

Expeditious selective access to functionalized platforms of A7B-type heteroleptic lanthanide double-decker complexes of phthalocyanine

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Materials and Methods

Solvents and chemicals were purchased from Aldrich or Alfa Aesar and used as received. Phthalonitriles **5**¹, **6**² and **7**³ were prepared according to reported literature protocols.

Mass spectra were recorded on a MALDI (matrix assisted laser desorption ionization) BRUKER Microflex LT using 2,5-dihydroxybenzoic acid as the matrix and on a BRUKER MicroTOFQ-II with an ESI (electrospray ionization) ion source in positive mode. In this latter case, the sample was infused at 150 $\mu\text{L}/\text{h}$ in 50:50 water and acetonitrile with 0.1% of formic acid. The gas flow of the sprayer is 0.6 bar, and the spray voltage is 3.5 kV. The capillary temperature is 200 $^{\circ}\text{C}$. The ions are transferred to the TOF by using mild conditions on ion optics (the two ion funnels, the hexapole, the quadrupole, and the collision cell) to preserve the complex. The mass range of the TOF is 50–5000 m/z and the calibration was done with cesium iodide.

FT-IR spectra were recorded between 4000 and 650 cm^{-1} using a Perkin-Elmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection (ATR) accessory featuring a zinc selenide (ZnSe) crystal.

Electronic absorption spectra were recorded at room temperature on a Shimadzu 2001 UV spectrophotometer using a 1 cm path length cuvette or on a Jasco V670 spectrophotometer between 290 and 2700 nm. The spectra of the neutral $[\text{Eu}(\text{Pc})_2]$ and oxidized species $[\text{Eu}(\text{Pc})_2]^+$ were recorded in chloroform. The oxidized species were generated *in-situ* by adding bromine. The spectra were corrected for the solvent absorption peaks at 1690 nm and 2350 nm. The spectra of the reduced species $[\text{Eu}(\text{Pc})_2]^-$ was recorded in THF. The reduced species were generated *in-situ* by adding a crystal of NaBH_4 .

NMR spectra were recorded on a 300 MHz spectrometer with the residual solvent peak (THF, ^1H : $\delta = 1.72$ ppm and 3.58 ppm) as the internal reference. The compound was dissolved in THF- d_8 and a crystal of NaBD_4 (98 atom % D for NMR, Acros) was added. The color immediately changed from dark green to green indicating the complete reduction. Chemical shifts are reported in parts per million (ppm, δ) relative to tetramethylsilane as an internal reference at 0.00 ppm.

Preparation of 1. A mixture of phthalonitriles **5** (2.35 g, 6.52 mmol, 20 equiv) and **6** (128 mg, 0.33 mmol, 1 equiv) was dissolved in a minimum amount of CH₂Cl₂ and evaporated to ensure of the homogeneous blending. Eu(OAc)₃ (422 mg, 1.28 mmol, 5 equiv regarding the total amount of phthalonitriles), dry pentanol (5 mL) and DBU (1 mL) were added, and the reaction mixture was refluxed under argon for 4 hours. The reaction mixture was cooled down to room temperature, poured into ethanol, filtered and recovered with dichloromethane. Dichloromethane was evaporated, and the product was purified on a silica gel column chromatography using an elution gradient (from hexane to CH₂Cl₂ / ethanol 50/1). Yield 11.5% (115 mg). Dark bluish grey waxy solid.

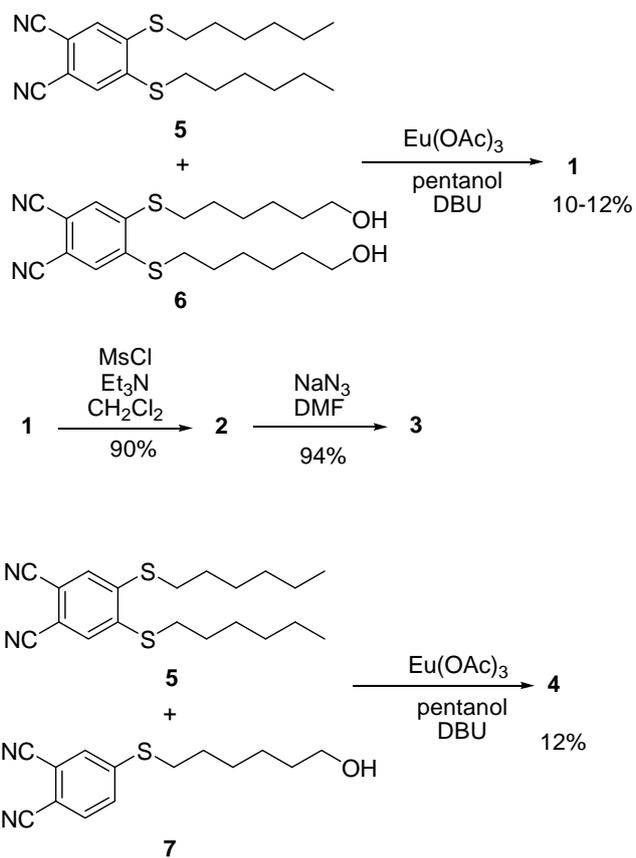
C₁₆₀H₂₂₄EuN₁₆O₂S₁₆, MW: 3068.60. MALDI-TOF-MS (*m/z*): 3037.065 [M+H]⁺. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₆₀H₂₂₄EuN₁₆O₂S₁₆H 3065.2721; Found 3065.2714. FT-IR (cm⁻¹): 3353, 3173, 3073, 2951, 2924, 2854, 1588, 1502, 1465, 1442, 1401, 1313, 1287, 1261, 1073, 1027, 941, 871, 796, 773, 753, 727, 697. ¹H NMR (300 MHz, THF-*d*₈ + NaBD₄): δ 11.13 (s, 16 H), 4.58, 4.38 (2 m, 38 H), 2.68, 2.32, 1.89 (3 m, 112 H), 1.15 (m, 42 H), 0.89 (q, 16 H). UV-vis (THF) λ nm, (log ε): 704.5 nm (4.80), 388.5 nm (4.56), 314.5 nm (4.60). UV-vis (CHCl₃) λ nm, (log ε): 712.5 nm (4.87), 390 (4.66), 318.5 nm (4.71).

Preparation of 2. Double-decker complex **1** (108 mg, 0.035 mmol) was dissolved in dichloromethane (5 mL) and triethylamine (1 mL, 7.17 mmol) in ice bath. Methanesulfonyl chloride (0.2 mL, 1.29 mmol) in dichloromethane (5 mL) was added drop by drop, then the ice bath was removed and the reaction mixture was stirred overnight at room temperature. The mixture was washed with water and dichloromethane phase was dried with Na₂SO₄. Dichloromethane was evaporated and the product was purified on a silica gel column chromatography using an elution gradient (from hexane to CH₂Cl₂). Yield 90% (101 mg). Dark bluish grey waxy solid. C₁₆₂H₂₂₈EuN₁₆O₆S₁₈, MW: 3224.78. MALDI-TOF-MS (*m/z*): 3221.414. HRMS (ESI-TOF) *m/z*: M⁺ Calcd for C₁₆₂H₂₂₈EuN₁₆O₆S₁₈ 3220.2194; Found 3220.2207. FT-IR (cm⁻¹): 3173, 3068, 2954, 2924, 2854, 2579, 2477, 2245, 2209, 2163, 1727, 1590, 1441, 1398, 1361, 1312, 1281, 1261, 1176, 1069, 1022, 941, 871, 832, 803, 753, 729, 695. ¹H NMR (300 MHz, THF-*d*₈ + NaBD₄): δ 11.21 (s, 16 H), 4.62, 4.41 2 (m, 36 H), 2.70, 2.47, 2.35, 2.04, 1.89, 1.29 (6 m, 118 H), 1.17 (m, 42H), 0.89 (q, 16 H). UV-vis (THF) λ nm, (log ε): 704.5 nm (4.54), 388 nm (4.36), 314 nm (4.45). UV-vis (CHCl₃) λ nm, (log ε): 713 nm (4.63), 391 (4.45), 317 nm (4.46).

Preparation of 3. Double-decker complex **2** (30 mg, 0.009 mmol) and NaN_3 (6 mg, 0.09 mmol) was dissolved in dry DMF (25 mL) and stirred for one day at 80°C . The reaction mixture was cooled down to room temperature, poured into water, filtered and recovered with dichloromethane. Dichloromethane was evaporated and dried with Na_2SO_4 , and the product was purified on a silica gel column chromatography using an elution gradient (from hexane to CH_2Cl_2 / ethanol 50/1). Yield 94% (26 mg). Dark bluish grey waxy solid. $\text{C}_{160}\text{H}_{222}\text{EuN}_{22}\text{S}_{16}$, MW: 3118.63. MALDI-TOF-MS (m/z): 3118.283 $[\text{M}]^+$. HRMS (ESI-TOF) m/z : M^+ Calcd for $\text{C}_{160}\text{H}_{222}\text{EuN}_{22}\text{S}_{16}$ 3114.2772; Found 3114.2803. FT-IR (cm^{-1}): 3172, 3073, 2953, 2923, 2854, 2580, 2480, 2209, 2162, 2090, 1588, 1442, 1401, 1362, 1313, 1286, 1260, 1072, 1023, 941, 871, 833, 801, 773, 753, 727, 695. ^1H NMR (300 MHz, $\text{THF-}d_8$ + NaBD_4): δ 11.16 (s, 16 H), 4.58, 4.36 (2 m, 36 H), 2.69, 2.50, 2.33, 1.89 (4 m, 112 H), 1.16 (t, 42 H), 0.89 (q, 16 H). UV-vis (THF) λ nm, ($\log \epsilon$): 705 nm (4.69), 388.5 nm (4.45), 315 nm (4.50). UV-vis (CHCl_3) λ nm, ($\log \epsilon$): 713.5 nm (4.56), 392 (4.33), 319.5 nm (4.40).

Preparation of 4.

A mixture of phthalonitriles phthalonitriles **5** (9000 mg, 24.96 mmol, 20 equiv) and **7** (330 mg, 1.27 mmol, 1 equiv) was dissolved in a minimum amount of CH_2Cl_2 and evaporated to ensure of the homogeneous blending. $\text{Eu}(\text{OAc})_3$ (1100 mg, 3.34 mmol), dry pentanol (5 mL) and DBU (1 mL) were added, and the reaction mixture was refluxed under argon for 4 hours. The reaction mixture was cooled down to room temperature, poured into ethanol, filtered and recovered with dichloromethane. Dichloromethane was evaporated, and the product was purified on a silica gel column chromatography using an elution gradient (from hexane to CH_2Cl_2 / hexane 9/1). Yield 12% (440 mg). Dark bluish grey waxy solid. $\text{C}_{154}\text{H}_{212}\text{EuN}_{16}\text{OS}_{15}$, MW: 2936.38. MALDI-TOF-MS (m/z): 2937.011 $[\text{M}+\text{H}]^+$. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{154}\text{H}_{212}\text{EuN}_{16}\text{OS}_{15}$ 2932,2034; Found 2932,1980. FT-IR (cm^{-1}): 3354, 3177, 3059, 2955, 2925, 2855, 1591, 1500, 1443, 1399, 1314, 1284, 1072, 941, 871, 833, 753, 733, 695. ^1H NMR (300 MHz, $\text{THF-}d_8$ + NaBD_4): δ 10.97 (m, 16 H), 8.77 (s, 1 H), 4.35, 4.16, 3.97 (3 m, 33 H), 2.43, 2.01, 1.61, 1.48 (4 m, 104 H), 0.88 (m, 42 H), 0.59 (m, 16 H). UV-vis (THF) λ nm, ($\log \epsilon$): 703 nm (4.82), 386 nm (4.63), 319 nm (4.68). UV-vis (CHCl_3) λ nm, ($\log \epsilon$): 711 nm (4.94), 390.5 (4.72), 318 nm (4.81)



Scheme S1. Preparation of functionalized heteroleptic double-decker complexes **1-4**.

