Supplementary Information For:

Lanthanide-corrole conjugates

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Synthesis of the corroles.

Synthesis of 5,15-bis-pentafluorophenyl-10-(4-nitrophenyl)-corrole (**1**).

5-(pentafluorophenyl)-dipyrromethane (624 mg, 2 mmol) and *p*-nitrobenzaldehyde (161 mg, 1 mmol) were dissolved in 100 ml of methanol, followed by addition of 5 ml of HCl (37%) in 100 ml of water. Reaction was performed under intensive stirring at room temperature for an hour, followed by extraction with DCM, washing of the organic phase with water for three times, drying of the DCM extracts with Na_2SO_4 and filtering. The organic fraction was concentrated to 50 ml with DCM, and DDQ (1 mmol, 222 mg) in 10 ml of THF was added gradually under stirring. After 10 minutes, the solution was evaporated to dryness, followed by the addition of 2 spoons of silica and 100 ml of DCM and evaporation to dryness. Fast column chromatography was performed using DCM:hexanes=1:1 as an eluent and 230-400 mesh silica as a sorbent. A second column chromatography was performed using DCM:hexanes=1:5 with the same sorbent. The product was recrystallized from hexanes and obtained as purple needles (220mg, 30%). ^{1}H NMR ($CDCl_3$) δ 9.14 (d, 2H, J=4.2Hz), 8.75 (d, 2H, J=3.8Hz), 8.62 (m, 6H), 8.37 (d, 2H, J=8.5Hz). ^{19}F NMR ($CDCl_3$) -137.9 (d, 4H, J=22.6Hz), -152.3 (s, 2H), -161.5 (t, 4H, J=16.2Hz). ESI-MS obsd 750.88 [M-H$^+$]; ESI-HR calc exact mass ($C_{37}H_{14}N_5O_2F_{10}$) 750.0988; found, 750.0981 [M-H$^+$]; $\lambda_{abs.}$ (nm(lgε), methanol) 412(5.08), 568(4.38), 615(4.26).

Synthesis of 5,15-bis-pentafluorophenyl-10-(4-aminophenyl)-corrole (**2**).

200 mg (0.27 mmol) of **1** and 610 mg of $SnCl_2 \cdot 2H_2O$ (2.7 mmol) were added to 50 ml of HCl (37%, aq.). This heterogeneous mixture was refluxed for 2 hours under Ar atmosphere and then it was cooled to RT, filtered, washed consequently with HCl (37%, aq.), $NaHCO_3$ solution, water and dried. Chromatography with DCM:hexanes=1:1 provided 185 mg (95% yield) of the title compound as a purple powder. ^{1}H NMR ($CDCl_3$) δ 9.09 (s, 2H), 8.76 (s, 2H), 8.70 (s, 2H), 8.55 (s, 2H), 7.93 (d, 2H, J=5.3Hz), 6.99 (d, 2H, J=6.3Hz). ^{19}F NMR ($CDCl_3$) -137.8 (d, 4H, J=18.2Hz), -153.0 (t, 2H, J=20.4Hz), -161.8 (t, 4H, J=18.5Hz). ESI-MS obsd 719.97 [M-H$^+$]; ESI-HR calc exact mass ($C_{37}H_{16}N_5F_{10}$) 720.1246; found, 720.1242 [M-H$^+$]; $\lambda_{abs.}$ (nm(lgε), methanol) 415(5.08), 568(4.38), 615(4.26). Calc for $C_{37}H_{17}F_{10}N_5$: C 61.59%, H 2.37%, N 9.71%. Found: C 61.91%, H 2.33%, N 9.60%.

Synthesis of {carboxymethyl-[2-(carboxymethyl-{[4-(5,10-diphenyl-corrol-5-yl)-phenylcarbamoyl]-methyl}-amino)-ethyl]-amino}-acetic acid, H_3edta-corrole (**3**).

