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Column chromatography separation of lanthanide(III) bisphthalocyaninate and phthalocyanine ligand

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Contents

Equipment and reagent

Elemental analysis of the synthesized compounds was carried out on a CHNS-OFlashEA, 1112 series analyzer. IR spectra were recorded on IRAffinity-1S spectrometer in the region of 450-4500 cm^{-1}. Electronic absorption (UV-vis) spectra were obtained using UNICO-2800 spectrophotometers at the wavelength range of 300-1000 nm utilizing quartz cuvettes of optical path length equal to 1 cm. Mass-spectra were obtained by means of time-of-flight mass-spectrometer «Simadzu Axima Confidence» (MALDI-TOF MS). Samples of approximately 10^{-3} M concentration were stored in chloroform and CHCA (alpha-cyano-4-hydrohycinnamic acid) was used as a matrix. NMR spectroscopy were studied on an AVANCE 500 spectrometer (Bruker, Hamburg, Germany) with TMS as inner standard, registering ^{1}H nuclei at 500 MHz. Purification of the complexes obtained was performed utilizing column (silica gel Kieselgel 60 (Merck), 230-400 mesh).

4-Nitrophthalonitrile (99%, «Sigma-Aldrich»), 2,4-dichlorophenol (for synthesis, «Sigma-Aldrich»), 2,4,5-trichlorophenol (95%, «Sigma-Aldrich»), erbium(III)/neodymium(III) chloride hexahydrate (99.9%, Sigma-Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (99%, Sigma-Aldrich), isoamyl alcohol (99.9%, Merck), chloroform (99%, Ecos-1), hydrazine monohydrate 64-65% (98%, Sigma Aldrich) were applied without additional purification.

Erbium (III), neodymium(III) and iron(III) acetylacetonate were obtained according to the procedure described in work.[S1]

4-(2,4-Dichlorophenoxy)phthalonitrile, 4-(2,4,5-trichlorophenoxy)phthalonitrile and 4-(4-cyclohexylphenoxy)phthalonitrile were obtained according to the methods.[S2-S4]

Synthesis

Novel bisphthalocyanine complexes were obtained by the following method. A mixture of phthalonitrile **1**, **2** or **3** (1.6 mmol), erbium(III) acetylacetonate or neodymium(III) acetylacetonate (0.8 mmol), DBU (0.2 g, 1.3 mmol), and isoamyl alcohol (10 ml) was refluxed for 12 h, cooled, and poured into an ethanol/water mixture (4:1). The formed precipitate was filtered off and washed with ethanol/water (4:1) until clear filtrates. The target product was extracted with chloroform. The products were separated on a chromatographic column filled with silica gel 60, eluent is chloroform (bis-phthalocyanine).

[S1] M. Chaudhari, S. Dehury, S. Dhar, U. Bora, B. Choudary, L. Mannepalli, US Patent 7282573, 2002
[S2] N. Nwaji, J. Mack, T. Nyokong, *New J. Chem.*, 2017, **41**, 14351
[S3] A. Botnar, T. Tikhomirova, K. Nalimova, D. Erzunov, M. Razumov, A. Vashurin, *J. Mol. Struct.*, 2020, **1205**, 127626
[S4] A. Botnar, T. Tikhomirova, K. Kazaryan, A. Bychkova, V. Maizlish, I. Abramov, A. Vashurin, *J. Mol. Struct.*, 2021, **1238**, 130438

Erbium(III) bis(2(3),9(10),16(17),23(24)-(2,4-dichlorophenoxy)phthalocyaninato) (**Er(Pc)$_2$1**). Yield: 0.22 g (25 %). IR spectrum, ν, cm^{-1}: 1095 (C-Cl), 1230 (Ar-O-Ar), 1319 (Pc$^{\cdot}$ radical). Mass spectrum (MALDI-TOF), m/z: 2483.0 $[M+3H]^+$. Found, %: C 54.20; H 2.00, N 9.03. $C_{112}H_{48}Cl_{16}ErN_{16}O_8$. Calculated, %: C 54.24; H 1.95; N 9.04. UV-vis ($CHCl_3$) λ_{max}, nm (lg ε): 326 (4.920), 356 (4.867), 466 (4.301), 608 (4.471), 673 (5.059), 920 (3.659). ^{1}H NMR (500 MHz, DMSO-d6:N_2D_4·D_2O 6:1 (v/v) ratio): δ, ppm. 46.90-34.04 (m, H_α, 16 H), 25.81-22.57 (m, H_β, 8 H), 20.74-13.45 (m, H_{Ar}, 24 H).

Erbium(III) bis(2(3),9(10),16(17),23(24)-(2,4,5-trichlorophenoxy)phthalocyaninato) (**Er(Pc)$_2$2**). Yield: 0.20 g (23 %). IR spectrum, ν, cm^{-1}: 1080 (C-Cl), 1246 (Ar-O-Ar), 1319 (Pc$^{\cdot}$ radical). Mass spectrum (MALDI-TOF), m/z: 2759.0 $[M+3H]^+$. Found, %: C 48.80; H 1.49, N 7.99. $C_{112}H_{40}Cl_{24}ErN_{16}O_8$. Calculated, %: C 48.82; H 1.46; N 8.13. UV-vis ($CHCl_3$) λ_{max}, nm (lg ε): UV-vis λ_{max}, nm (lg ε): 326 (4.937), 353 (4.858), 465 (4.307), 606 (4.456), 671 (5.061), 918 (3.616). ^{1}H NMR (500 MHz, DMSO-d6:N_2D_4·D_2O 6:1 (v/v) ratio): δ, ppm. 41.68-36.38 (m, H_α, 16 H), 21.92-19.90 (m, H_β,8 H), 16.44-12.73 (m, H_{Ar}, 16 H).