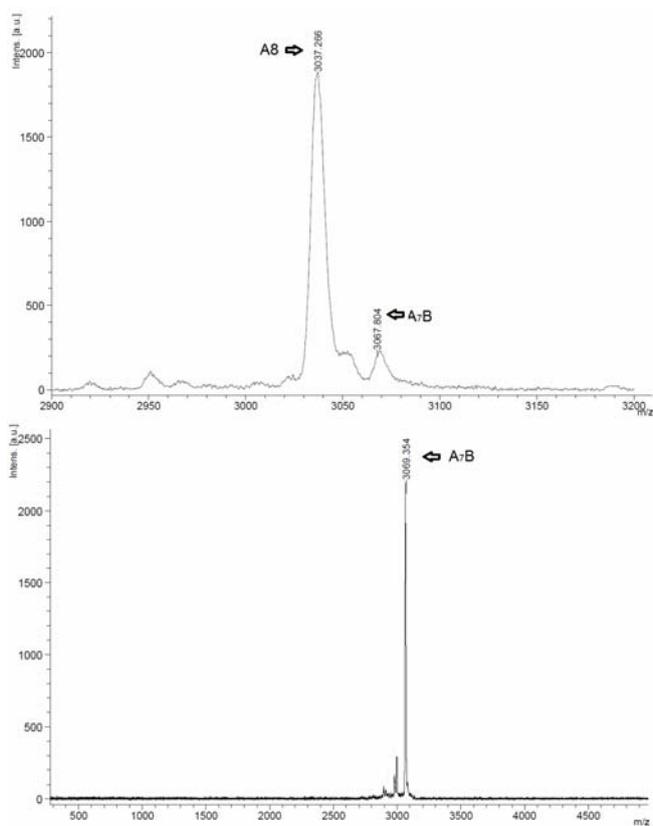


Figure S1. MALDI-TOF spectra of the resulting mixture of phthalocyanines (top) and of the isolated desired dihydroxylated double-decker **1** (bottom)

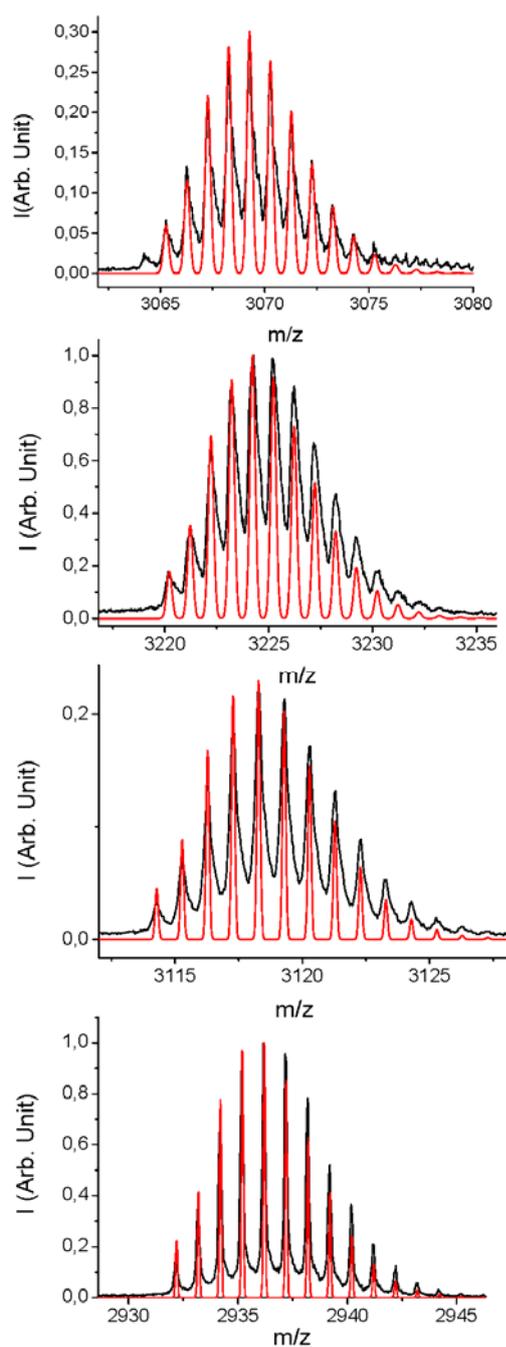


Figure S2. High resolution mass spectra (ESI-TOF) (from top to bottom: complex **1**, **2**, **3** then **4**): theoretical (red) and experimental (black) isotopic patterns. The observed molecular ions in ESI are M^+ (for complex **4** it is a mixture of M^+ and $[M+H]^+$).

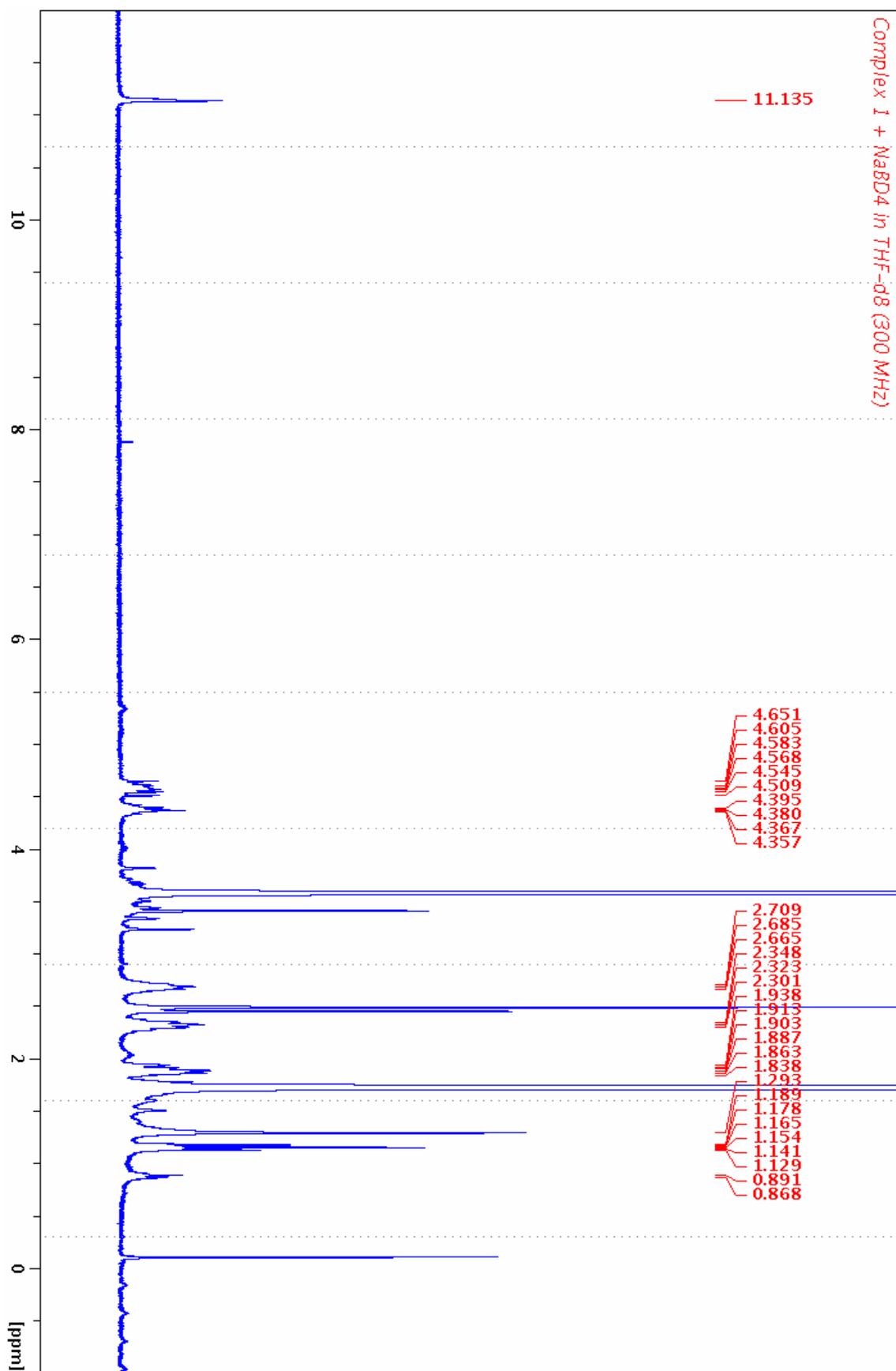


Figure S5. ¹H NMR spectrum of complex **1** recorded at 300 MHz in THF-d₈. The species was generated *in-situ* with NaBD₄

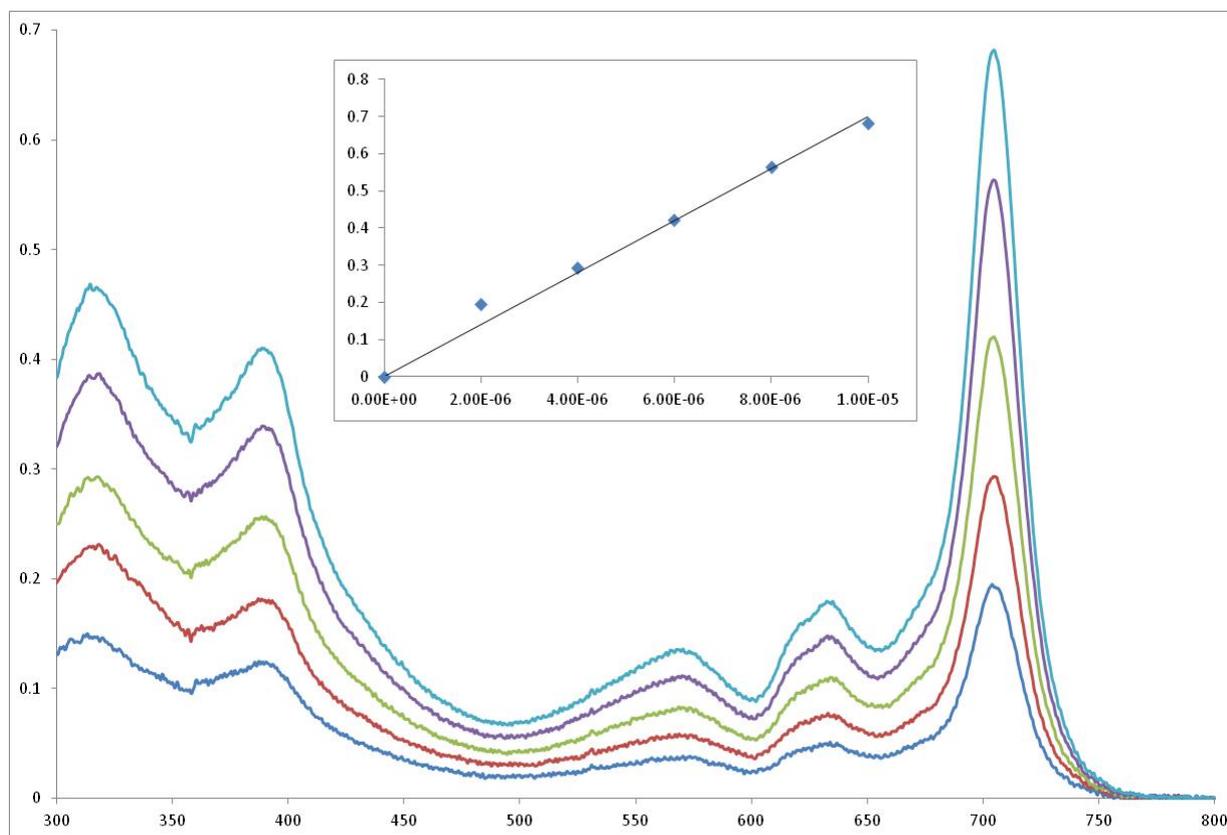


Figure S6a. UV-Vis spectrum of complex **1** in THF at different concentrations (2 to 10 μM).
Inset: Plot of the Q band absorption intensity vs concentration.

