

Electronic Supporting Information

Bis(tetrabenzotriazaporphyrinato) and (tetrabenzotriazaporphyrinato)(phthalocyaninato) lutetium(III) complexes – novel sandwich-type tetrapyrrolic ligand based NIR absorbing electrochromes

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Experimental details

General: Gel permeation chromatography was accomplished on the polymeric support Bio-Beads S-X1 (BIORAD) with C_6H_6 as eluent. Preparative TLC was performed on flexible plates Merck Silica Gel 60 and Merck Silica Gel 60 F₂₅₄ with C_6H_6 as eluent. The electrolyte $[Bu_4N][BF_4]$ (Sigma-Aldrich) was recrystallized twice from ethyl acetate/hexane (9/1) and dried under vacuum at 80 °C. *o*-Dichlorobenzene (DCB, 99%, Sigma-Aldrich, HPLC grade) for voltammetric and spectroelectrochemical studies was used as received. All other reagents and solvents were obtained or distilled according to standard procedures. The lutetium salt $[Lu(acac)_3] \cdot 3H_2O$ was dried immediately before use in vacuum desiccator for 5 h at 50 °C. The reactions were monitored by TLC and UV/Vis spectroscopy and were continued until complete disappearance of starting reagents was observed if not additionally specified.

Measurements: Electronic absorption (UV/Vis) spectra were recorded with a ThermoSpectronic Helios- α spectrophotometer by using 0.5 cm quartz cells with samples dissolved in CCl_4 , THF, C_6H_6 or DCB. UV/Vis/NIR measurements were made with a Hitachi U-4100 instrument by using 0.5 cm quartz cells with samples dissolved in CCl_4 . The concentrations were varied in the range from $1.5 \cdot 10^{-5}$ to $4 \cdot 10^{-5}$ M. MALDI-TOF mass spectra were taken with a VISION-2000 mass spectrometer with 2-[(2E)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]-malonitrile (DCTB) as matrix. High-resolution MALDI mass spectra were recorded with a Bruker ULTRAFLEX II TOF/TOF instrument with DCTB as the matrix. 1H NMR and 1H - 1H COSY spectra were recorded with a Bruker AVANCE 600 spectrometer (600.12 MHz) with samples dissolved in $[D_6]DMSO$ to which $N_2H_4 \cdot H_2O$ (1–2 vol%) was added at 20 °C, unless otherwise specified. Chemical shifts are given in ppm relative to $SiMe_4$. Coupling constants, J , are given in Hz.

Quantum-chemical calculations were performed with density functional theory (DFT) method. Perdew–Burke–Ernzerhof (PBE) functional and PRIRODA software package supplied with three exponent TZ2P basis set including twice polarized Gauss-type functions were used for optimization of the structure geometries. Hessian calculations were used to prove the structures to be minima on the PES. The size of the basis set used was – (11s6p2d):[6s3p2d] for C and N, (5s1p):[3s1p] for H and (10s10p9d7f):[5s5p3d4f] for Lu atom correspondingly.

Electrochemical measurements were carried out with IPC-Pro (Econix, Moscow, Russia) and EmStat (Palm Instrument BV, Utrecht, the Netherlands) electrochemical interfaces. Cyclic voltammetry (CV) and square-wave voltammetry (SWV) were performed in a conventional three-electrode cell with a Pt-disk (2.0 mm in diameter) working and Pt-foil counter electrodes. The calomel reference electrode (SCE, 3.5 M KCl) was connected to the solution through a salt bridge and a Luggin capillary, the tip of which was placed close to the working electrode. Each time after a series of measurements, the junction potential of the reference electrode was corrected to a ferrocenium⁺/ferrocene (Fc⁺/Fc) couple. The samples (1.0×10^{-4} to 5.0×10^{-4} M) were dissolved in a 0.15 M solution of $[Bu_4N][BF_4]$ in DCB, and the solution was purged with argon for 20 min before measurements were taken. The open-circuit potential of the working electrode when immersed in the TBTAP solutions was approximately +0.4 V. The scan rate in CVA measurements was varied from 0.02 to 1.00 Vs^{-1} . A frequency of 10 Hz and an amplitude potential of 0.05 V were used for SWV. All measurements were performed at ambient temperature ($22 \pm 1^\circ C$).

Spectroelectrochemical experiments were performed with a quartz electrochemical cell composed of three separated compartments. The rectangular compartment with a path length of 9.3 mm contained a Pt-net working electrode, which was placed near the sidewall of the cell to avoid its interfering with the light beam. A Luggin capillary and a capillary for argon purging were placed close to the working electrode. A reference SCE electrode was installed in

the separate compartment and connected to the working part through a salt bridge. A Pt counter electrode with a surface area larger than the area of the working electrode was placed in a separate compartment and connected to the working space through a glass tube fitted with a frit. Sample solutions (1.0×10^{-5} to 2.0×10^{-5} M) contained 0.2 M of $[\text{Bu}_4\text{N}][\text{BF}_4]$. Pure argon was passed through the sample solution to remove oxygen and to stir the solution gently during the electrolysis process.