Neodymium (III) bis(2(3),9(10),16(17),23(24)-(4-cyclohexylphenoxy)phthalocyaninato) (**Nd(Pc)$_2$3**). Yield: 0.17 g (16 %). IR spectrum, ν, cm^{-1}:1223 (Ar-O-Ar), 1314 (Pc$^{\cdot}$ radical), 2847 (CH_2), 2915 (CH_2). Mass spectrum (MALDI-TOF), m/z: 2564.8 $[M+2H]^+$. Found, %: C 74.95; H 5.69, N 8.71. $C_{160}H_{144}N_{16}NdO_8$. Calculated, %: C 74.97; H 5.66; N 8.74. UV-vis ($CHCl_3$) λ_{max}, nm (lg ε): 330 (5.136), 366 (5.013), 486 (4.494), 625 (4.811), 693 (5.129), 920 (3.587). ^{1}H NMR (500 MHz, DMSO-d6:N_2D_4·D_2O 6:1 (v/v) ratio): δ, ppm. 7.04-6.49 (m, H_α, H_β, 24 H), 6.34-5.72 (m, H_{Ar}, 32 H), 1.29-0.68 (m, $H_{Cycloalk}$, 88 H).

2(3),9(10),16(17),23(24)-(2,4-Dichlorophenoxy)phthalocyanine (**H$_2$Pc1**). Yield: 0.01 g (1 %). IR spectrum, ν, cm^{-1}: 1010 (H_2Pc), 1089 (C-Cl), 1231 (Ar-O-Ar), 3193 (N-H). Mass spectrum (MALDI-TOF), m/z: 1159.5 $[M+H]^+$. Found, %: C 58.10; H 2.29, N 9.68. $C_{56}H_{26}Cl_8N_8O_4$. Calculated, %: C 58.06; H 2.26; N 9.67.

2(3),9(10),16(17),23(24)-(2,4,5-Trichlorophenoxy)phthalocyanine (**H$_2$Pc2**). Yield: 0.01 g (1 %). IR spectrum, ν, cm^{-1}: 1010 (H_2Pc), 1080 (C-Cl), 1247 (Ar-O-Ar), 3189 (N-H). Mass spectrum (MALDI-TOF), m/z: 1297.5 $[M+H]^+$. Found, %: C 51.86; H 1.74, N 8.62. $C_{56}H_{22}Cl_{12}N_8O_4$. Calculated, %: C 51.89; H 1.71; N 8.64.

2(3),9(10),16(17),23(24)-(4-Cyclohexylphenoxy)phthalocyanine (**H$_2$Pc3**). Yield: 0.01 g (3 %). IR spectrum, ν, cm^{-1}: 1007 (H_2Pc), 1222 (Ar-O-Ar), 2848 (CH_2), 2919 (CH_2), 3150 (N-H). Mass spectrum (MALDI-TOF), m/z: 1212.1 $[M+H]^+$. Found, %: C 79.34; H 6.18, N 9.28. $C_{80}H_{74}N_8O_4$. Calculated, %: C 79.31; H 6.16; N 9.25.

Separation

Further, on the example of **Er(Pc)$_2$1** (Fig. S6), the amounts of reagents required for column chromatography are described in the details. Hydrazine hydrate 1 mmol (50 μl) was added to the prepared solution of the complex containing $4 \cdot 10^{-4}$ mmol (0.001 g) of the macrocycle and chloroform (2.7 ml). The color of the solution changed from green to blue. The solution was kept for 15 min in order to completely convert the green neutral-radical form into the reduced blue one. The solution of silica gel in chloroform was placed into a chromatographic column with the diameter of 3 cm and the height of 7.5 cm. Next, blue macrocycle solution was added into the column. Eluting with chloroform, the free phthalocyanine ligand was isolated. Further, the prepared solution of iron(III) acetylacetonate containing 0.3 mmol (0.1 g) of the iron complex and 2.7 ml of chloroform was added to the column. As the result of the redox reaction, the reduced form of the sandwich type macrocycle passed into the neutral radical one. Finally, the green form of bisphthalocyaninate was isolated by elution with chloroform.

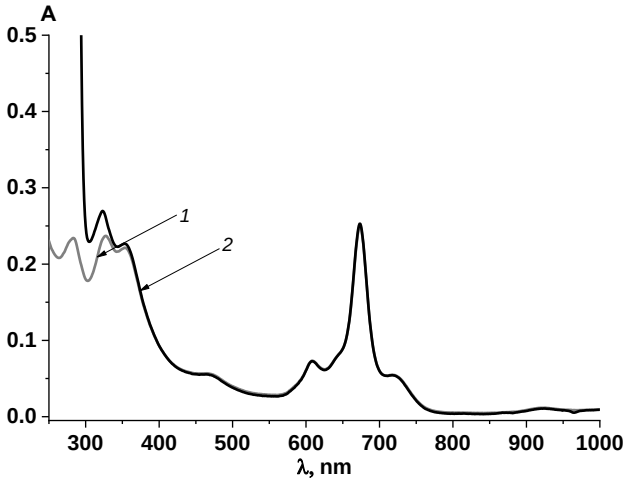


Figure S1. UV-vis spectra for mixture **Er(Pc)$_2$1** and **H$_2$Pc1** in chloroform (*1*) and for mixture **Er(Pc)$_2$1** and **H$_2$Pc1** in chloroform with the addition of pyridine (*2*).

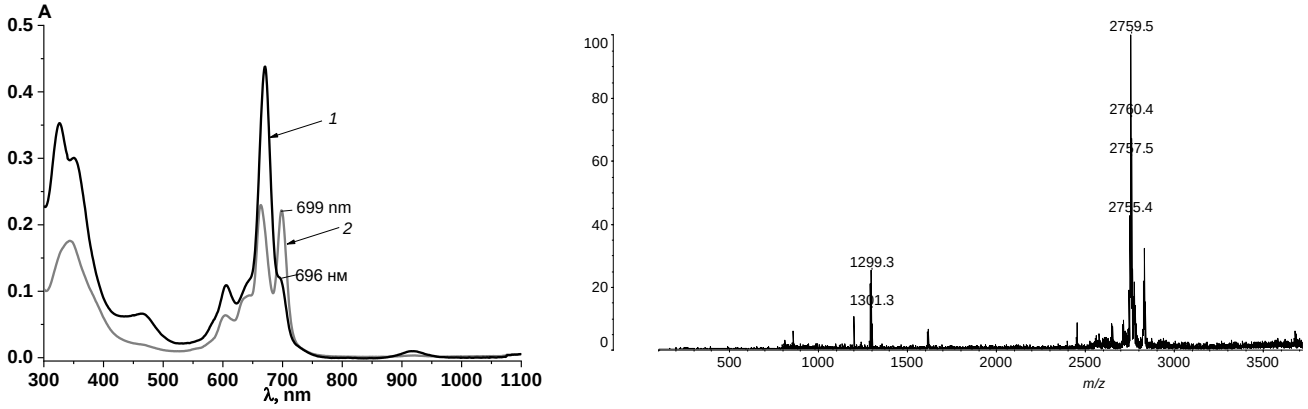


Figure S2. (*a*) UV-vis spectra for mixture **Er(Pc)$_2$2** and **H$_2$Pc2** (*1*) and the corresponding phthalocyanine ligand **H$_2$Pc2** (*2*) in chloroform, (*b*) mass spectrum for mixture **Er(Pc)$_2$2** and **H$_2$Pc2** after primary purification by column chromatography on silica gel.