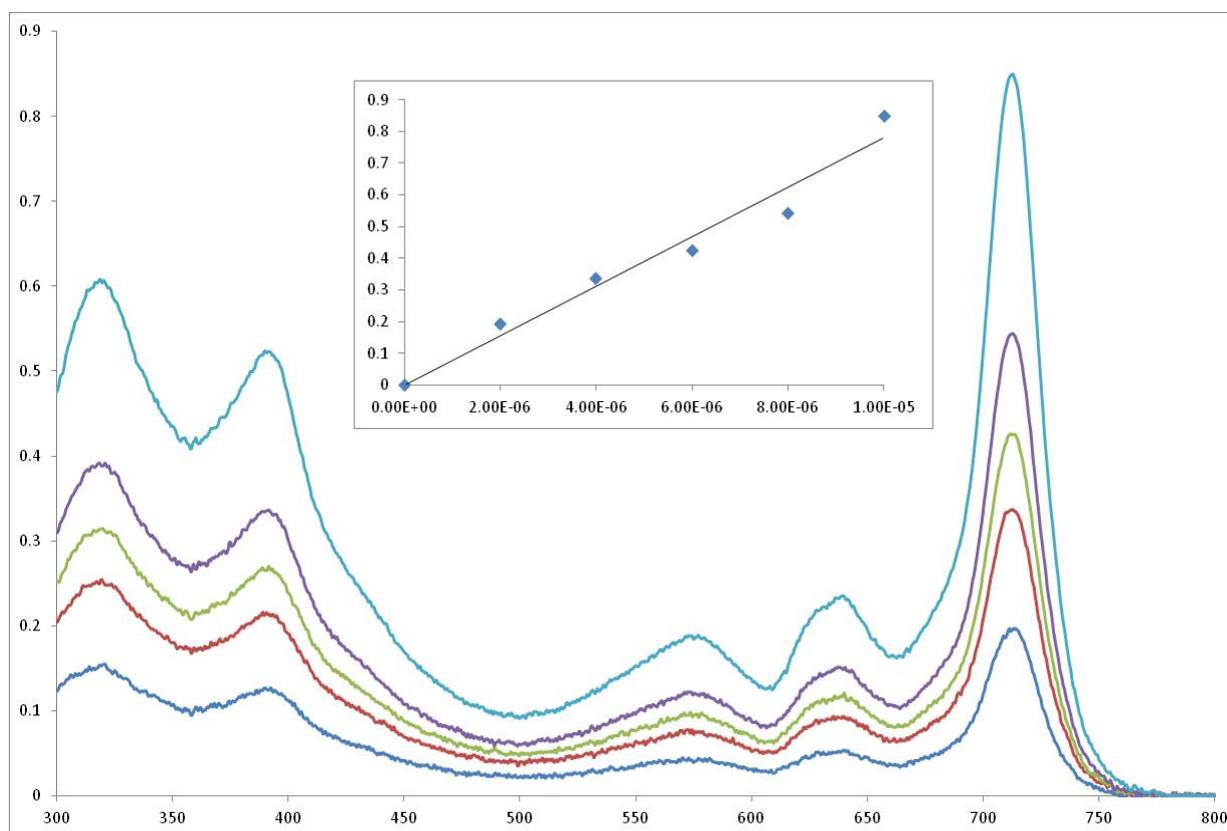


Figure S6b. UV-Vis spectrum of complex **1** in CHCl_3 at different concentrations (2 to 10 μM).
Inset: Plot of the Q band absorption intensity vs concentration.

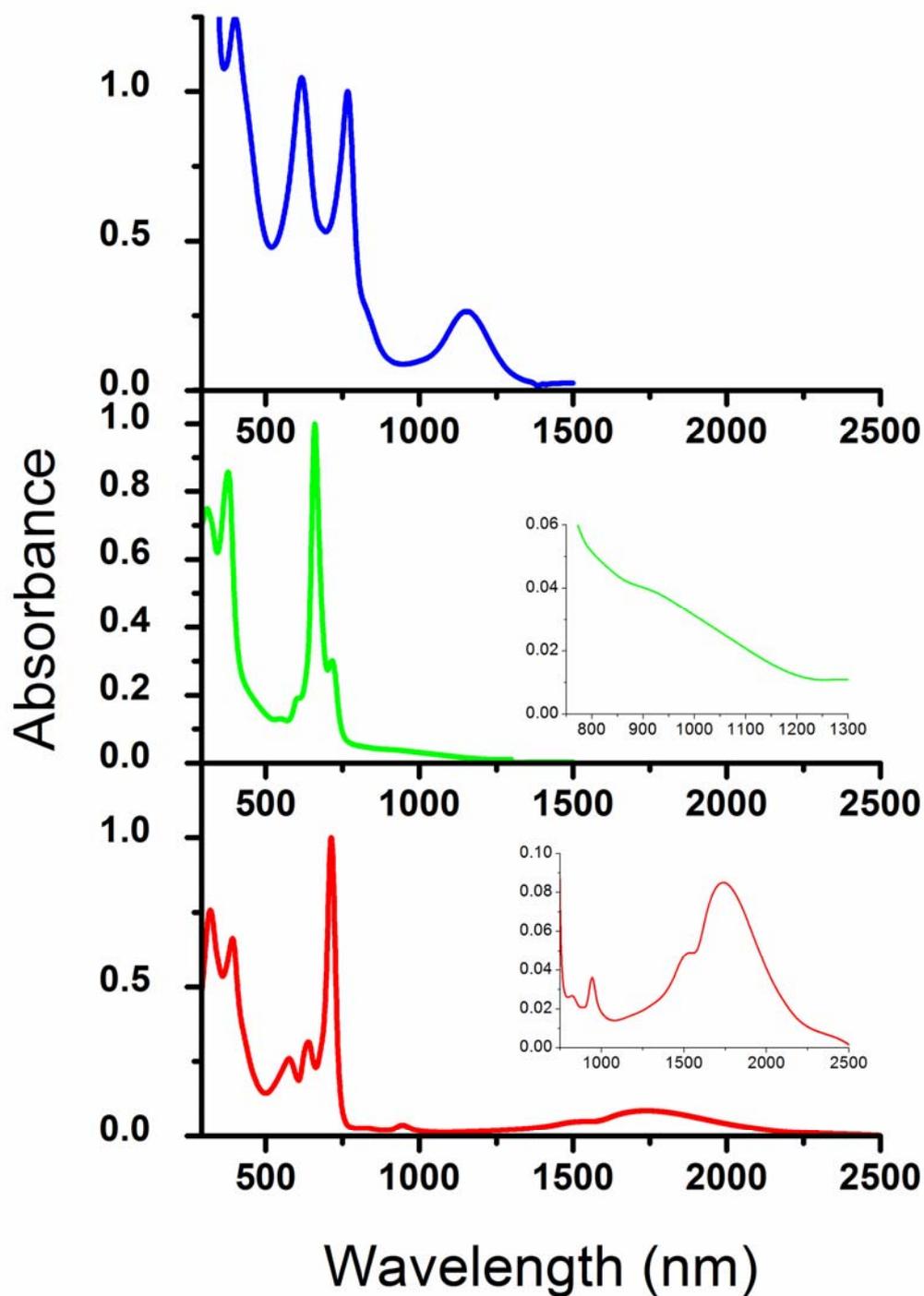


Figure S7. Electronic absorption spectra of complex **1**. (Top) Oxidized species $[\text{Pc}_2\text{Eu}]^+$ generated *in-situ* in CHCl_3 by adding Br_2 . (Middle) Reduced $[\text{Pc}_2\text{Eu}]^-$ species generated *in-situ* in THF by adding NaBH_4 . Inset: magnified view of the 750-1300 nm range. (Bottom) Neutral species $[\text{Pc}_2\text{Eu}]$. Inset: magnified view of the 750-2700 nm range.

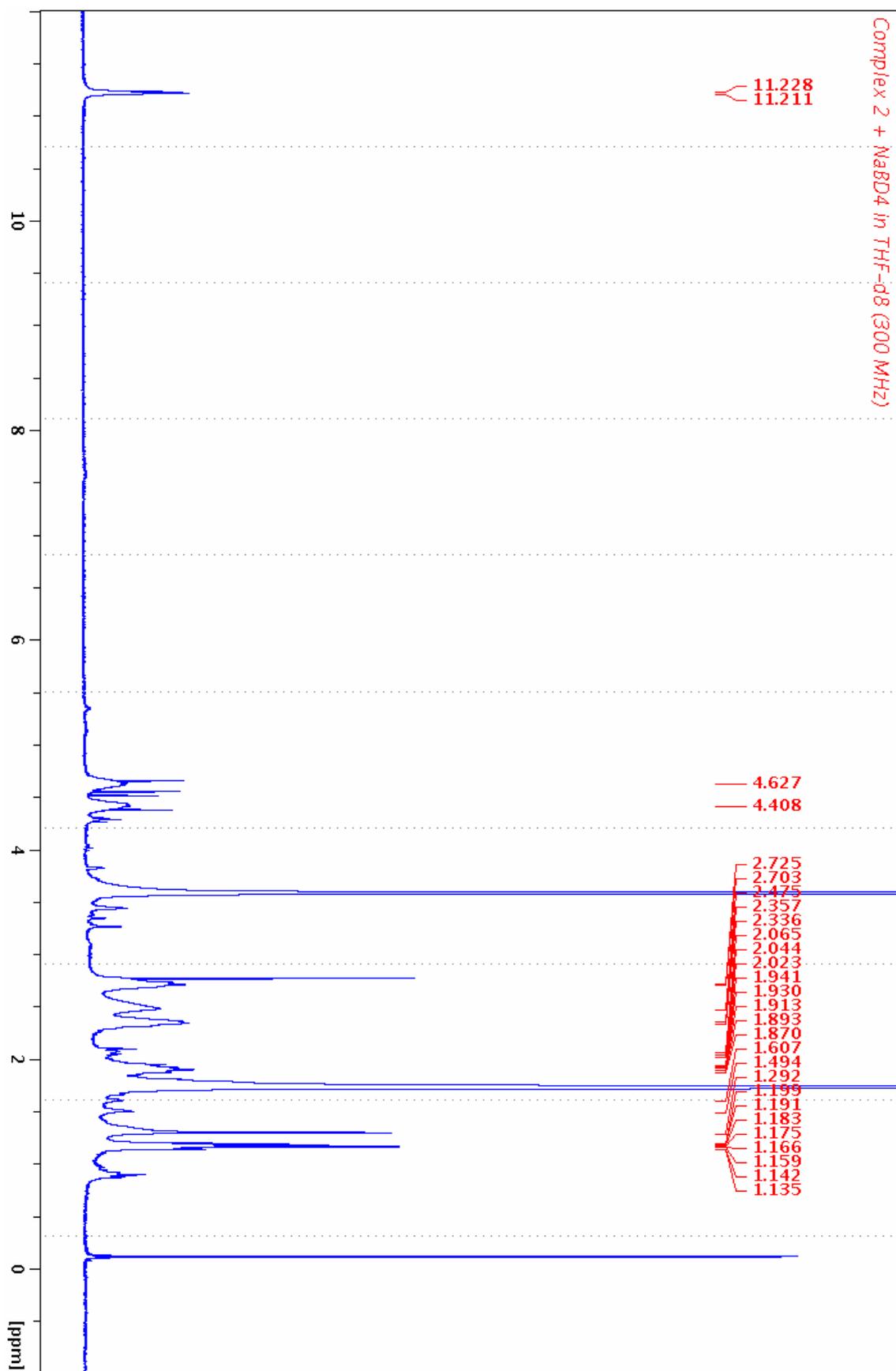


Figure S10. ¹H NMR spectrum of complex **2** recorded at 300 MHz in THF-d₈. The species was generated *in-situ* with NaBD₄.