27-phenyl-29H,31H-tetrabenzob[*b,g,l,q*][5,10,15]triazaporphyrine (^{Ph}TBTAPH₂, **1):** A mixture of preliminarily synthesized^{3b} ^{Ph}TBTAP zinc complex (62 mg, 0.095 mmol), pyridine-HCl (33 mg, 0.285 mmol) in pyridine (2 mL) was heated under reflux for about 3 h. The reaction was removed from the heat, allowed to cool to the room temperature, and then poured into water (10 mL). The resulting precipitate was collected by filtration, washed consecutively with H₂O to neutral pH and 80% aqueous MeOH (3×10 ml), and finally dried *in vacuo* to yield 54 mg of **1** (96%). UV/VIS (THF): λ_{max} (I/I_{max}) = 379 (0.492), 590 (0.176), 616 (0.292), 643 (0.678), 684 (1.000) nm. UV/Vis (C₆H₆): λ_{max} (I/I_{max}) = 381 (0.502), 592 (0.233), 617 (0.324), 645 (0.664), 686 (1.000) nm. MS (MALDI-TOF): calcd. for C₃₉H₂₃N₇ [M⁺] 589.2; found 589.0.

(^{Ph}TBTAP)₂Lu (2**):** A mixture of ligand **1** (25 mg, 0.042 mmol), MeOLi (5 mg, 0.126 mmol), [Lu(acac)₃]·3H₂O (11 mg, 0.021 mmol) and 100 mg of *n*-hexadecanol (cetyl alcohol) was heated under argon to 220 °C and held for 30 min. The mixture was cooled to room temperature and then diluted with THF (5 ml), the insoluble components were filtered off, and the solvents evaporated. The residue was repeatedly washed with boiling MeOH (4×30 ml) and dried *in vacuo*. The greenish solid that was obtained was dissolved in THF and subjected to gel permeation chromatography, from which one narrow green band containing target double-decker was generally collected. Preparative TLC was applied for final purification of the compound to yield 22.9 mg of **2** (81%).

Data for 2: ¹H NMR ([D₆]DMSO with the addition of 1–2 vol% N₂H₄·H₂O): δ = 8.70–8.98 (m, 12 H, α^1 -H, α^2 -H), 8.17–8.27 (m, 8 H, β^1 -H), 7.70–7.93 (m, 8 H, β^2 -H, m^o -H, *p*-H), 7.44–7.61 (m, 4 H, β^3 -H), 7.25–7.31 (m, 2 H, m^i -H), 6.80–6.94 (m, 2 H, o^o -H), 6.38–6.54 (m, 4 H, α^3 -H), 6.07–6.18 (m, 2 H, o^i -H). Protons are denoted in accordance with Figs. S4, S5. UV/Vis/NIR (C₆H₆): λ_{max} (I/I_{max}) = 339 (1.000), 387 sh (0.550), 448 sh (0.289), 573 (0.185), 600 sh (0.214), 629 (0.583), 652 (0.752), 829 (0.049), 896 (0.060) nm. UV/Vis/NIR (CCl₄): λ_{max} (I/I_{max}) = 338 (1.000), 386 sh (0.551), 447 sh (0.298), 572 (0.187), 599 sh (0.215), 630 (0.587), 652 (0.769), 828 (0.050), 897 (0.062), 1231 sh (0.124), 1339 (0.197), 1491 (0.178) nm. HR MS (MALDI-TOF/TOF): calcd. for C₇₈H₄₂N₁₄Lu [M]⁺ 1349.3125; found 1348.9894.

(^{Ph}TBTAP)Lu(Pc) (3**):** A mixture of ligand **1** (25 mg, 0.042 mmol), MeOLi (5 mg, 0.126 mmol), PcLu(OAc) (31 mg, 0.042 mmol) preliminarily synthesized by known procedure^{5a}, 100 mg of *n*-hexadecanol (cetyl alcohol) and 0.1 mL of 1,2,4-trichlorobenzene (TCB) was heated under argon to 220 °C and held for 30 min. The mixture was cooled to room temperature and then diluted with THF (5 ml), the insoluble components were filtered off, and the solvents evaporated. The residue was repeatedly washed with boiling MeOH (4×30 ml) and dried *in vacuo*. The greenish solid that was obtained was dissolved in THF and subjected to gel permeation chromatography, from which one narrow green band containing target double-decker was generally collected. Preparative TLC was applied for final purification of the compound to yield 38.5 mg of **3** (72%).

Data for 3: ¹H NMR ([D₆]DMSO with the addition of 1–2 vol% N₂H₄·H₂O): δ = 8.74–8.92 (m, 14 H, α^1 -H, α^2 -H, α^{Pc} -H), 8.10–8.27 (m, 12 H, β^1 -H, β^{Pc}), 7.81–7.85 (m, 4 H, β^2 -H, m^o -H, *p*-H), 7.50–7.54 (br. t, J = 7.3 Hz, 2 H, β^3 -H), 7.29–7.33 (m, 1 H, m^i -H), 7.00–7.03 (m, 1 H, o^o -H), 6.48 (d, J = 8 Hz, 2 H, α^3 -H), 6.17–6.19 (br. d, J = 7.3 Hz, 1 H, o^i -H). Protons are denoted in accordance with Figs. 2, S6. UV/Vis/NIR (C₆H₆): λ_{max} (I/I_{max}) = 329 (1.000), 455

(0.280), 586 (0.199), 604 sh (0.203), 644 (0.718), 659 (0.989), 858 (0.040), 920 (0.056) nm. UV/Vis/NIR (CCl₄):
 λ_{\max} (I/I_{\max}) = 329 (1.000), 452 (0.286), 585 (0.194), 603 sh (0.201), 642 (0.705), 658 (0.944), 856 (0.043), 917
(0.053), 1263 sh (0.092), 1361 (0.140), 1498 (0.097) nm. HR MS (MALDI-TOF/TOF): calcd. for C₇₁H₃₇N₁₅Lu [M]⁺
1274.2764; found 1274.1014.