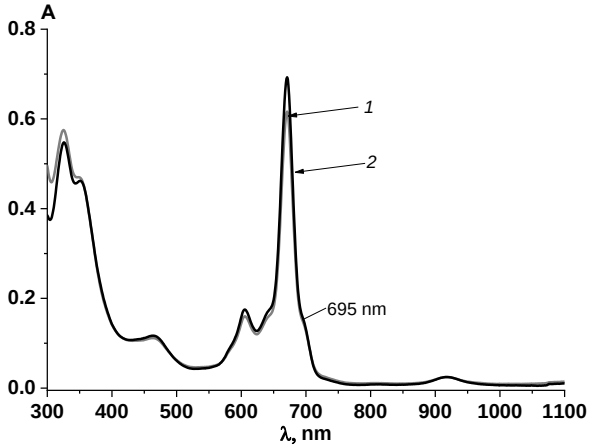


Figure S3. UV-vis spectra for mixture **Er(Pc)$_2$2** and **H$_2$Pc2** in chloroform after primary (*1*) and secondary purification (*2*) using Bio-Beads.

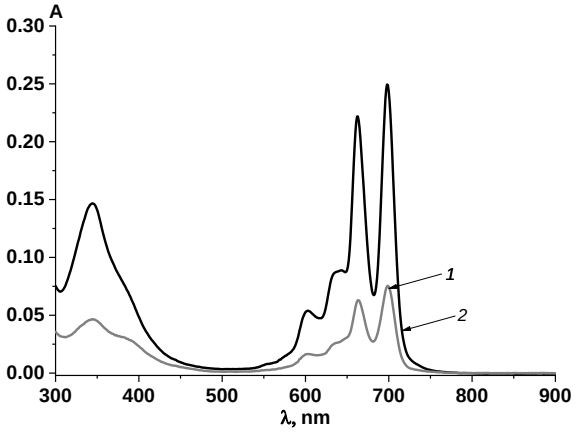


Figure S4. UV-vis spectra for **H$_2$Pc1** (*1*) and **H$_2$Pc2** (*2*) in chloroform

a)

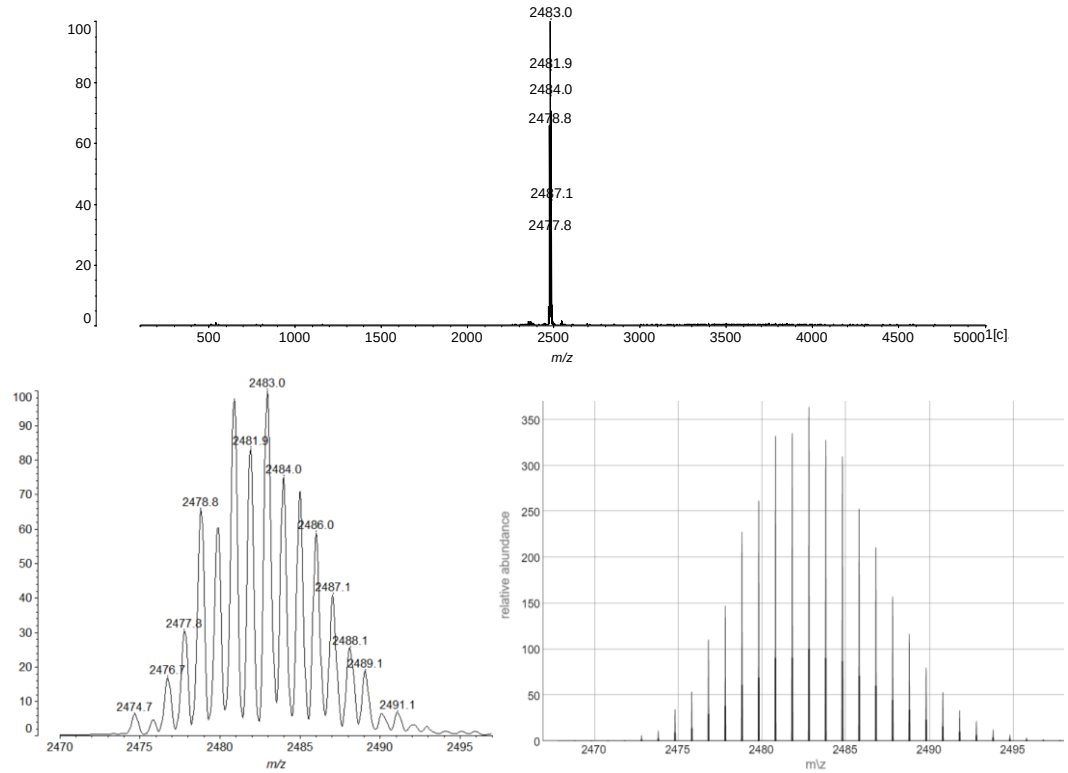


Figure S5a. Mass spectrum, isotopic resolution of the MALDI-TOF main peak (bottom left) and calculated isotopic patterns (bottom right) for **Er(Pc)$_2$1**.

b)

