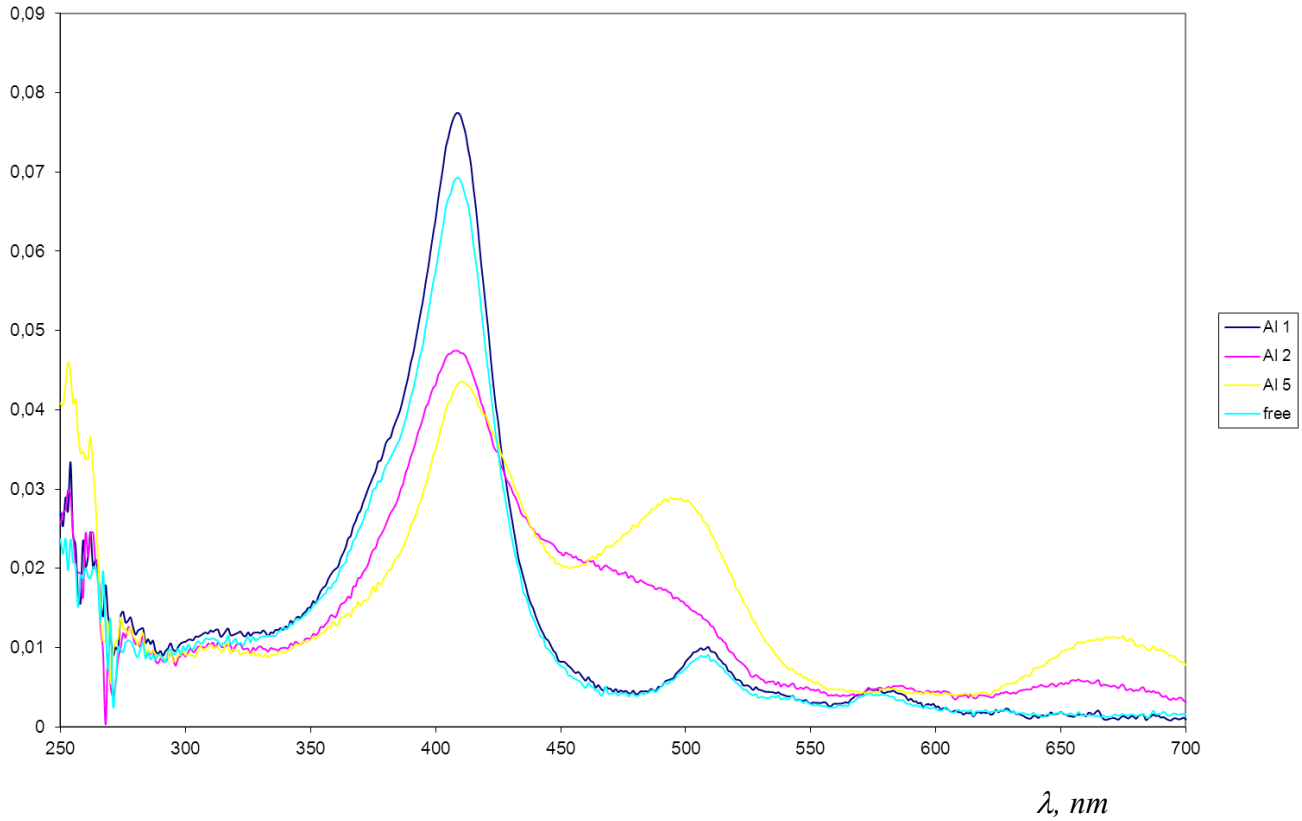

Figure S5 Evolution of UV-vis spectrum of trismacrocycle **10** after addition of 1, 2 and 5 equiv. $Al(ClO_4)_3$ (MeCN, C = $6.4*10^{-7}$ M).

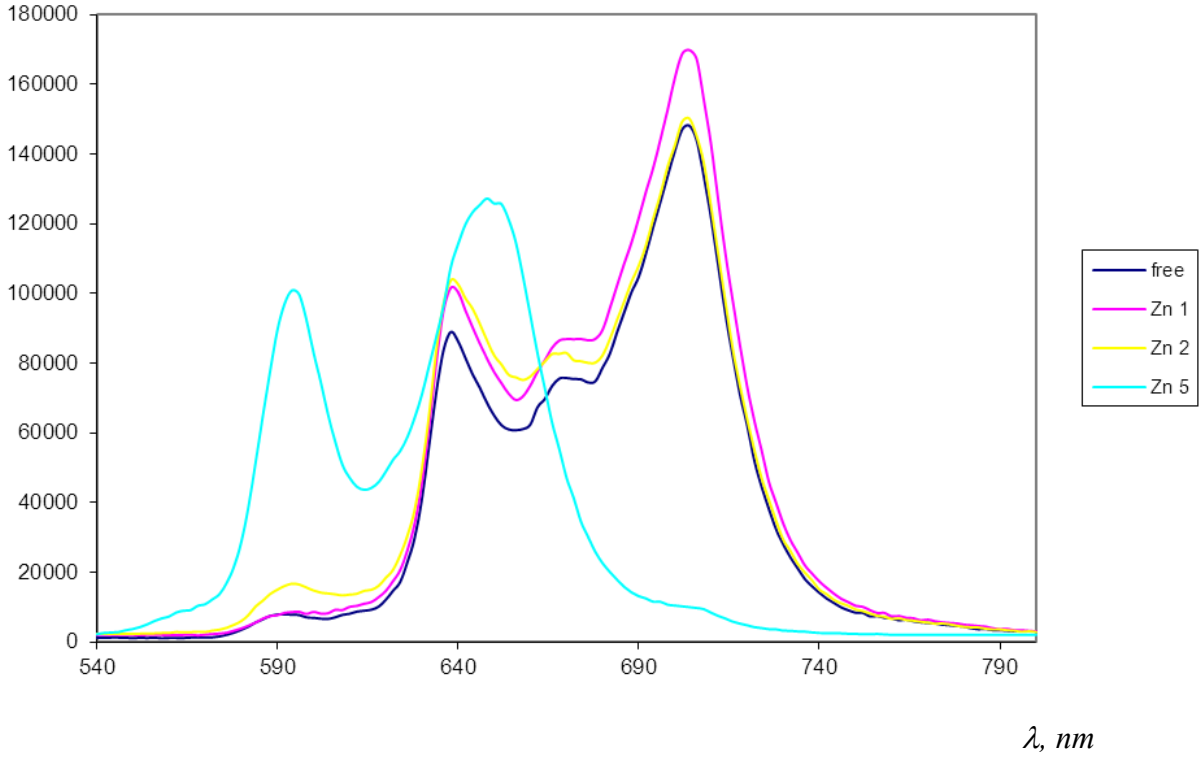

Figure S6 Evolution of the fluorescence of trismacrocycle **10** after addition of 1, 2 and 5 equiv. $Zn(ClO_4)_2$ (MeCN, C = $6.4*10^{-7}$ M, λ_{ex} 409 nm).