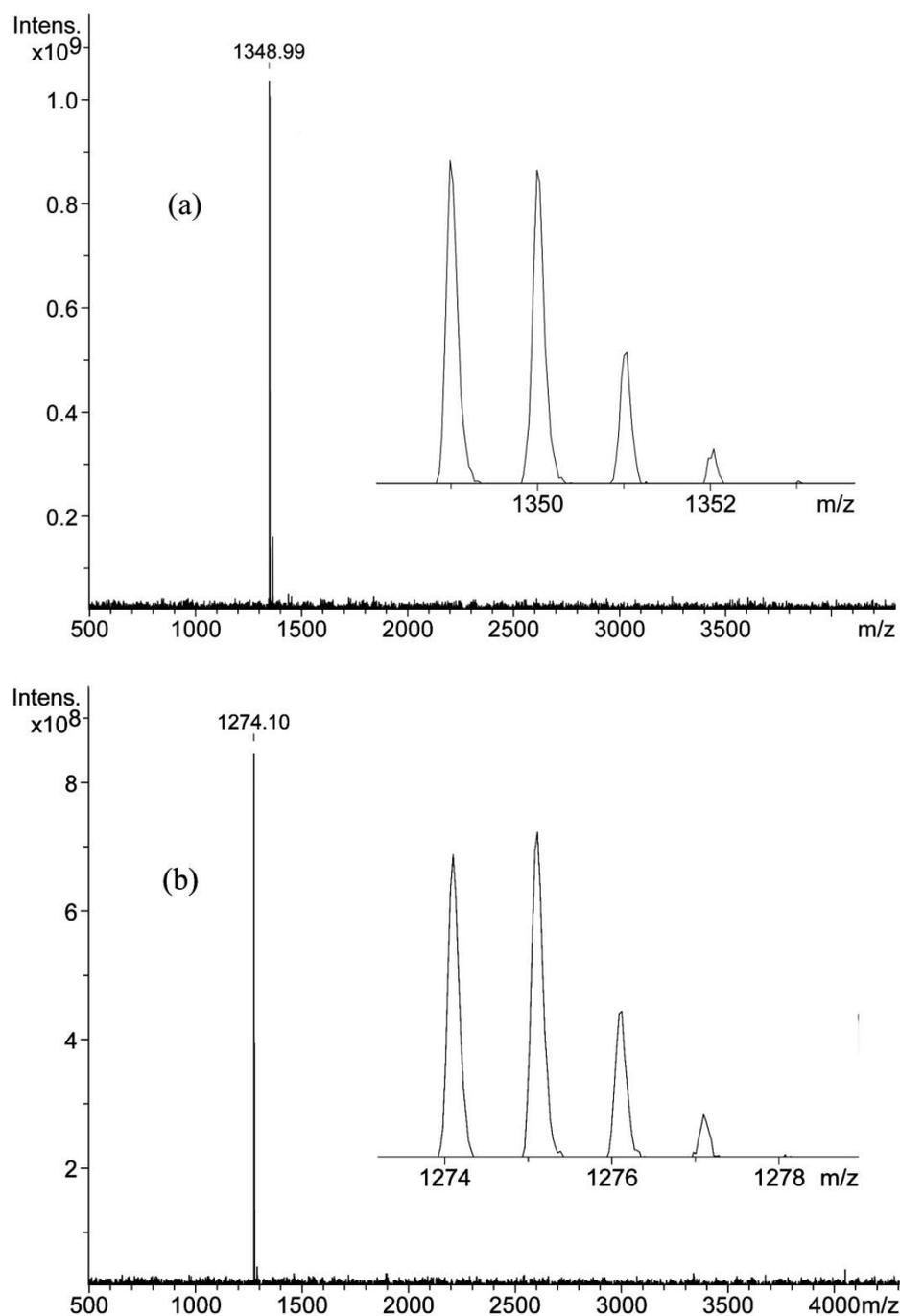


Fig. S1 MALDI-TOF mass spectra of **2** (a) and **3** (b) with DCTB as the matrix; isotopic patterns for the corresponding molecular ions are shown in insets.