A solution of **2** (150 mg, 0.14 mmol) in dry DMF was added dropwise to a stirred solution (80°C) of H_4edta dianhydride (52 mg, 0.2 mmol) in dry DMF, containing a catalytic amount of triethylamine, during 10 minutes. After adding, the reaction was continued at the same conditions for 1 hour until the starting corrole was not determined by TLC in the reaction mixture. Crude product was precipitated by water, filtered and dried to provide the title compound as a purple powder in 90% yield (185 mg). ^{1}H NMR (MeOD) δ 9.06 (s, 2H), 8.77 (s, 2H), 8.60 (s, 4H), 8.10 (dd, 4H, J=21.6Hz, J=7.4Hz), 3.79 (s, 4H), 3.66 (s, 2H), 3.57 (s, 2H), 3.30 (s, 2H), 3.16 (s, 2H). ^{19}F NMR (MeOD) -140.8 (d, 4H, J=18Hz), -155.7 (s, 2H), -164.7 (s, 4H). ESI-MS obsd 994.03 [M-H$^+$]; ESI-HR calc exact mass ($C_{47}H_{30}N_7O_7F_{10}$) 994.2047; found, 994.2012 [M-H$^+$]; $\lambda_{abs.}$ (nm(lgε), methanol) 410(5.08), 568(4.38), 615(4.26). Calc for $C_{47}H_{31}N_7O_7F_{10}$: C 56.69%, H 3.14%, N 9.85%. Found: C 56.39%, H 3.09%, N 9.74%.

Synthesis of ((2-{[2-(Bis-carboxymethyl-amino)-ethyl]-carboxymethylamino}-ethyl)-{[4-(5,15-diphenyl-corrol-5-yl)-phenylcarbamoyl]-methyl}-amino)-acetic acid, H_4dtpa-corrole (**4**).

A solution of **2** (150 mg, 0.14 mmol) in dry DMF was added dropwise to a stirred solution (80°C) of H_5dtpa dianhydride (70 mg, 0.2 mmol) in dry DMF, containing a catalytic amount of triethylamine, during 10 minutes. After adding, the reaction was continued at the same conditions for 1 hour until the starting corrole was not determined by TLC in the reaction mixture. Crude product was precipitated by water, filtered and dried to provide the title compound as a purple powder in 89% yield (250 mg). ^{1}H NMR (MeOD) δ 8.97 (d, 2H), 8.72 (s, 2H), 8.57 (s, 2H), 8.52 (s, 2H), 8.05 (dd, 4H, J=33Hz, J=7Hz), 3.79 (s, 2H), 3.63 (s, 2H), 3.55 (s, 6H), 3.27 (s, 4H), 3.17 (s, 4H). ^{19}F NMR (MeOD) -140.8 (d, 4H, J=18Hz), -156.2 (s, 2H), -165.0 (s, 4H). ESI-MS obsd 1095.06 [M-H$^+$]; ESI-HR calc exact mass ($C_{51}H_{39}F_{10}N_8O_9$) 1097.2680; found, 1097.2683 [M+H$^+$]; $\lambda_{abs.}$ (nm(lgε), methanol) 410(5.08), 568(4.38), 615(4.26). Calc for $C_{51}H_{38}F_{10}N_8O_9$: C 55.85%, H 3.49%, N 10.22%. Found: C 55.34%, H 3.23%, N 9.89%.

Synthesis of the lanthanide-corrole conjugates.

General procedures for the syntheses of complexes **5-12**.

A. Syntheses were carried out by interaction of 0.05 mmol of **3** (**4**) with 0.05 mmol of $LnX_3 \cdot 6H_2O$ (Ln = Nd, Er, Yb, Lu; X = Cl or NO_3) in methanol at room temperature under stirring for 10 minutes. Obtained solutions were used for NMR and MS characterization.

B. Syntheses were carried out by interaction of 0.05 mmol of **3** (**4**) with 0.05 mmol of $LnX_3 \cdot 6H_2O$ (Ln = Nd, Er, Yb, Lu; X = Cl or NO_3) in DMF at room temperature under stirring for 10 minutes. Then the crude product was precipitated with water, filtered and dried to give quantitative yield of the title compounds as purple powders.

Nd-edta-corrole (**5**).