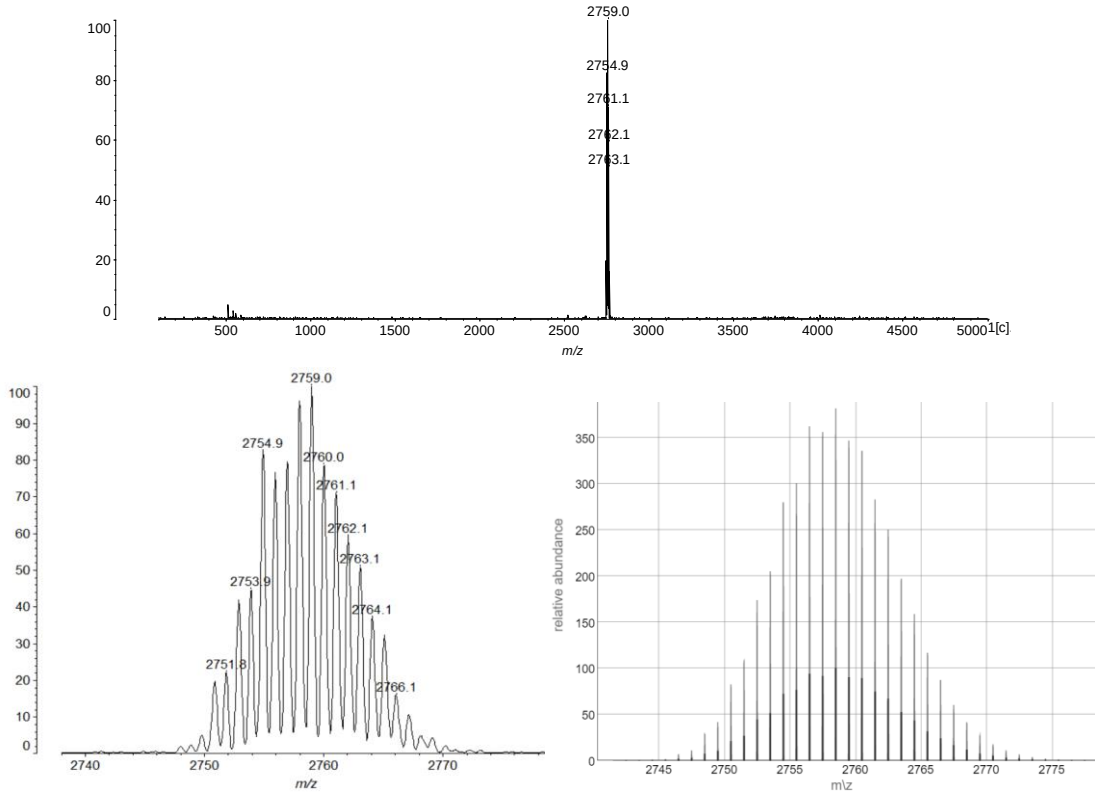


Figure S5b. Mass spectrum, isotopic resolution of the MALDI-TOF main peak (bottom left) and calculated isotopic pattern (bottom right) for **Er(Pc)$_2$2**.

c)

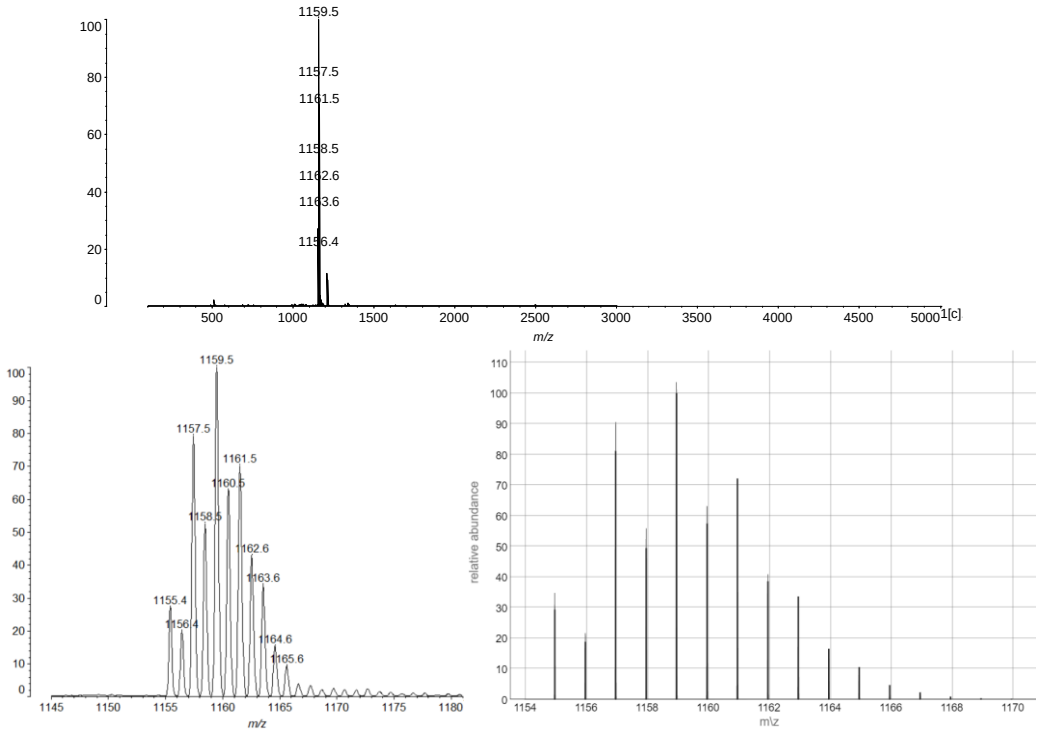


Figure S5c. Mass spectrum, isotopic resolution of the MALDI-TOF main peak (bottom left) and calculated isotopic pattern (bottom right) for **H_2Pc1**.

d)