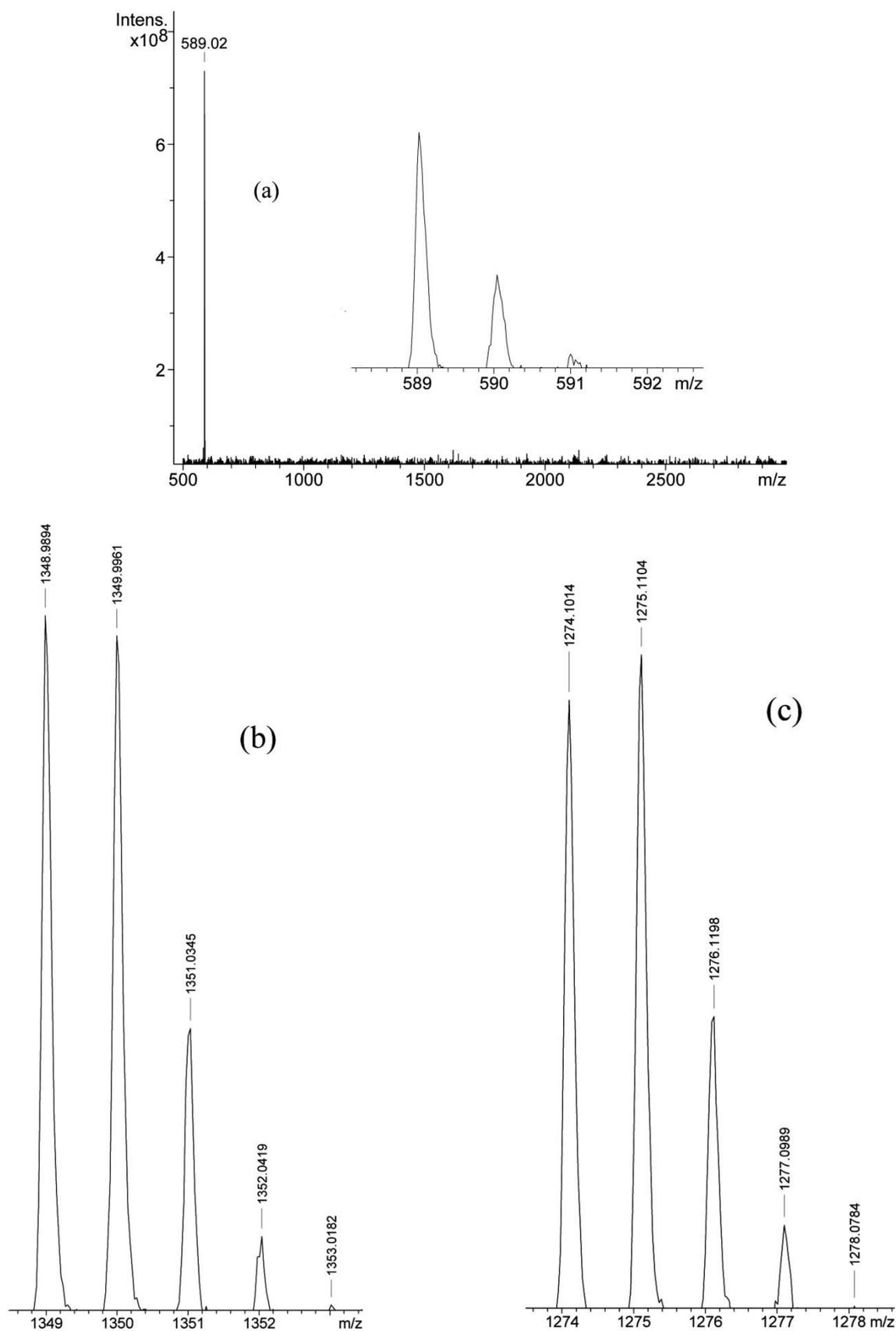
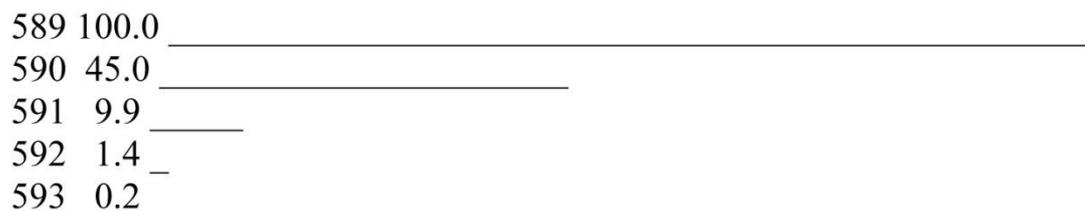


Fig. S2 MALDI-TOF mass spectrum of **1** with isotopic pattern for the molecular ion shown in inset (a) with DCTB used as matrix; the isotopic distributions for the molecular ions of compounds **2** (b) and **3** (c) by HR-MS mass spectrometry.