Yield 59 mg. ^{19}F NMR (MeOD) δ -141.38 (d, 4H, J=18Hz), -154.15 (t, 2H, J=20 Hz), -164.22 (t, 4H, J=16Hz). MALDI-MS obsd 1170.97 [M-H$^+$]; MALDI-MS calc ($C_{47}H_{31}F_{10}N_7NdO_9$) 1171.04; ESI-MS obsd 1194.79 [M+Na$^+$]; ESI-MS calc

($C_{47}H_{32}F_{10}N_7NdO_9$+$Na^+$) 1195.11; $\lambda_{abs.}$ (nm(lgε), methanol) 410(5.08), 568(4.38), 615(4.26).

Er-edta-corrole (**6**).

Yield 60 mg. ESI-MS obsd 1215.81 [M+Na^+]; ESI-MS calc ($C_{47}H_{31}ErF_{10}N_7O_9$+$Na^+$) 1216.12; $\lambda_{abs.}$ (nm(lgε), methanol) 410(5.08), 568(4.38), 615(4.26).

Yb-edta-corrole (**7**).

Yield 60 mg. ^{19}F NMR (MeOD) δ -140.70 (s, 4H), -156.81 (s, 2H), -165.36 (s, 4H). ESI-MS obsd 1203.14 [M+H^+]; ESI-MS calc ($C_{47}H_{33}F_{10}N_7O_9Yb$) 1203.16; $\lambda_{abs.}$ (nm(lgε), methanol) 410(5.08), 568(4.38), 615(4.26).

Lu-edta-corrole (**8**).

Yield 60 mg. ^{1}H NMR (MeOD) δ 9.51 (d, 2H, J=4Hz), 9.14 (d, 2H, J=4Hz), 8.94 (d, 2H, J=3.5Hz), 8.77 (d, 2H, J=4.5Hz), 8.51 (d, 2H, J=8.1Hz), 8.34 (d, 2H, J=8.1Hz), 4.36 (d, 1H, J=16.2Hz), 4.17 (d, 1H, J=16.5Hz), 3.98-3.56 (m, 6H), 3.2-3.1 (m, 4H). ^{19}F NMR (MeOD) δ -141.47 (d, 4H, J=18Hz), -154.19 (t, 2H, J=20Hz), -164.26 (t, 4H, J=18Hz). ESI-MS obsd 1208.81 [M+Na^+]; ESI-MS calc ($C_{47}H_{30}F_{10}LuN_7O_8$+$Na^+$) 1208.13; $\lambda_{abs.}$ (nm(lgε), methanol) 410(5.08), 568(4.38), 615(4.26).

Nd-dtpa-corrole (**9**).

Yield 62 mg. ^{19}F NMR (MeOD) δ -141.51 (d, 4H, J=16Hz), -154.16 (m, 2H), -164.28 (t, 4H, J=17Hz). ESI-MS obsd 1236.00 [M-H^+]; ESI-MS calc ($C_{51}H_{34}F_{10}N_8NdO_9$) 1236.14; $\lambda_{abs.}$ (nm(lgε), methanol) 410(5.08), 568(4.38), 615(4.26).

Er-dtpa-corrole (**10**).

Yield 63 mg. ESI-MS obsd 1260.1 [M-H^+]; ESI-HR obsd 1260.1632 [M-H^+]; ESI-HR calc exact mass ($C_{51}H_{34}ErF_{10}N_8O_9$) 1260.1626; $\lambda_{abs.}$ (nm(lgε), methanol) 410(5.08), 568(4.38), 615(4.26).

Yb-dtpa-corrole (**11**).

Yield 63 mg. ^{19}F NMR (MeOD) δ -139.05 (s, 4H), -156.21 (s, 2H), -164.40 (s, 4H). ESI-MS obsd 1287.67 [M-2H^{+}+Na^{+}]; ESI-MS calc ($C_{51}H_{33}F_{10}N_8O_9Yb+Na^{+}$) 1288.14; $\lambda_{abs.}$ (nm(lgε), methanol) 410(5.08), 568(4.38), 615(4.26).

Lu-dtpa-corrole (**12**).