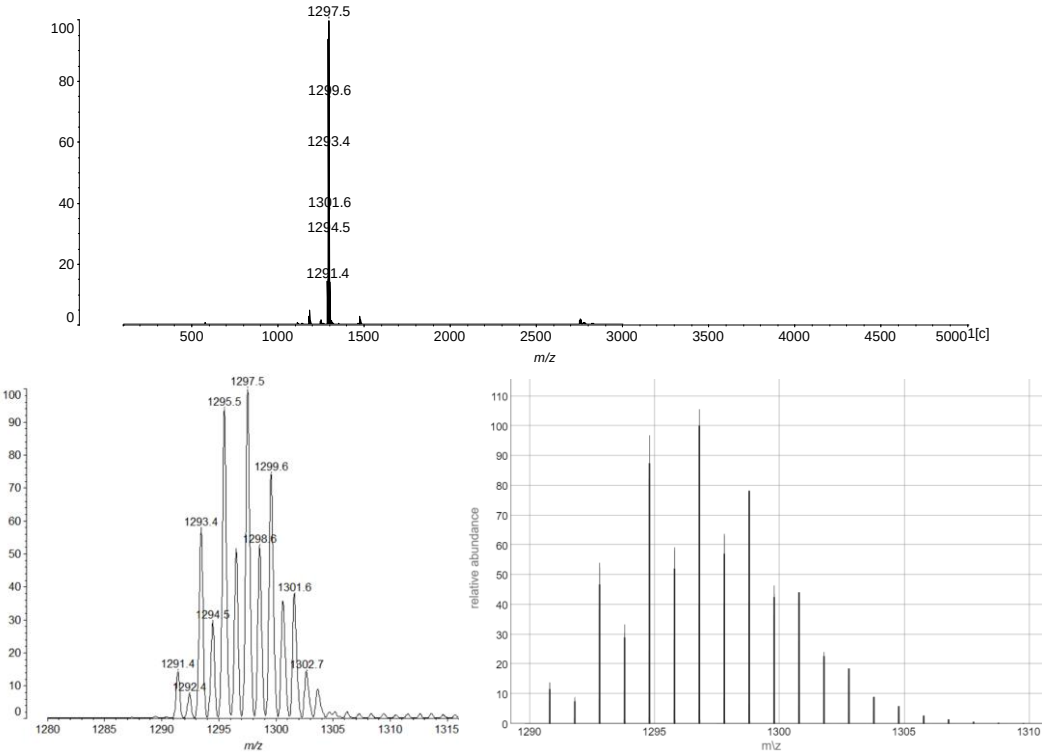


Figure S5d. Mass spectrum, isotopic resolution of the MALDI-TOF main peak (bottom left) and calculated isotopic pattern (bottom right) for **H_2Pc2.**

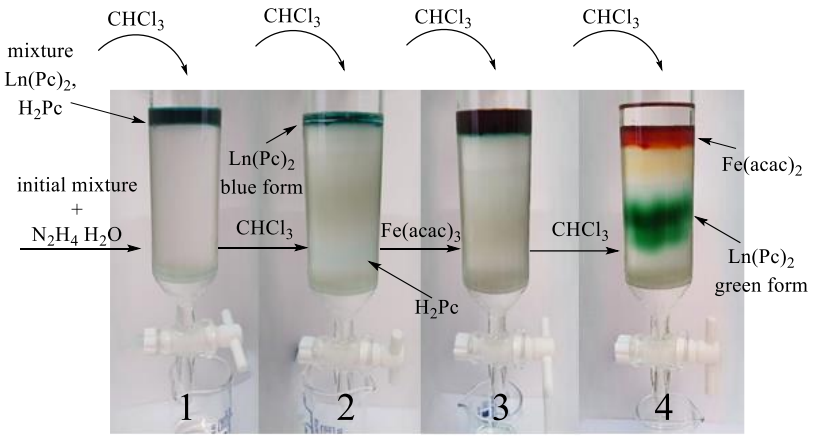
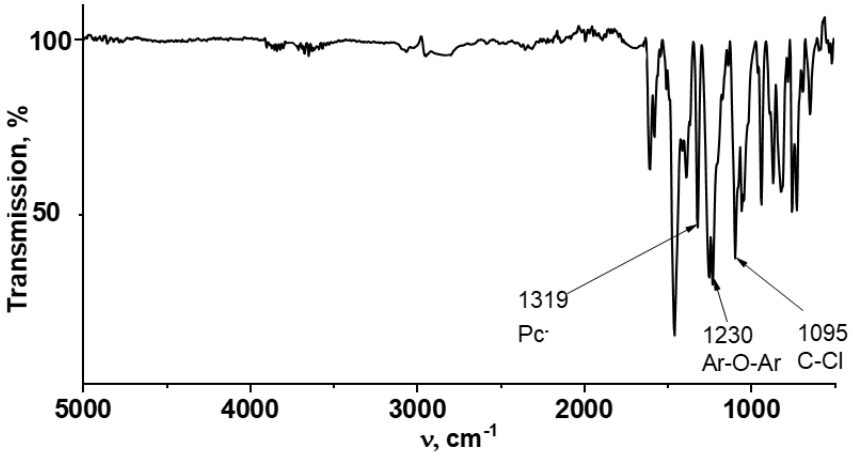
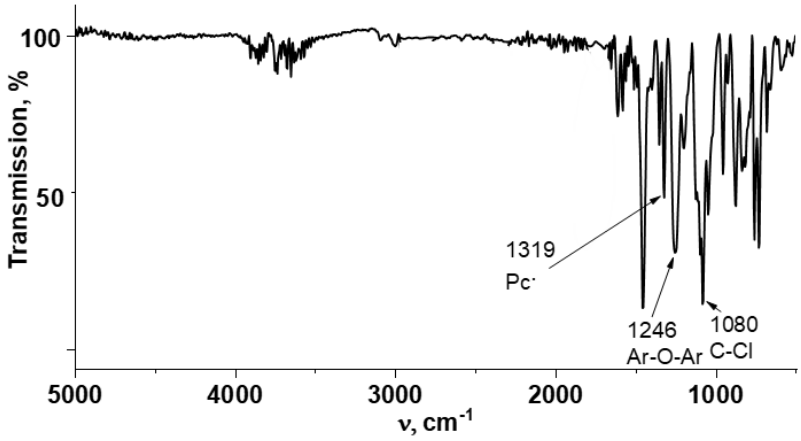


Figure S6. Picture of the column chromatography process for mixture of **Er(Pc)$_2$1** and **H$_2$Pc1**.

a)



b)