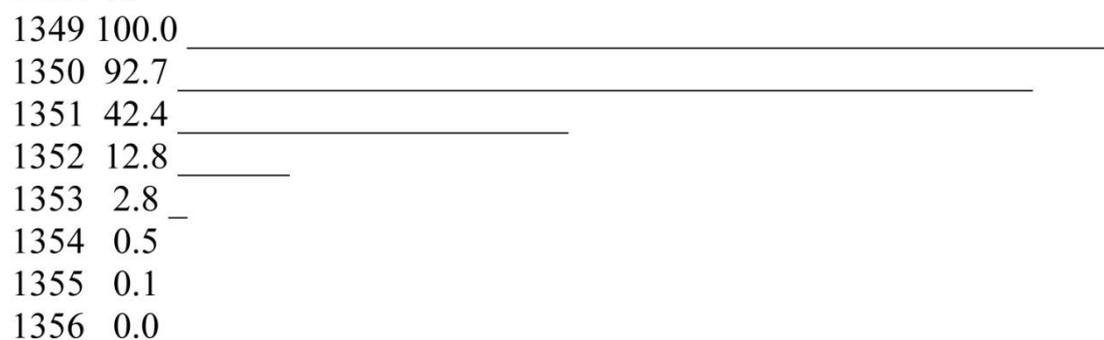
(1) $C_{39}H_{23}N_7, [M]^+$

mass %



(2) $C_{78}H_{42}N_{14}Lu, [M]^+$

mass %



(3) $C_{71}H_{37}N_{15}Lu, [M]^+$

mass %

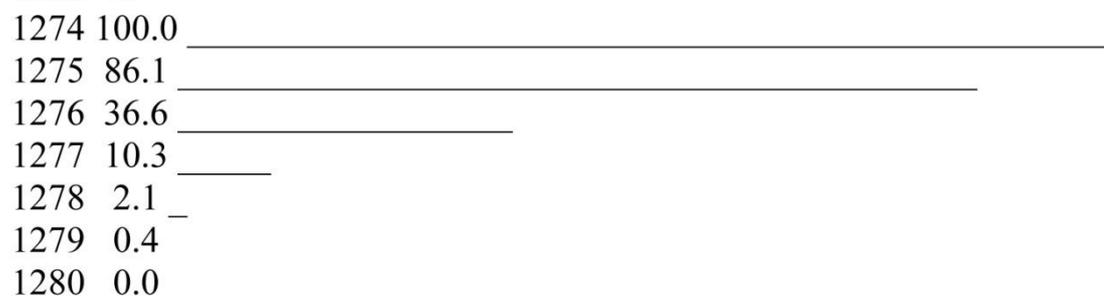


Fig. S3 Corresponding simulated MS patterns of the molecular ions for complexes 1–3.

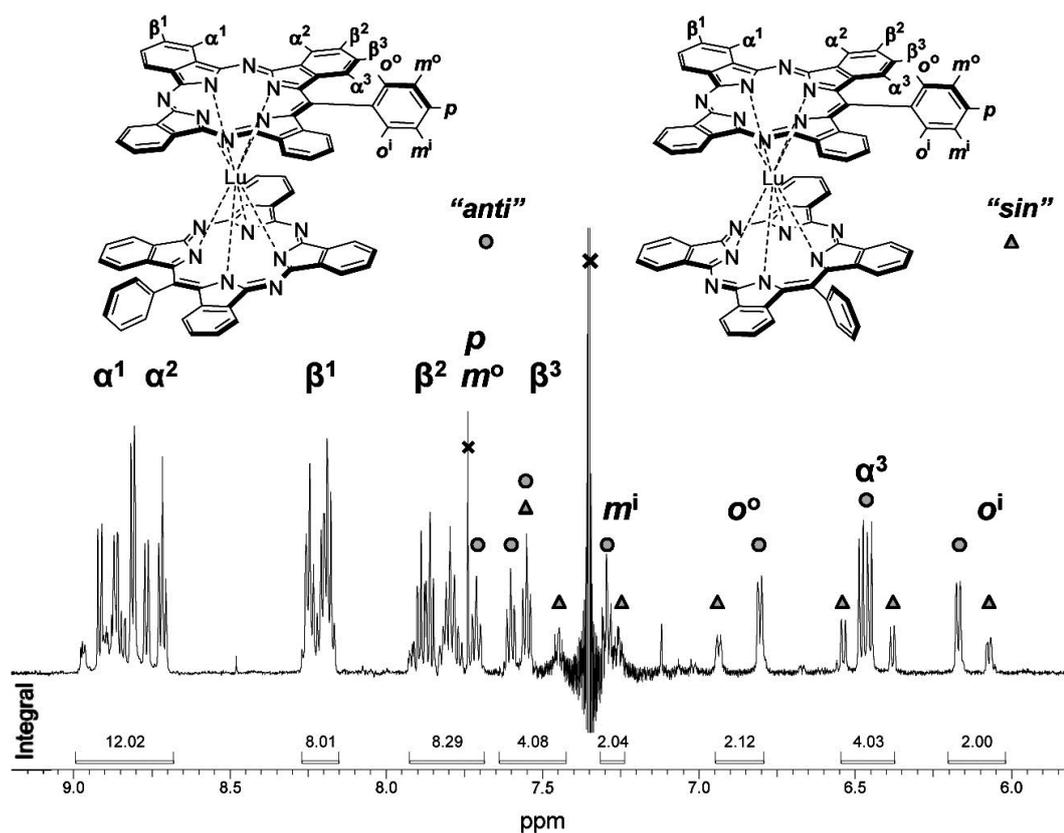


Fig. S4 ¹H NMR spectrum of compound **2** (aromatic region) in [D₆]DMSO with the addition of 1–2 vol% N₂H₄·H₂O; distinct signals of the main “anti” and minor “sin” rotamer are marked with circles and triangles respectively; “x” indicates signals from residual solvents.