Yield 63 mg. ^{1}H NMR (MeOD) δ 9.52 (d, 2H, J=4.4Hz), 9.15 (d, 2H, J=4.2Hz), 8.96 (d, 2H, J=4.2Hz), 8.79 (d, 2H, J=4.7Hz), 8.50 (d, 2H, J=8.1Hz), 8.30 (d, 2H, J=8.3Hz), 4.6-3.9 (m, 4H), 3.9-3.5 (m, 8H), 3.25-3.1 (m, 4H). ^{19}F NMR (MeOD) δ -141.49 (d, 4H, J=17Hz), -154.17 (t, 2H, J=20.5Hz), -164.27 (m, 4H). ESI-MS obsd 1268.21 [M^{+}]; ESI-MS calc ($C_{51}H_{35}F_{10}LuN_8O_9$) 1268.18; $\lambda_{abs.}$ (nm(lgε), methanol) 410(5.08), 568(4.38), 615(4.26).

NMR spectra were recorded on spectrometer Bruker Avance 400 and Bruker Avance 600.

ESI mass spectra were recorded on spectrometer Waters ESI TOF Premier. MALDI mass spectra were recorded on Waters Micromass Maldi Micro MX mass spectrometer using TOF electron negative mode.

UV/VIS absorption spectral measurements were recorded with an Agilent 8453 spectrophotometer.

Elemental analysis was performed on CHNS analyzer Flash 2000 Thermo Scientific.

Luminescent measurements

Spectra of molecular fluorescence, 4f-luminescence and excitation spectra were recorded on spectrofluorimeter "Fluorolog FL 3-22" "Horiba Jobin Yvon" (Xe-lamp 450 W). Spectra of 4f-luminescence of Yb^{3+} ions (transition $^2F_{5/2}\rightarrow{}^2F_{7/2}$) were registered at 950-1050 nm region and of Nd^{3+} at 850-1350 nm (transitions $^4F_{3/2}\rightarrow{}^4I_{13/2}$, $^4F_{3/2}\rightarrow{}^4I_{11/2}$ и $^4F_{3/2}\rightarrow{}^4I_{9/2}$). Spectra of molecular fluorescence of corroles were registered at 550-800 nm (S-S transitions).

Luminescence integral intensity was measured using software of the device. The relative quantum yield of molecular fluorescence was determined using solution of Zn-tpp in ethanol as a primary reference (0.022). Determination of the relative quantum yield of molecular fluorescence and 4f-luminescence was made using formula:

$$\varphi_x = \varphi_0 I_x A_0 n_x^2/(I_0 A_x n_0^2),$$

where φ_0 and φ_x – luminescence quantum yield of the reference and of the sample respectively,

A_0 and A_x – absorption at the Soret band of the reference and of the sample respectively,

I_x and I_0 – integral luminescence intensity of the reference and of the sample respectively,

n_0 and n_x – refractive index of the reference solvent and of the sample solvent respectively.

Fluorescence lifetime was measured under excitation at the Soret band.