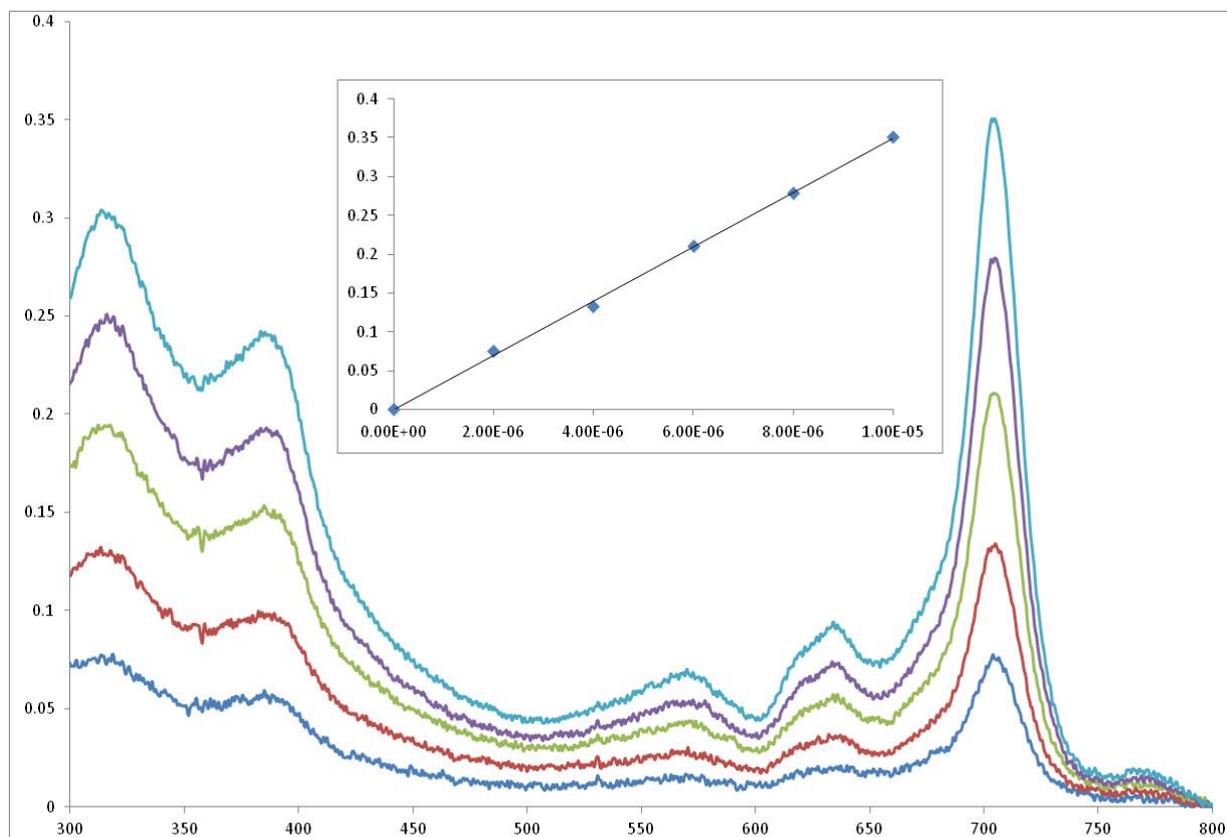


Figure S11a. UV-Vis spectrum of complex **2** in THF at different concentrations (2 to 10 μM). Inset: Plot of the Q band absorption intensity vs concentration.

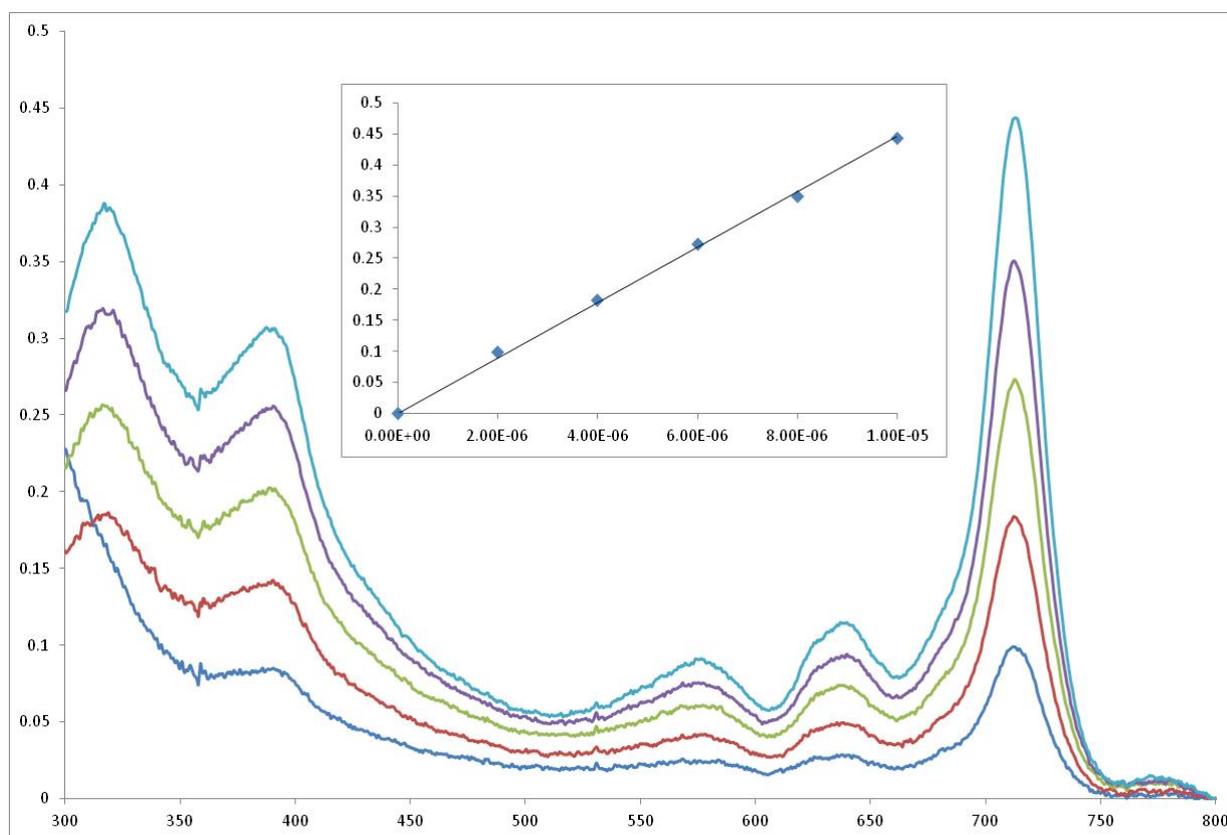


Figure S11a. UV-Vis spectrum of complex **2** in CHCl_3 at different concentrations (2 to 10 μM). Inset: Plot of the Q band absorption intensity vs concentration.

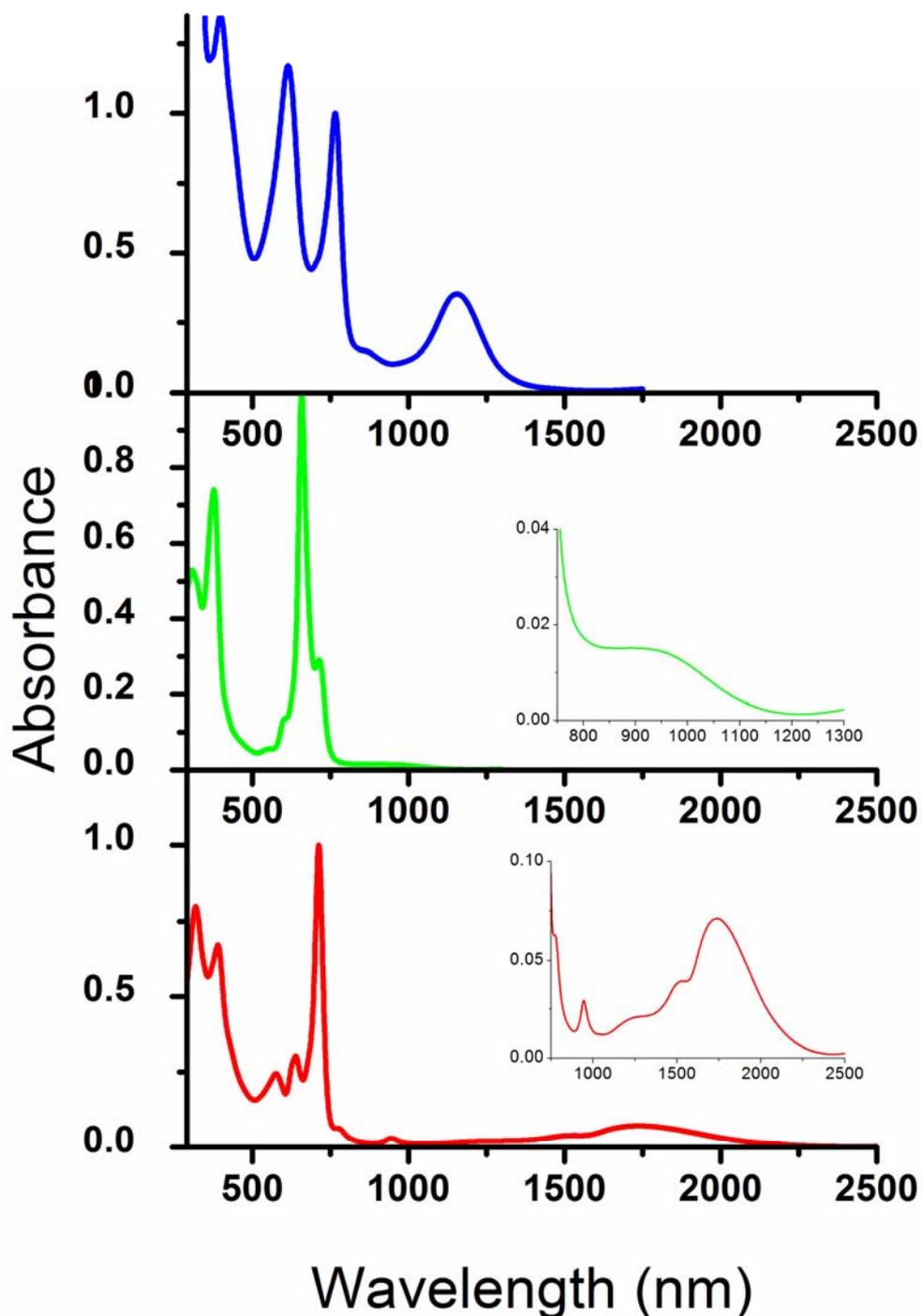


Figure S12. Electronic absorption spectra of complex **2**. (Top) Oxidized species $[\text{Pc}_2\text{Eu}]^+$ generated *in-situ* in CHCl_3 by adding Br_2 . (Middle) Reduced $[\text{Pc}_2\text{Eu}]^-$ species generated *in-situ* in THF by adding NaBH_4 . Inset: magnified view of the 750-1300 nm range. (Bottom) Neutral species $[\text{Pc}_2\text{Eu}]$. Inset: magnified view of the 750-2700 nm range.