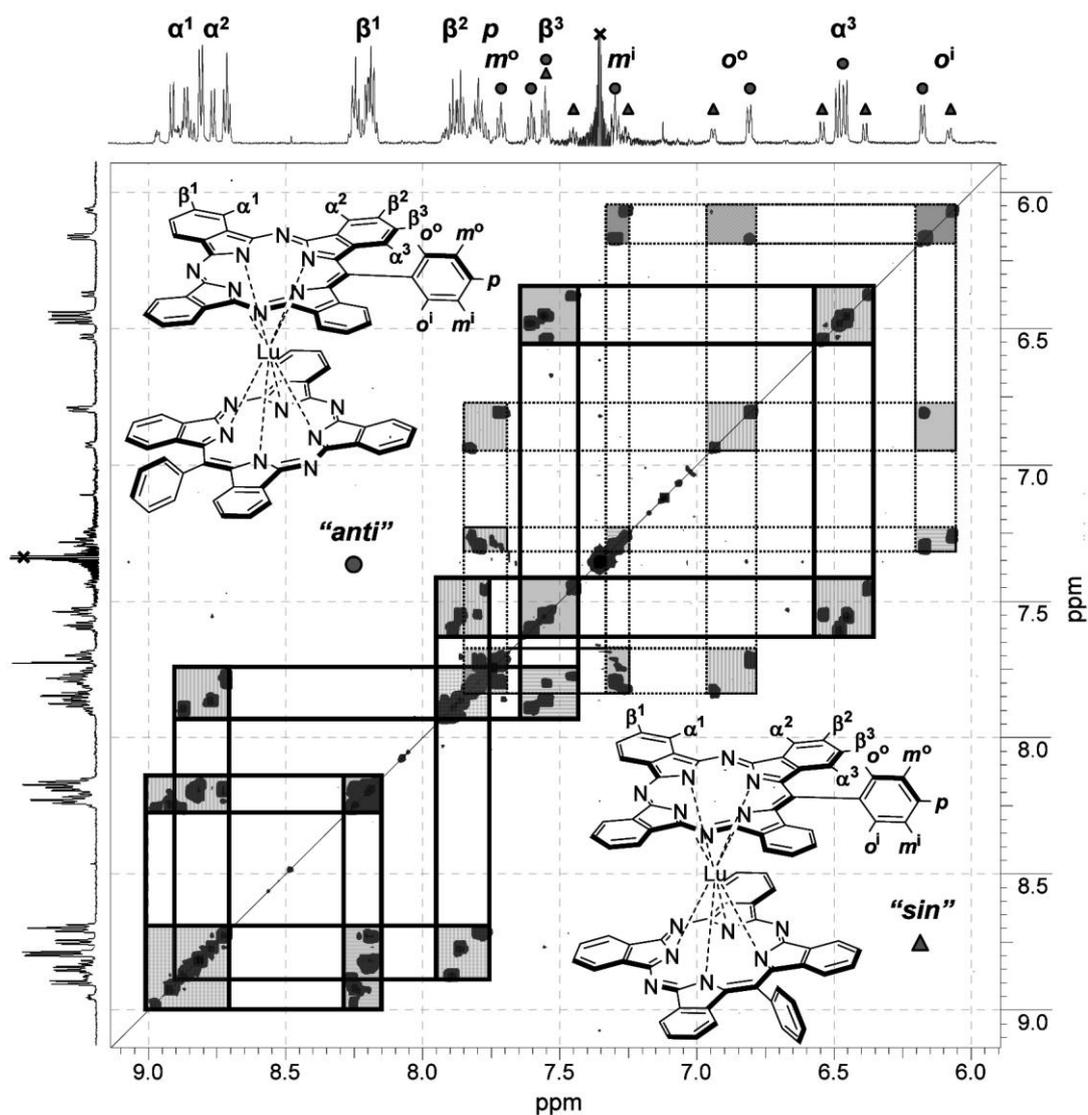


Fig. S5 ^1H - ^1H COSY NMR spectrum of compound **2** (aromatic region) in $[\text{D}_6]\text{DMSO}$ with the addition of 1–2 vol% $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$; distinct signals of the main “anti” and minor “sin” rotamer are marked with circles and triangles respectively; “x” indicates signals from residual solvents.