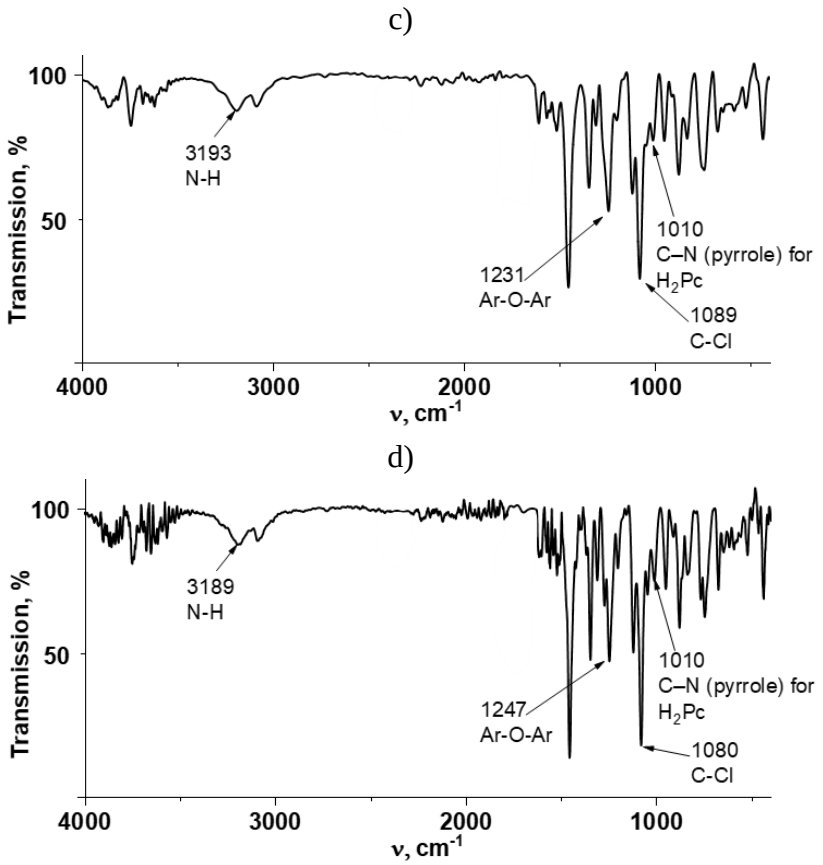


Figure S7. IR spectra for **Er(Pc)$_2$1** (a), **Er(Pc)$_2$2** (b) and the corresponding phthalocyanine ligands **H$_2$Pc1** (c) and **H$_2$Pc2** (d).

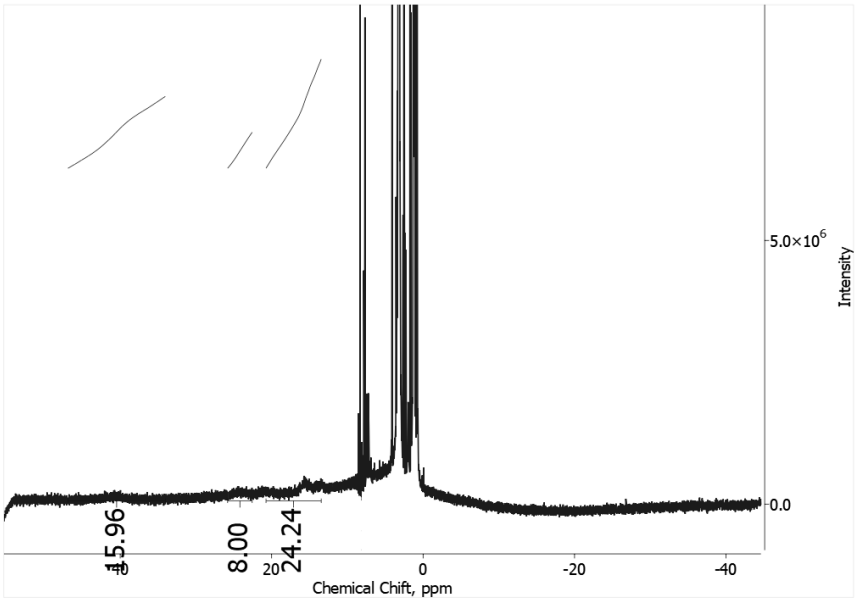


Figure S8. ^{1}H NMR spectrum for **Er(Pc)$_2$1** (DMSO-d$_6$: N_2D_4·D_2O 6 : 1 (v/v) ratio).

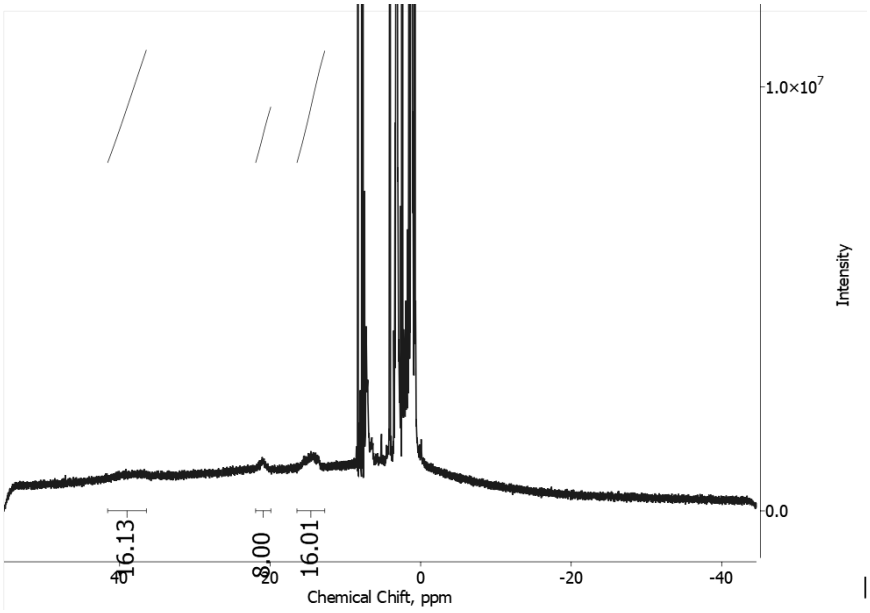


Figure S9. ^{1}H NMR spectrum for **Er(Pc)$_2$2** (DMSO-d$_6$: N_2D_4·D_2O 6 : 1 (v/v) ratio).

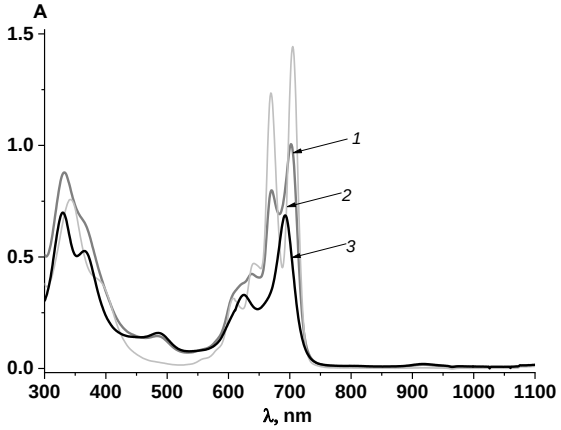


Figure S10. UV-vis spectra for mixture **Nd(Pc)$_2$3** and **H$_2$Pc3** (*1*), **H$_2$Pc3** (*2*) and **Nd(Pc)$_2$3** (*3*) in chloroform.