Characterization of complex 3.

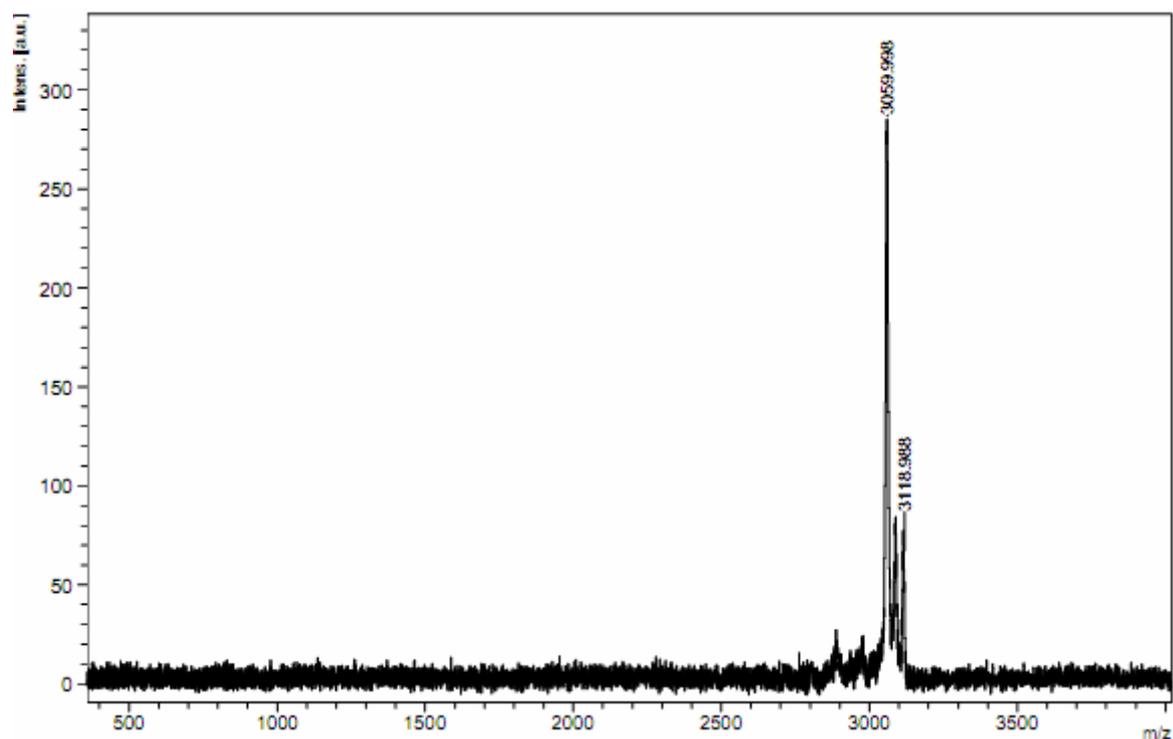


Figure S13. MALDI-TOF spectrum of complex 3. Matrix: DHB.

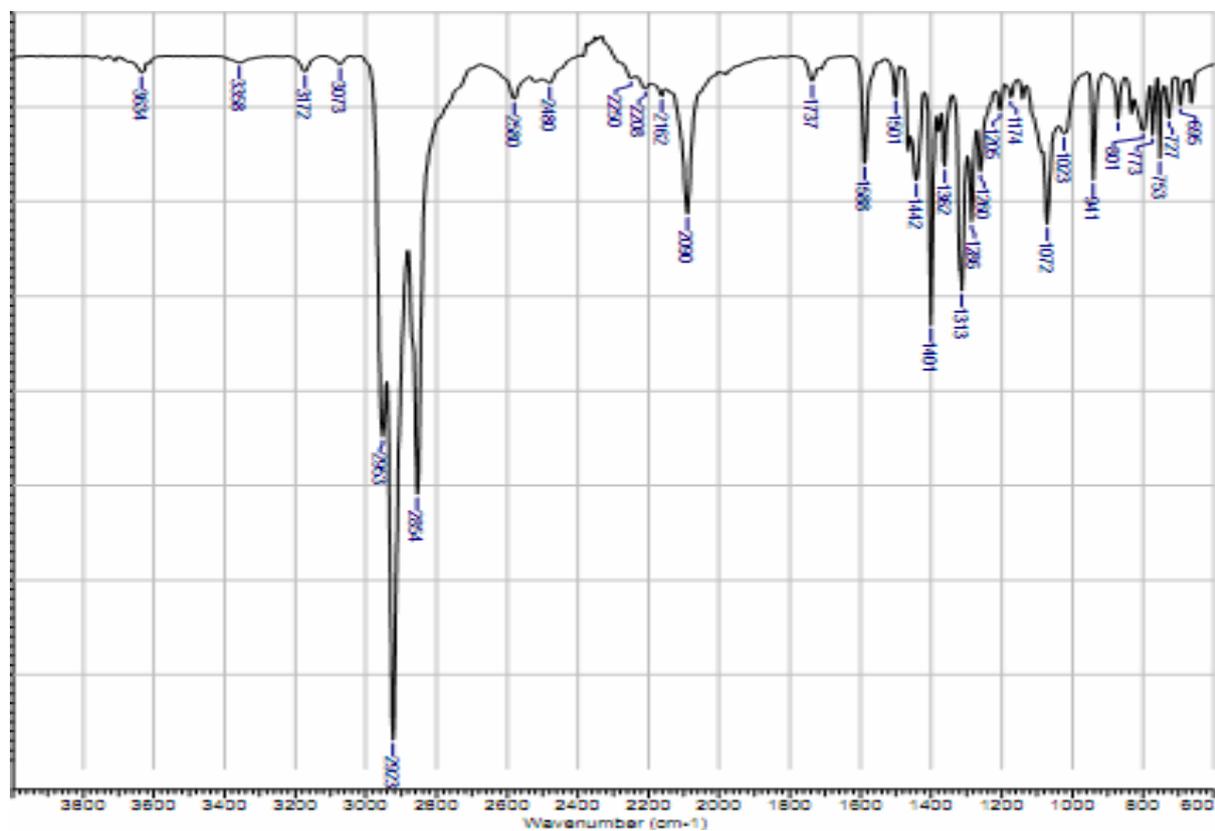


Figure S14. FT-IR spectrum of complex 3.

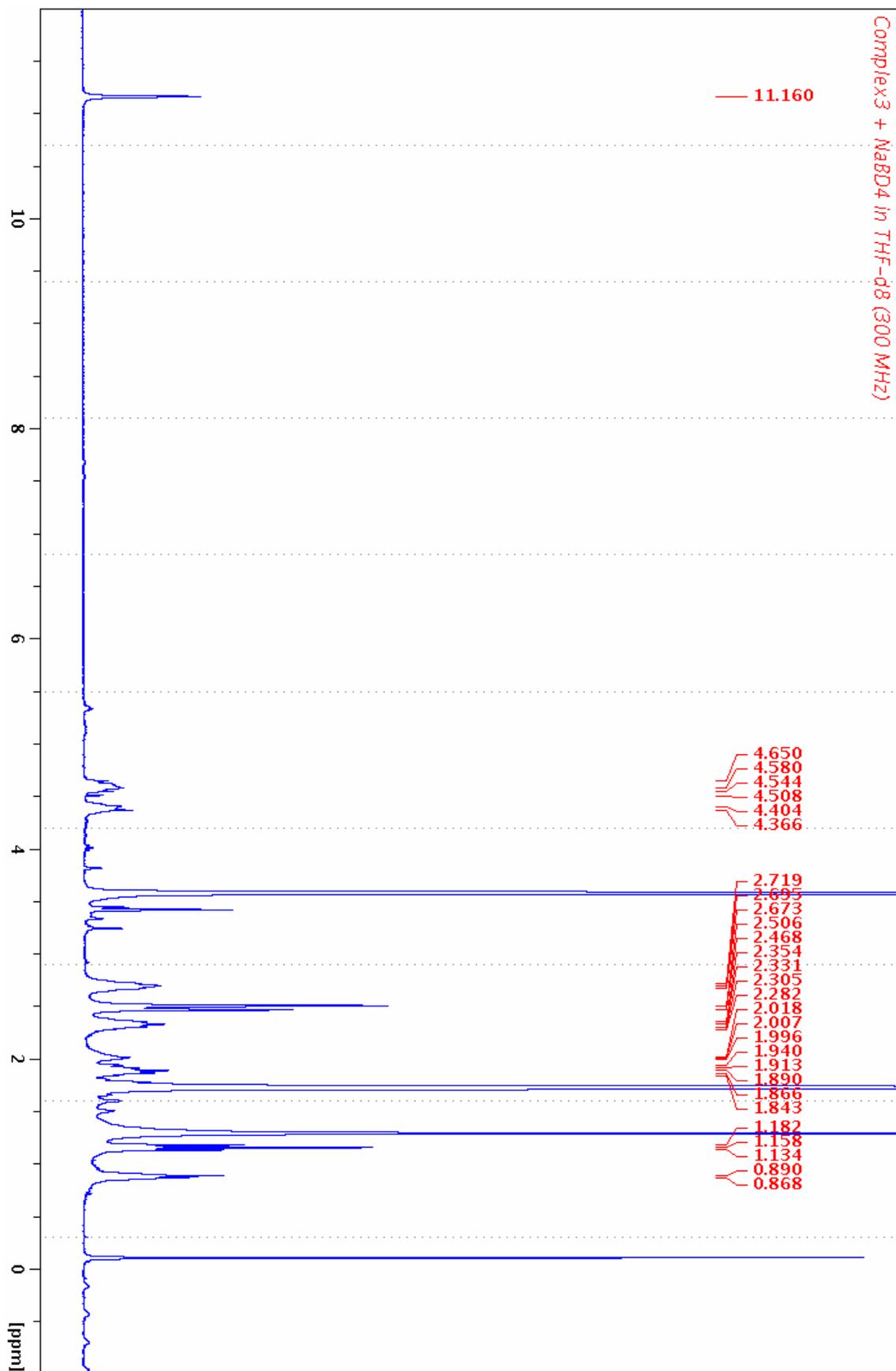


Figure S15. ¹H NMR spectrum of complex **3** recorded at 300 MHz in THF-d₈. The species was generated *in-situ* with NaBD₄.