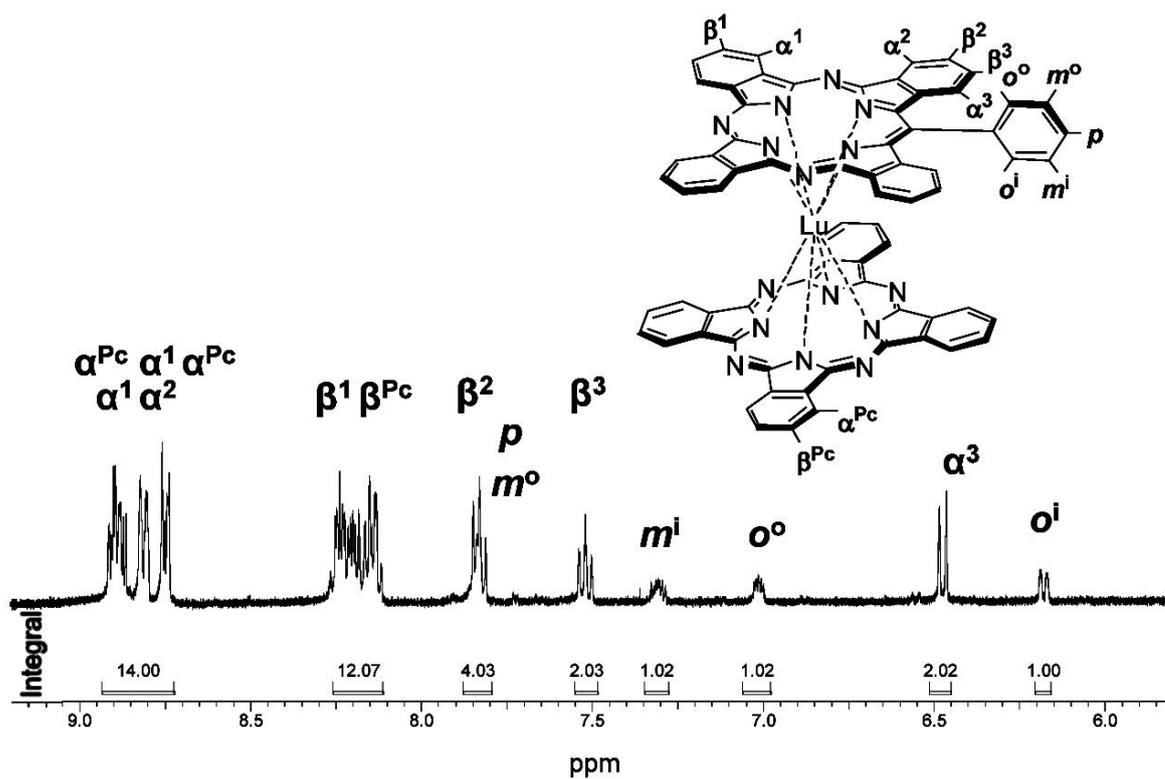


Fig. S6 ¹H NMR spectrum of compound 3 (aromatic region) in [D₆]DMSO with the addition of 1–2 vol% N₂H₄·H₂O.

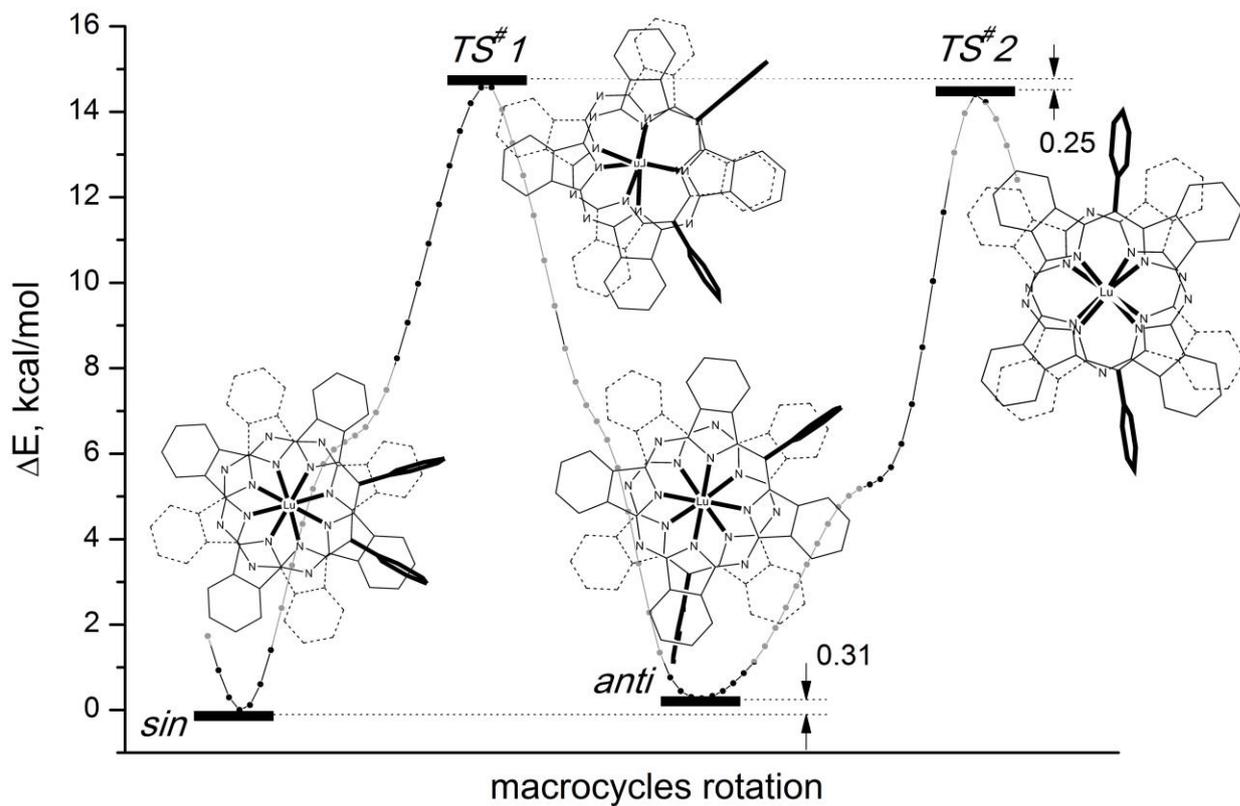


Fig. S7 Dependence of the potential energy (ΔE) on the skew angle between Ph^{h} TBTAP planes for the model of complex **2** by theoretical calculations (DFT//PBE/TZ2P). *Staggered* rotamer with 45° angle between *meso*-phenyl groups is denoted as “sin” form; *staggered* rotamer with 135° angle between *meso*-phenyl groups is denoted as “anti” form. Abbreviations TS1 and TS2 denote respective *eclipsed* transition states.