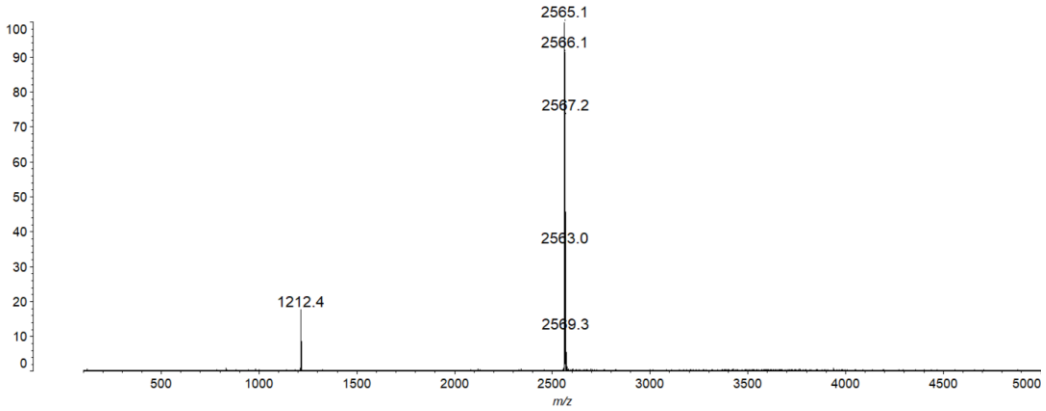


Figure S11. Mass spectrum for mixture **Nd(Pc)$_2$3** and **H$_2$Pc3**.

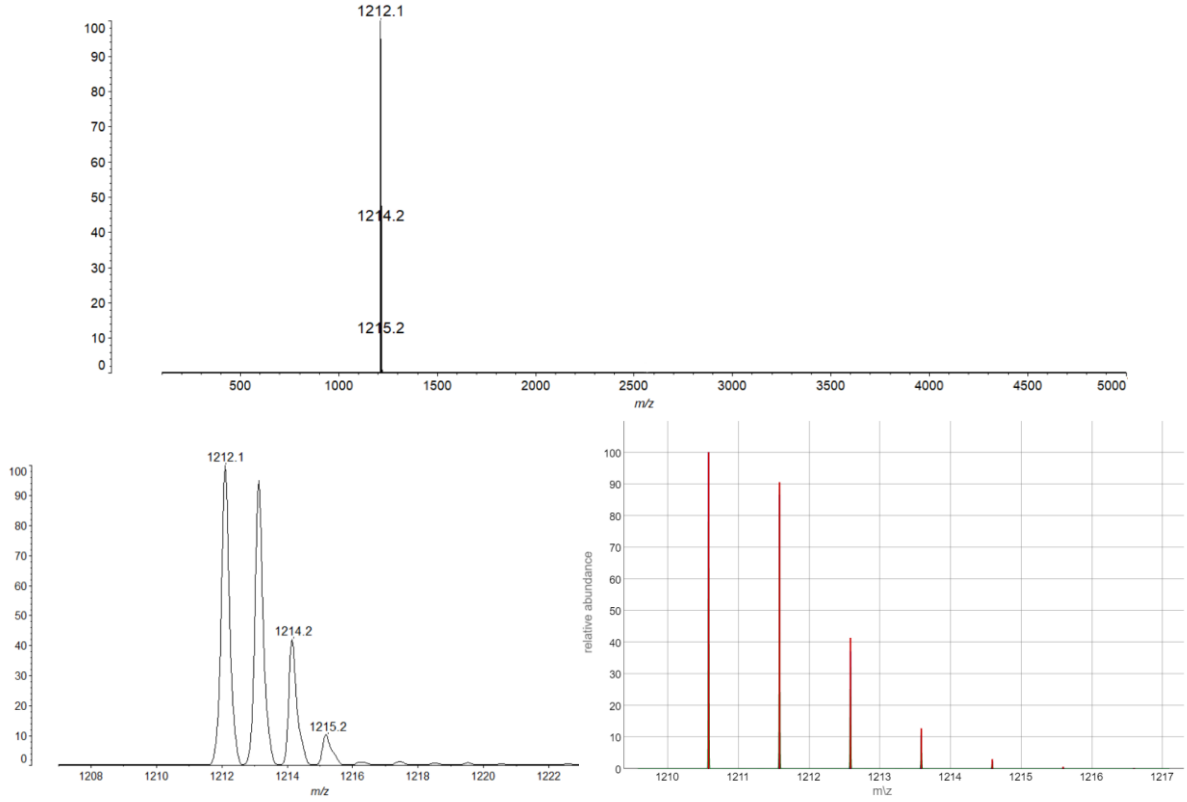


Figure S12, *a*. Mass spectrum, isotopic resolution of the MALDI-TOF main peak (bottom left) and calculated isotopic pattern (bottom right) for **H_2Pc3**.