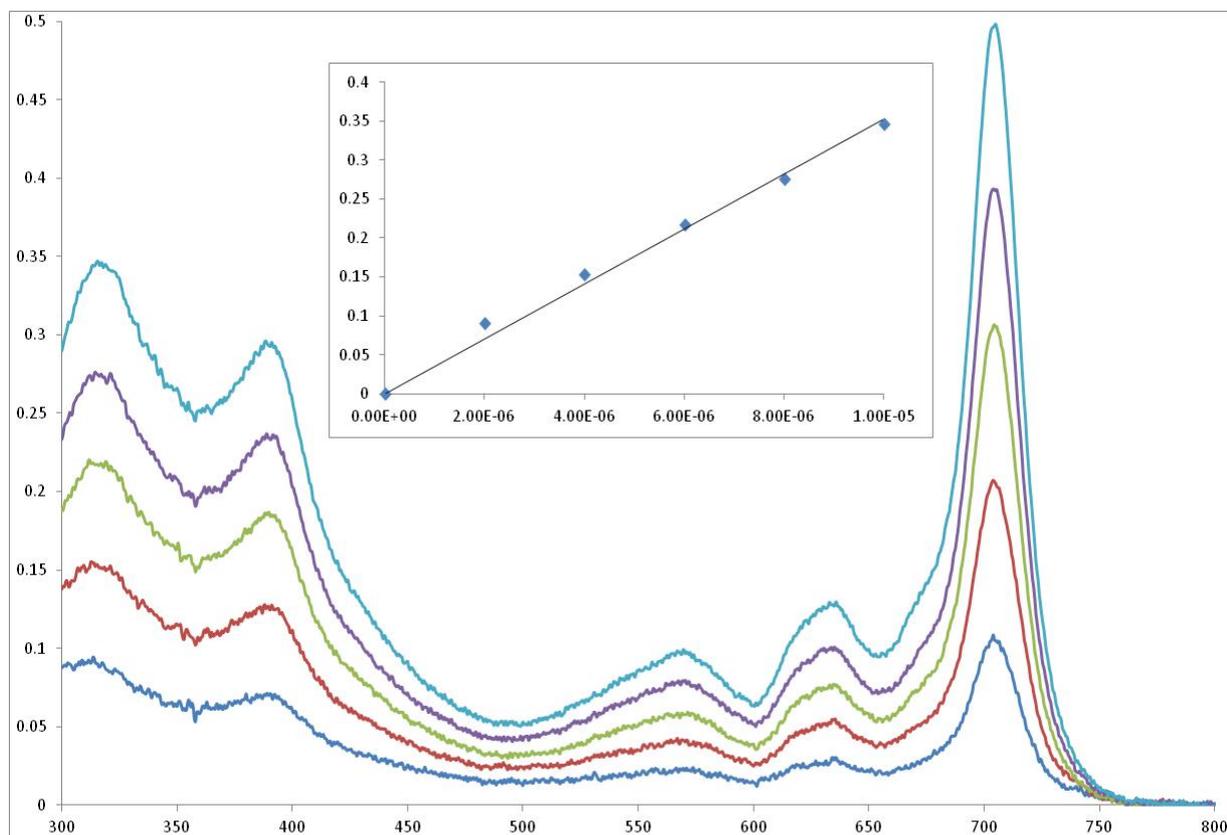


Figure S16a. UV-Vis spectrum of complex **3** in THF at different concentrations (2 to 10 μM). Inset: Plot of the Q band absorption intensity vs concentration.

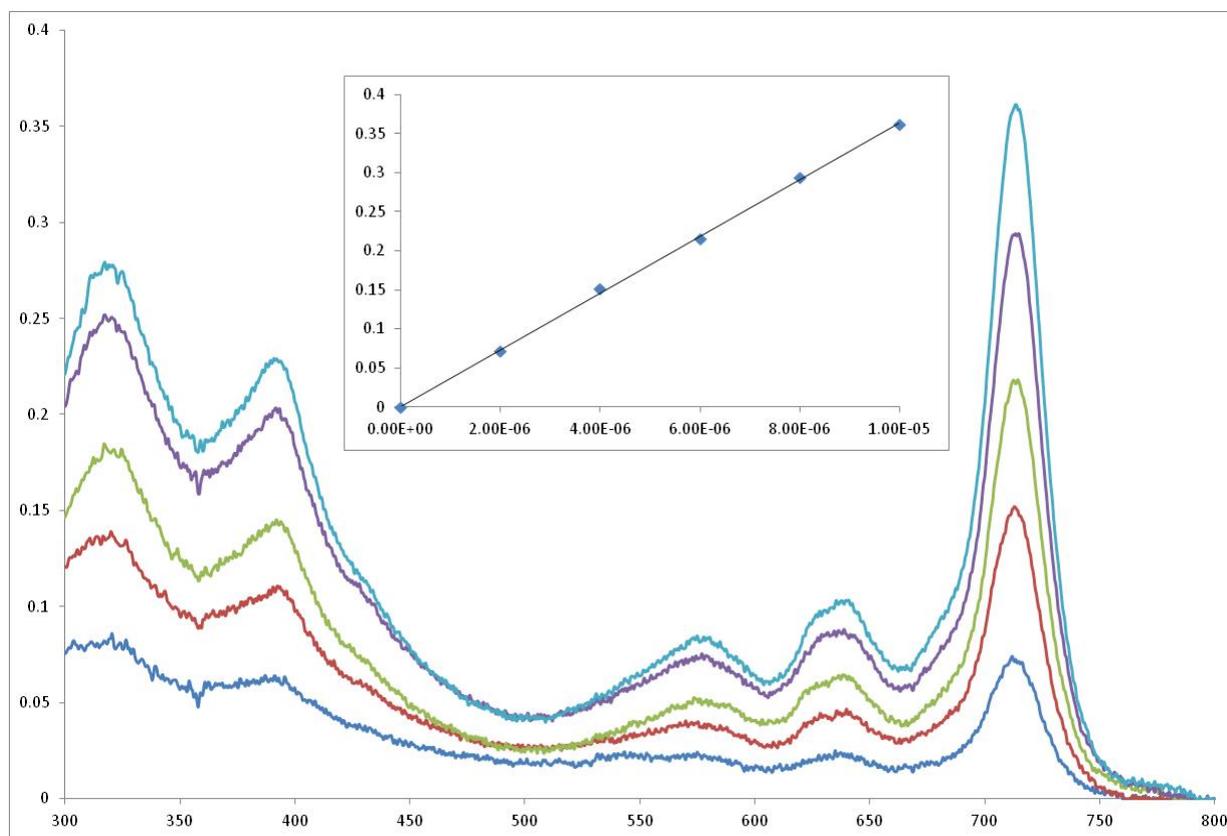


Figure S16b. UV-Vis spectrum of complex **3** in CHCl_3 at different concentrations (2 to 10 μM). Inset: Plot of the Q band absorption intensity vs concentration.

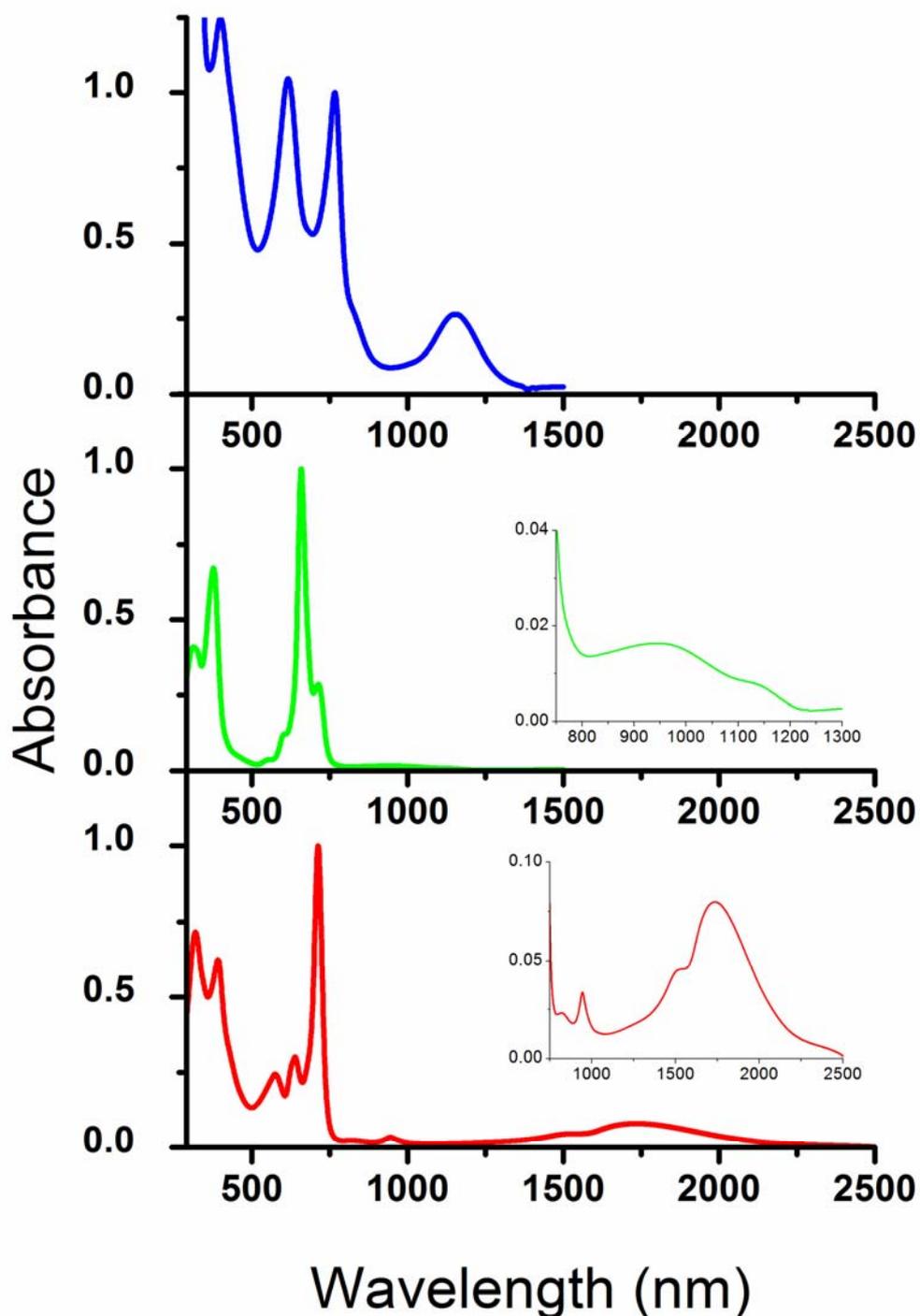


Figure S17. Electronic absorption spectra of complex **3**. (Top) Oxidized species $[\text{Pc}_2\text{Eu}]^+$ generated *in-situ* in CHCl_3 by adding Br_2 . (Middle) Reduced $[\text{Pc}_2\text{Eu}]^-$ species generated *in-situ* in THF by adding NaBH_4 . Inset: magnified view of the 750-1300 nm range. (Bottom) Neutral species $[\text{Pc}_2\text{Eu}]$. Inset: magnified view of the 750-2700 nm range.

