

Supporting Information

**Novel phenyl-substituted pyrazinoporphyrazine complexes
of rare-earth elements: optimized synthetic protocols and
physicochemical properties**

A.D. Kosov^a, T.V. Dubinina^{a,b@}, N.E. Borisova,^{a,c} A.V. Ivanov^a, K.A. Drozdov^a, S.A. Trashin^d, K. De Wael^d, M.S. Kotova^a, and L.G. Tomilova^{a,b}

[a] *Department of chemistry, Lomonosov Moscow State University, 119991 Moscow, Russian Federation.*

[b] *Institute of physiologically Active Compounds, Russian Academy of Science, 142432 Chernogolovka, Moscow Region, Russian Federation.*

[c] *A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Science, 28 Vavilov Str. 119334 Moscow, Russian Federation*

[d] *AXES research group, University of Antwerp, 2020 Antwerp, Belgium.*

@Corresponding author E-mail: dubinina.t.vid@gmail.com

Contents list

Figure S1. ^1H NMR spectra of complexes **2a**, **2d**, **2f** in $[\text{D}_5]\text{Py}$ and $^1\text{H}-^1\text{H}$ COSY NMR spectrum of complex **2b** in $[\text{D}_7]\text{DMF}$.

Figure S2. FT-IR spectra of ligand **4** in ZnSe.

Figure S3. Effect of the scan rate on the peak current Red_1 and Red_1' (A) and the same voltammograms normalized on square root of the scan rate.

Table S1. Oxidation-reduction potentials $E_{1/2}$ (V) for complex **2e** in comparison with analogous complexes.

Supporting references.

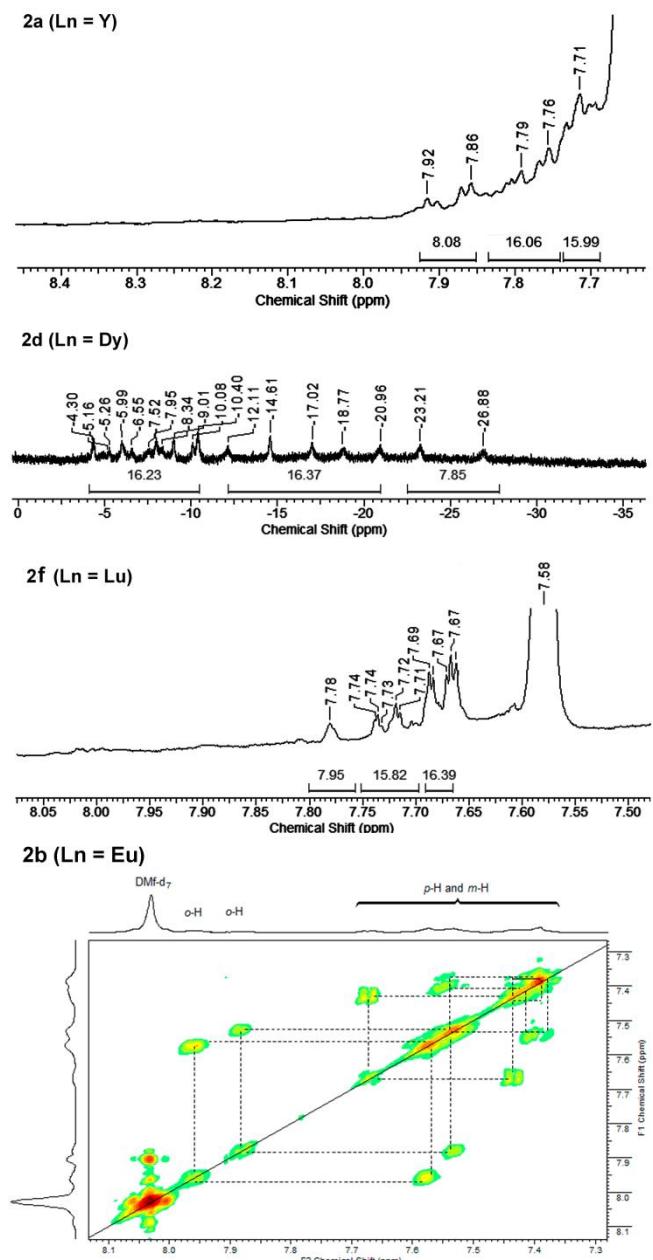


Figure S1. ^1H NMR spectra of complexes **2a**, **2d**, **2f** in $[\text{D}_5]\text{Py}$ and $^1\text{H}-^1\text{H}$ COSY NMR spectrum of complex **2b** in $[\text{D}_7]\text{DMF}$.