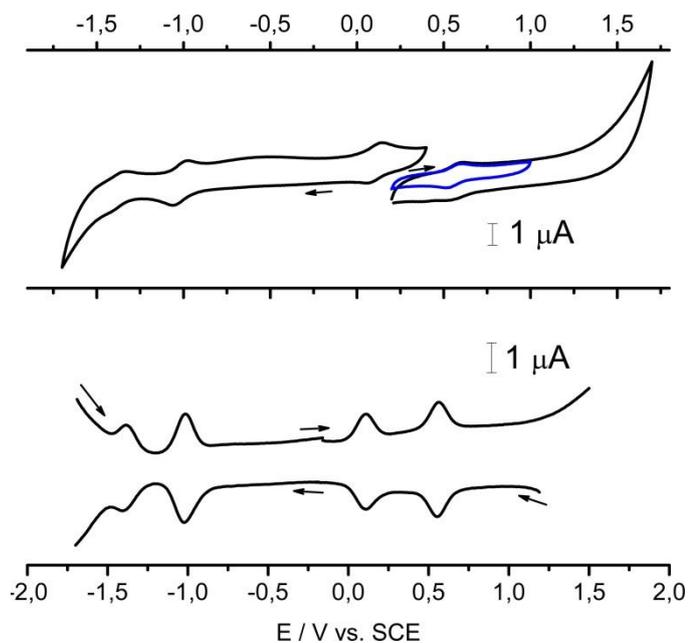


Fig. S8 CVA (scan rate 0.10 V s^{-1}) and SWVA for complex **3** in DCB containing 0.15 M $[\text{BuN}_4][\text{BF}_4]$.

Table S1 Half-wave potentials in DCB.

	$E_{1/2}$ [V] vs. SCE ^[a]				$\Delta E_{1/2}$ ^[b]
	R_3	R_2	R_1	Ox_1	
2	-1.456 (-2.064)	-1.085 (-1.693)	0.044 (-0.564)	0.501 (-0.107)	0.457
3	-1.385 (-2.027)	-1.019 (-1.661)	0.112 (-0.530)	0.559 (-0.083)	0.447
4 ^[c]	-1.370	-1.020	0.130	0.530	0.400

[a] Values versus Fe/Fc^+ given in parentheses. [b] $\Delta E_{1/2} = \text{Ox}_1 - R_1$.

[c] Values correspond to the data of Ref. [8b].

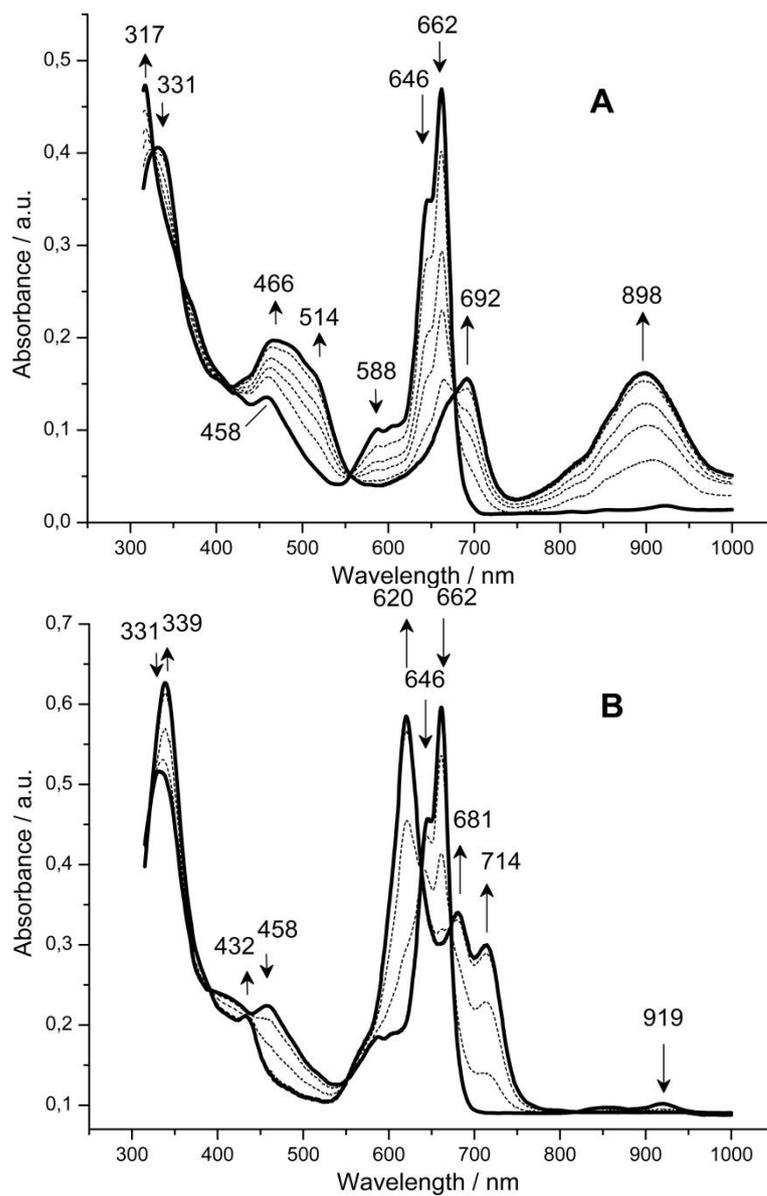


Fig. S9 UV/Vis spectral changes for **3** in DCB containing 0.2 M [BuN₄][BF₄] during controlled-potential oxidation at +0.8 V (A) and reduction at -0.4 V (B).