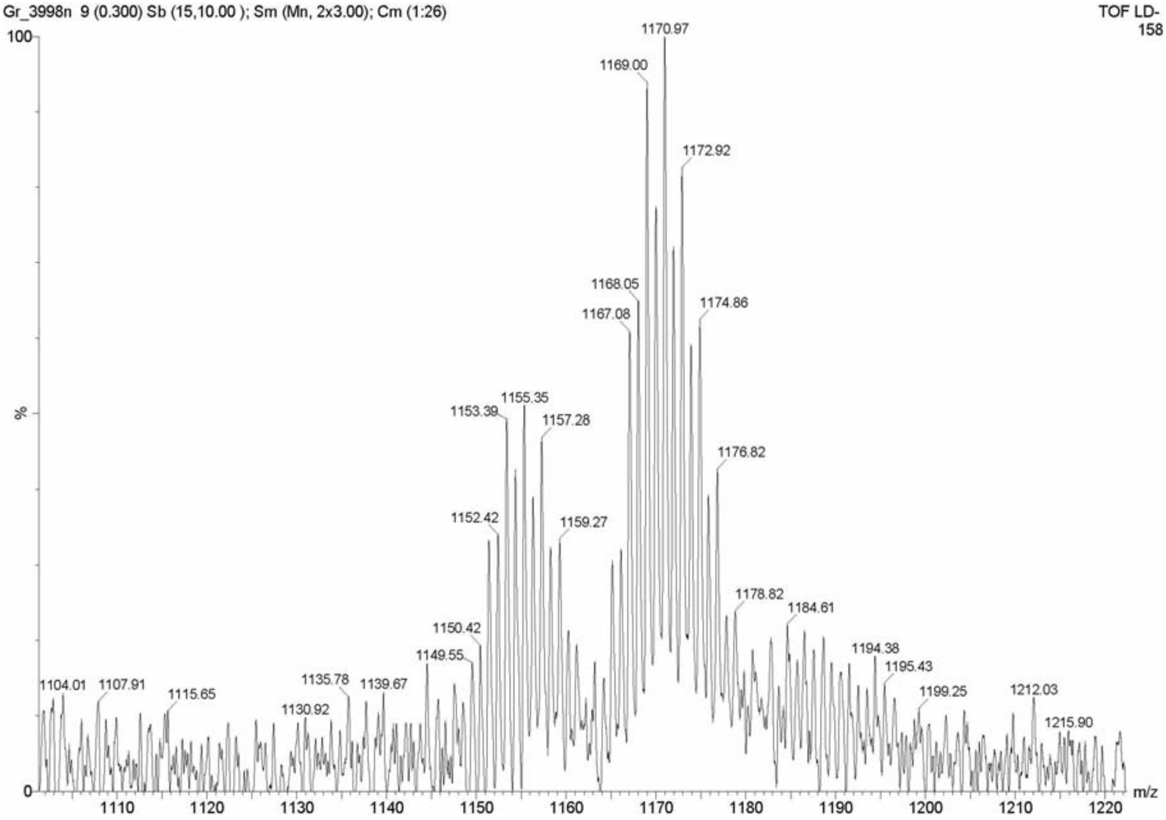

Figure S1. MALDI mass spectrum of Nd-edta-corrole.