Characterization spectra of complex 4

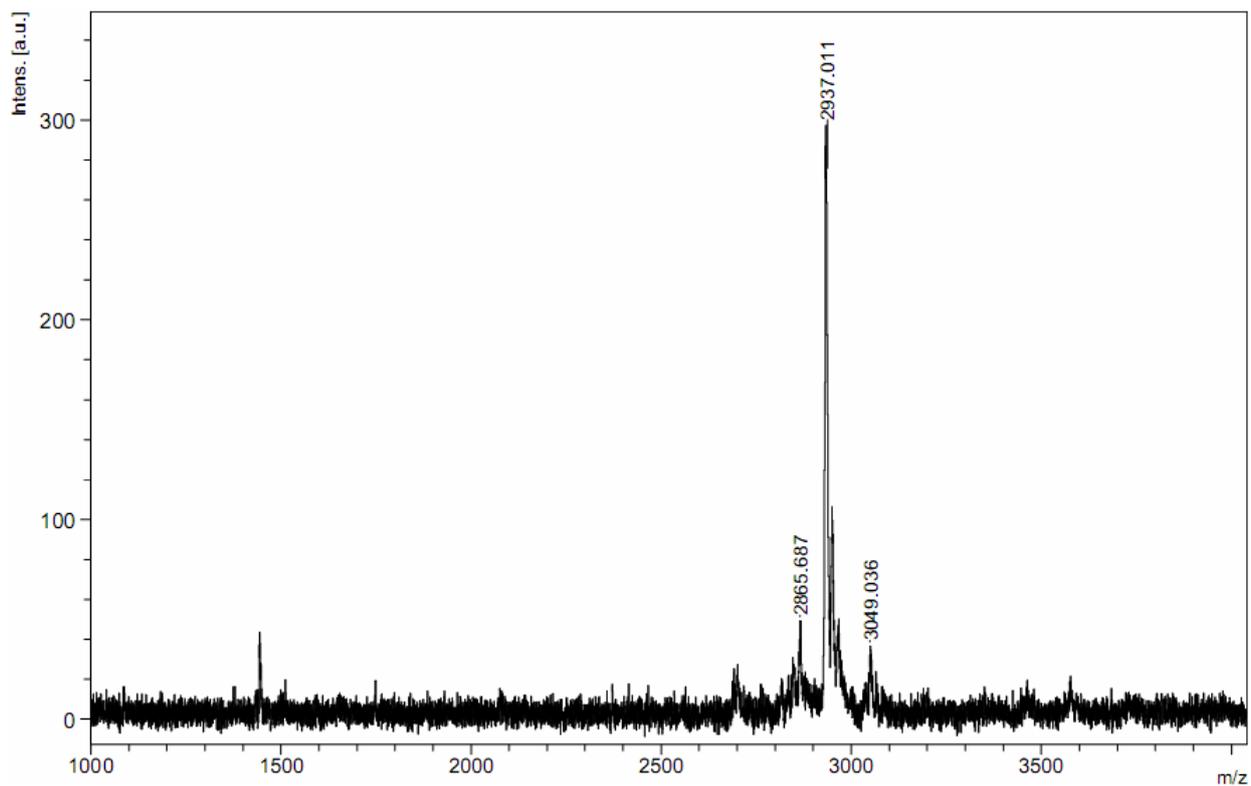


Figure S18. MALDI-TOF spectrum of complex 4. Matrix: DHB.

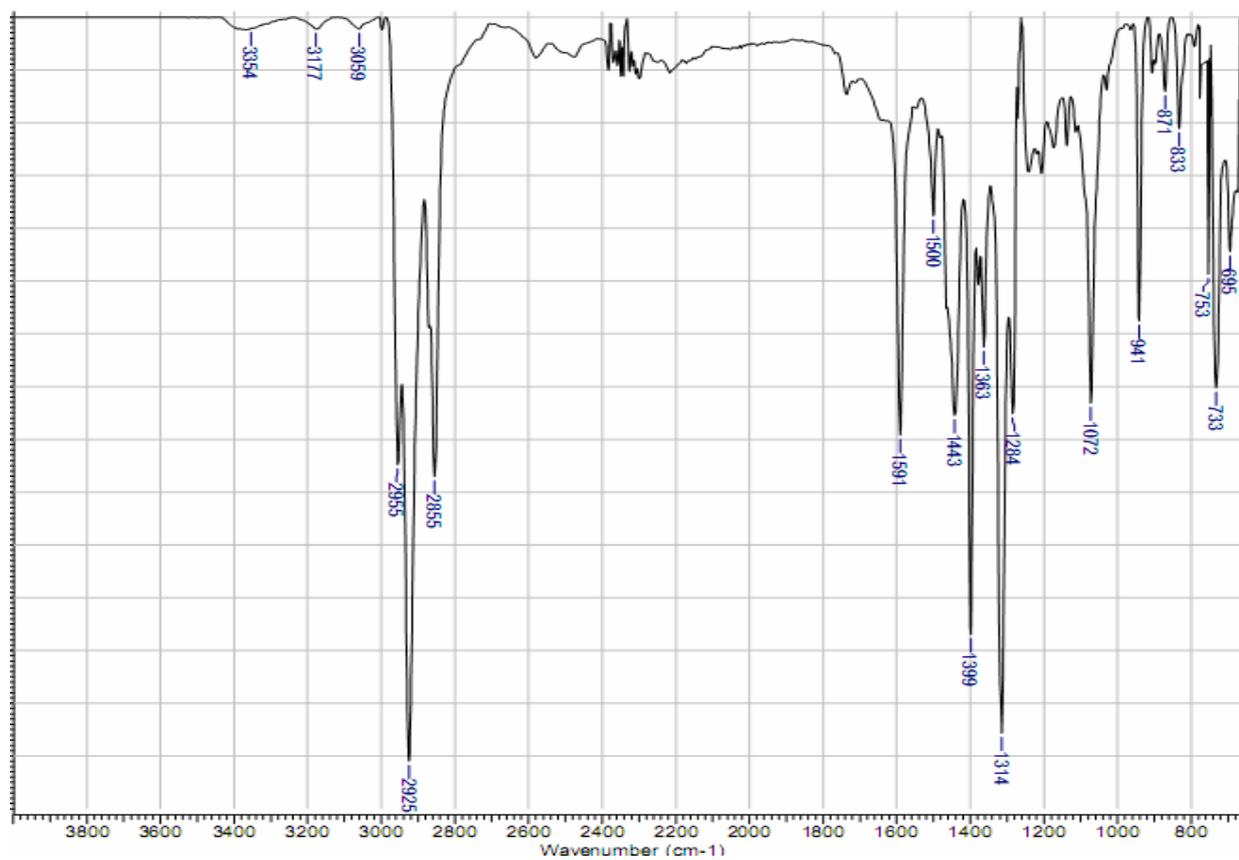


Figure S19. FT-IR spectrum of complex 4.

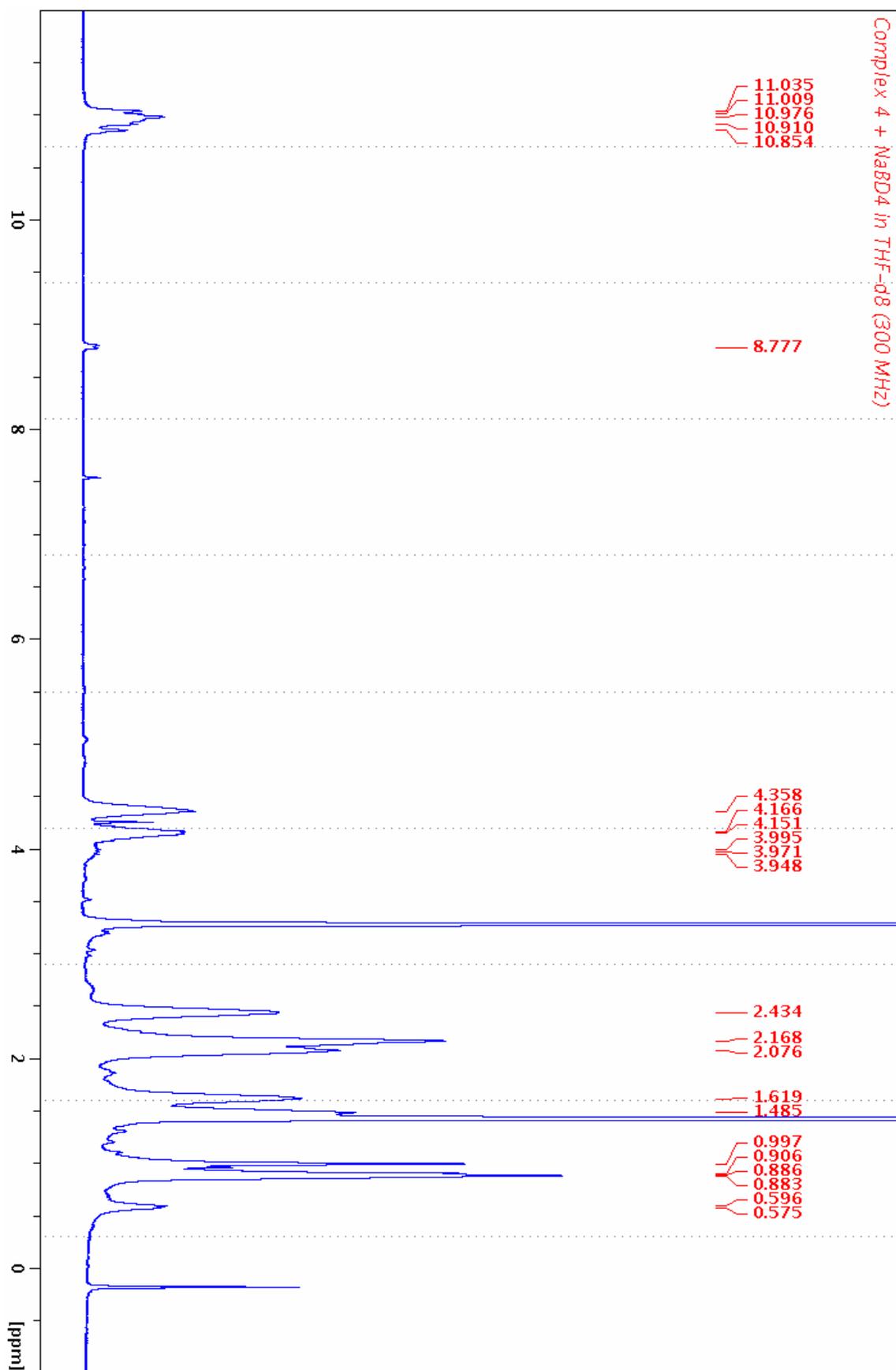


Figure S20. ¹H NMR spectrum of complex **4** recorded at 300 MHz in THF-d₈. The species was generated *in-situ* with NaBD₄.