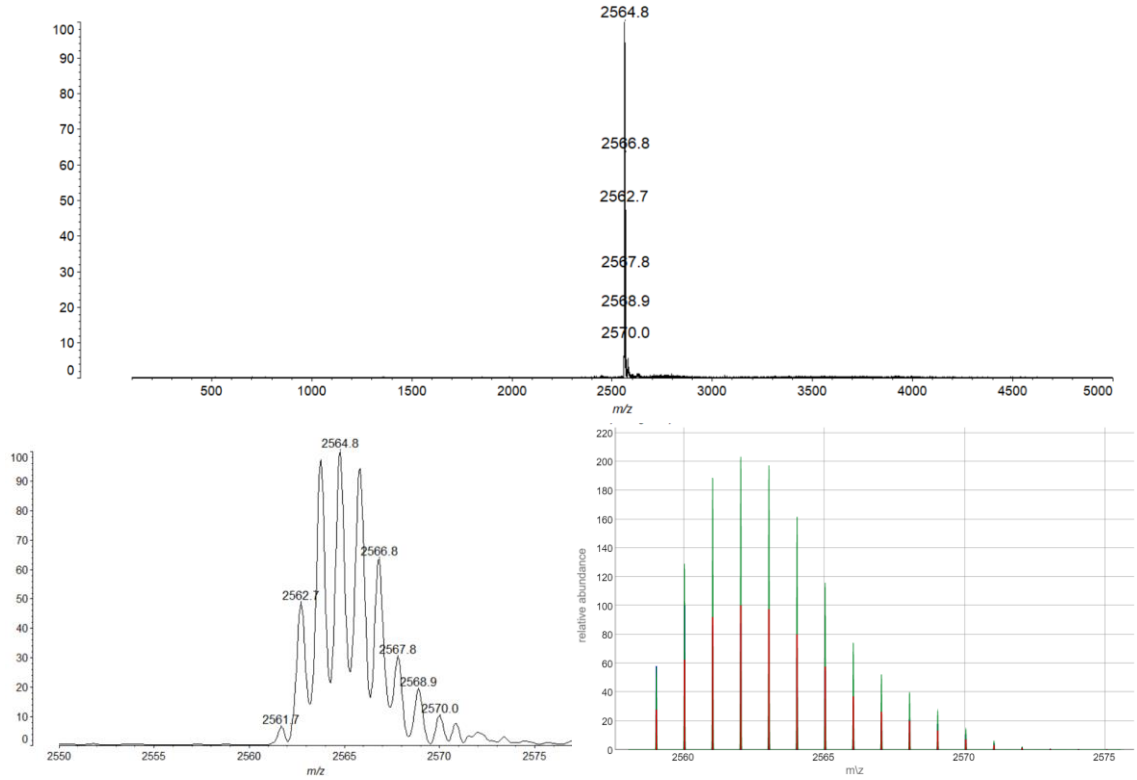
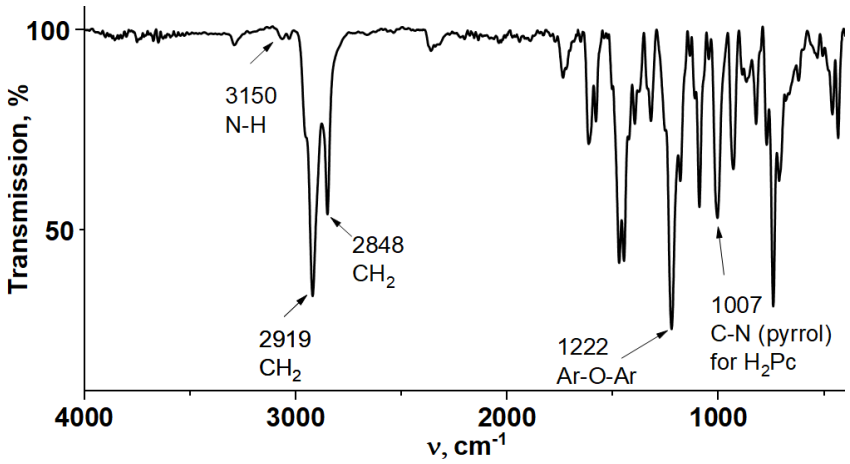


Figure S12, *b*. Mass spectrum, isotopic resolution of the MALDI-TOF main peak (bottom let) and calculated isotopic pattern (bottom right) for **Nd(Pc)$_2$3**.

a)



b)

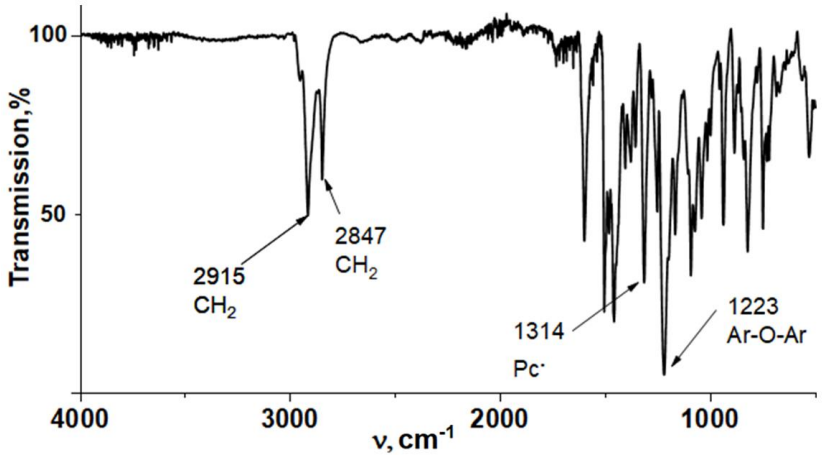


Figure S13. IR spectra for **H_2Pc3** (a) and **Nd(Pc)$_2$3** (b).

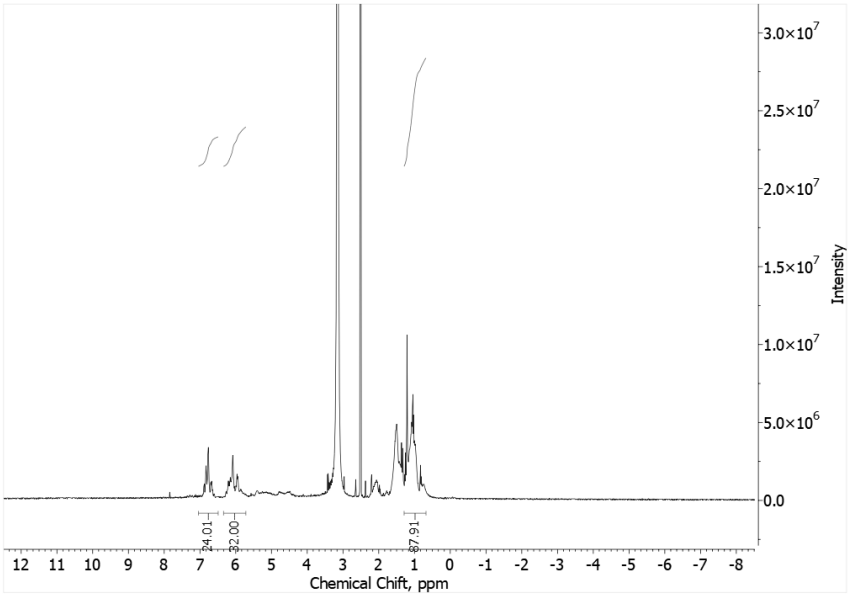


Figure S14. ^{1}H NMR spectrum for **Nd(Pc)$_2$3** (DMSO-d_6 : N_2D_4·D_2O 6 : 1 (v/v) ratio).