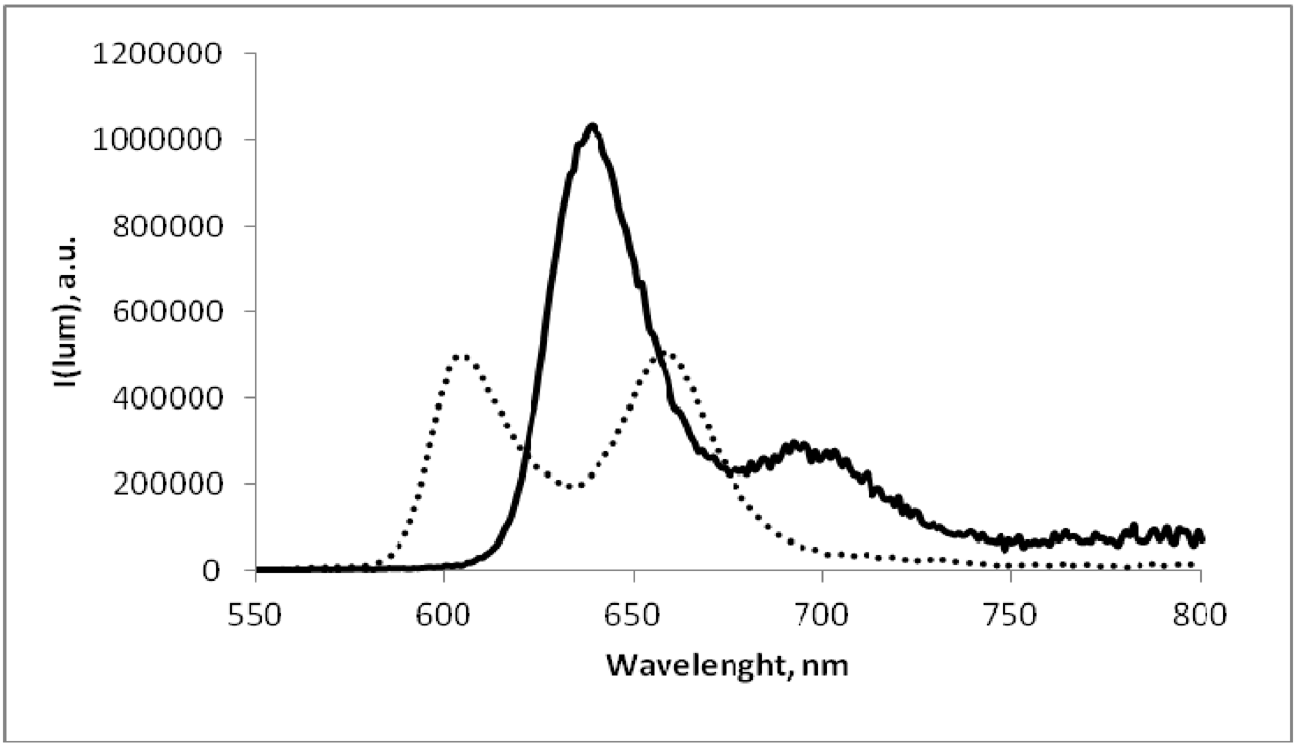

Figure S2. Molecular fluorescence of **13** (Zn-tpp, dotted line) and **3** (edta-corrole, solid line). C=10^{-5}M, RT, DMF, $\lambda_{exc.}$=Soret band (Table 1).

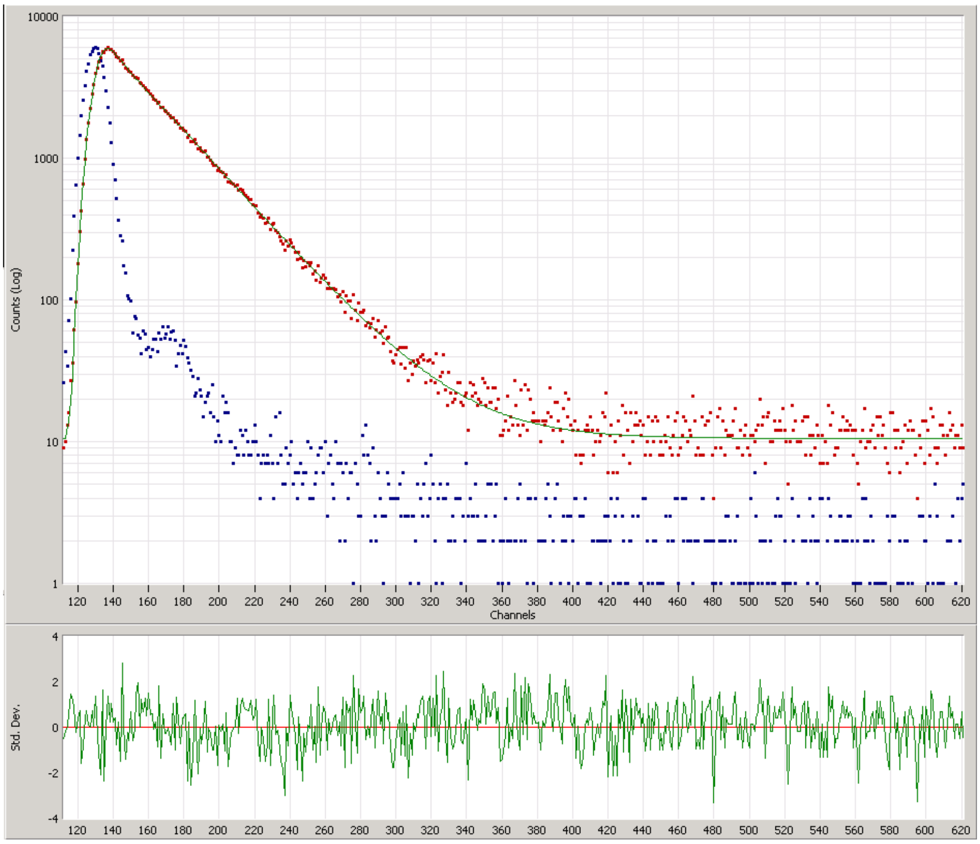

Figure S3. Lifetime measurement of molecular fluorescence of **6**