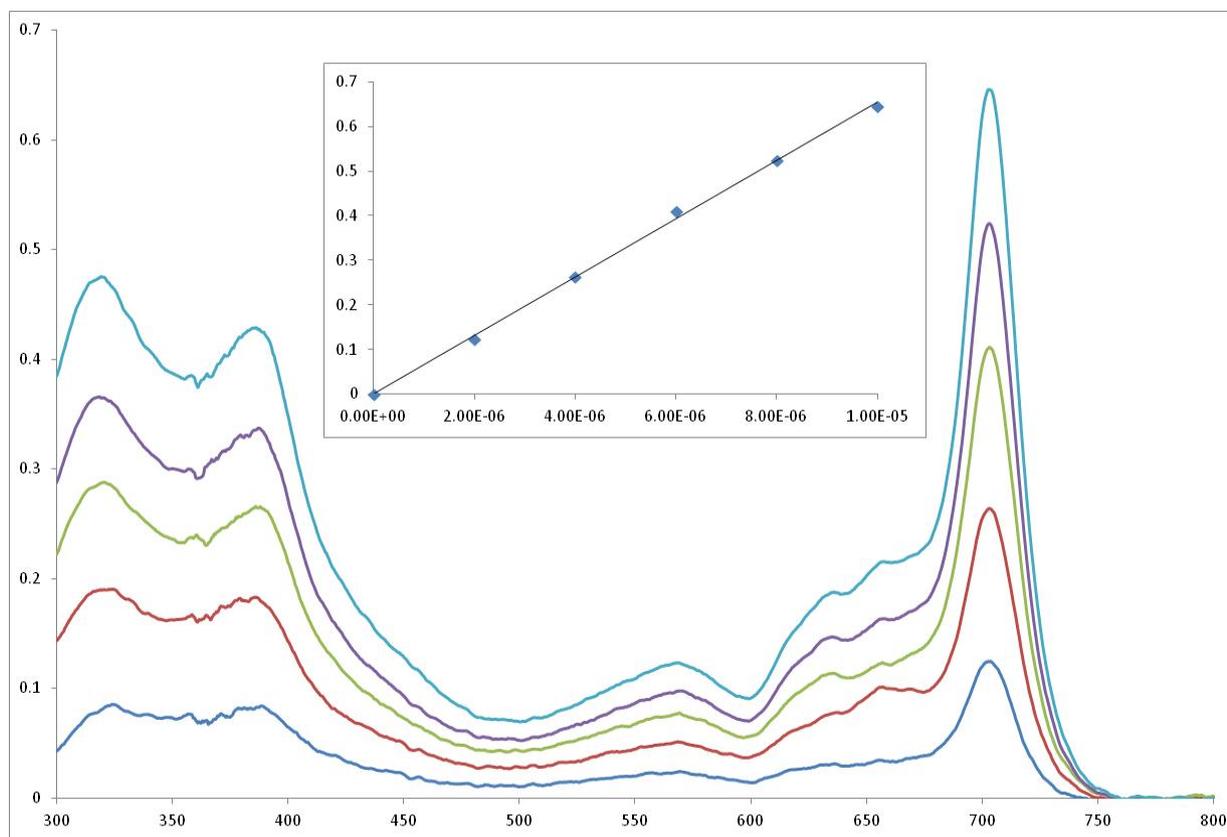


Figure S21a. UV-Vis spectrum of complex **4** in THF at different concentrations (2 to 10 μM). Inset: Plot of the Q band absorption intensity vs concentration.

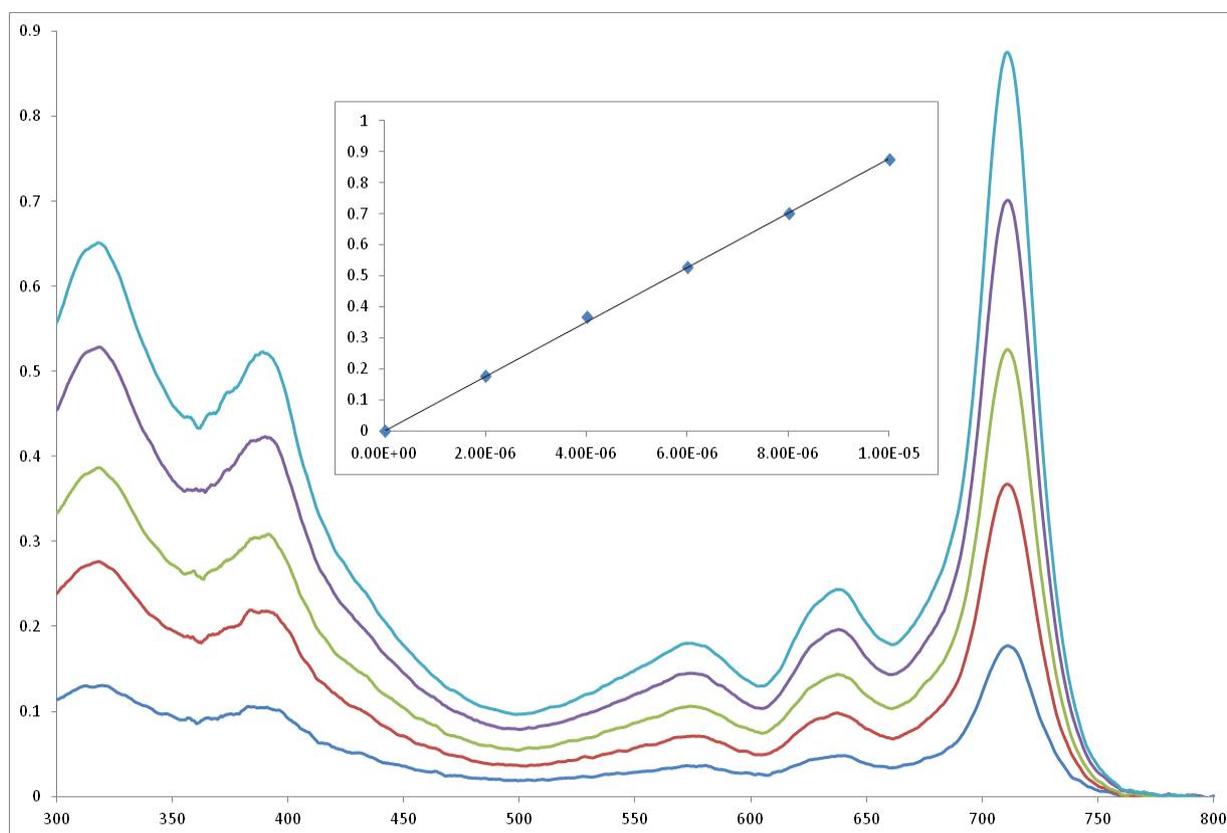


Figure S21b. UV-Vis spectrum of complex **4** in CHCl_3 at different concentrations (2 to 10 μM). Inset: Plot of the Q band absorption intensity vs concentration.

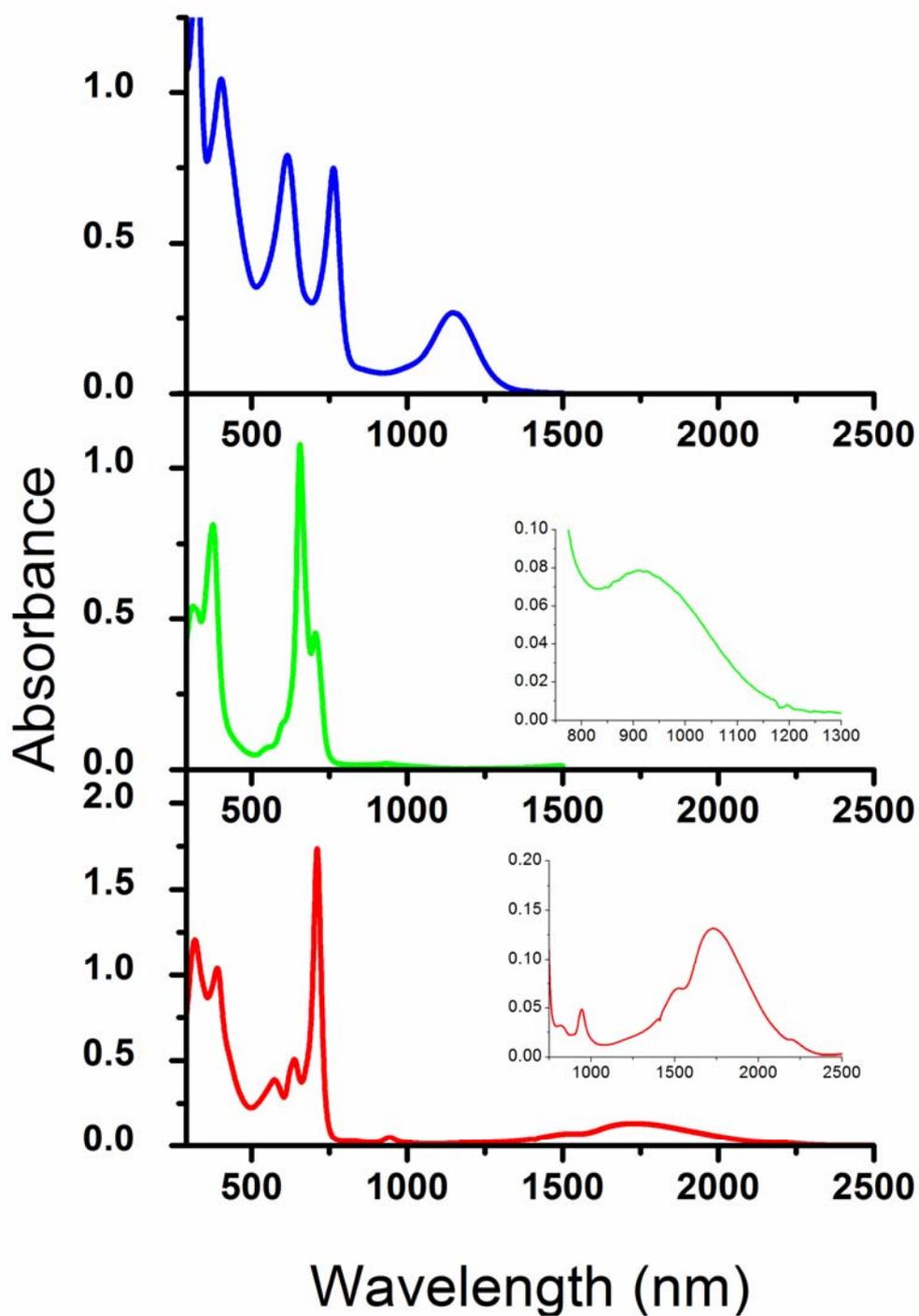


Figure S22. Electronic absorption spectra of complex **4**. (Top) Oxidized species $[\text{Pc}_2\text{Eu}]^+$ generated *in-situ* in CHCl_3 by adding Br_2 . (Middle) Reduced $[\text{Pc}_2\text{Eu}]^-$ species generated *in-situ* in THF by adding NaBH_4 . Inset: magnified view of the 750-1300 nm range. (Bottom) Neutral species $[\text{Pc}_2\text{Eu}]$. Inset: magnified view of the 750-2700 nm range.

References

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- (1) Gürek, A. G.; Bekarođlu, Ö. *J. Chem. Soc. Dalton Trans.* **1994**, 1419.
 - (2) Kandaz, M.; Bilgicli, A. T.; Altindal, A. *Synthetic Metals* **2010**, 160, 52.
 - (3) Kandaz, M.; Koca, A.; Yarasir, M. N.; Salih, B. *Polyhedron* **2007**, 26, 1139.