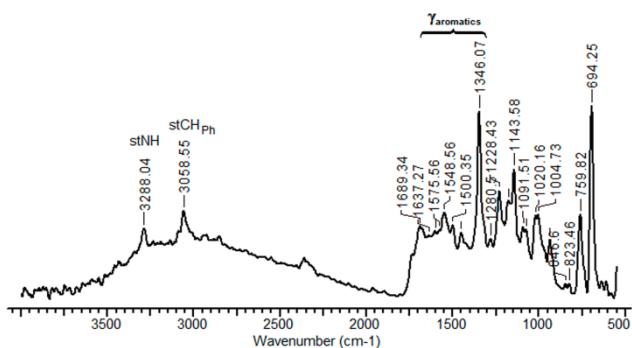


Figure S2. FT-IR spectra of ligand **4** in ZnSe.

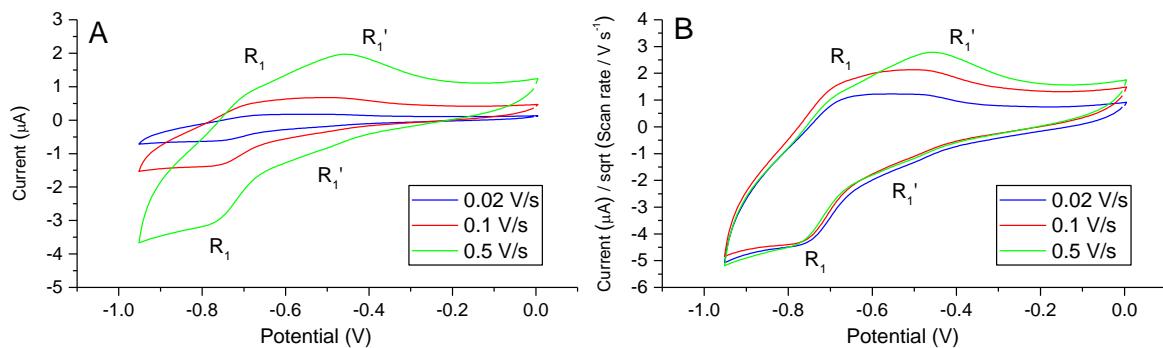


Figure S3. Effect of the scan rate on the peak current Red_1 and Red_1' (A) and the same voltammograms normalized on square root of the scan rate.

Table S1. Oxidation-reduction potentials $E_{1/2}$ (V) for complex **2e** in comparison with analogous complexes.

Compound	Solvent	Red_3	Red_2	Red_1	Ox_1	Ox_2	Fc^+/Fc	$\Delta E_{\text{Red}_1-\text{Ox}_1}$	Reference
2e	Pyridine	-1.24	-0.98	-0.74	+0.86	+1.20	0.610	1.60	This work
$^{Ph_8}PcLuOAc$	<i>o</i> -DCB	-	-1.32	-0.85	+0.75	+1.44	0.640	1.60	[1]
$^{Ph_8}DzPzZn$	Pyridine	-1.33 ^[a]	-1.04	-0.72	+0.64	+0.96	0.55 ^[b]	1.36	[2]
$^{Py_8}TPyzPzZn$	Pyridine	-1.38 ^[c]	-0.72	-0.34	-	-	0.55	-	[3,4]
$^{Py_8}TPyzPzMg$	Pyridine	-1.43 ^[d]	-0.79	-0.40	-	-	0.55	-	[3,4]
$^{Cl_8}TPyzPAH_2$	DMSO	-0.89	-0.38	-0.04	-	-	0.465	-	[5]
$(C_{12H_{25}})_8PyzPAH_2$	CH_2Cl_2	-	-	-0.41	-	-	ca. 0.5 ^[e]	-	[6]

^[a] two additional reduction process (Red_4 and Red_5) observed at -1.49 and -1.72 V; ^[b] the value of 0.55 V for Fc^+/Fc couple was reported in followed publication of the same authors as in the original publication values were measured vs SCE; ^[c] two additional reduction processes (Red_4 and Red_5) observed at -1.66 and -1.83 V; ^[d] additional reduction process (Red_4) observed -1.70 V; ^[e] reported vs SCE, a recommended value for Fc^+/Fc is given [7] as the value was reported vs SCE.

Abbreviations for the compounds:

2e = Octaphenyl-octaazaphthalocyaninato erbium(III) acetate

$^{Ph_8}PcLuOAc$ = Octaphenyl-phthalocyaninato lutetium(III) acetate

$^{Ph_8}DzPzZn$ = Tetrakis-2,3-(5,7-diphenyl-1,4-diazepino)porphyrzinato zinc(II)

$^{Py_8}TPyzPzZn$ = Tetrakis-2,3-[5,6-di(2-pyridyl)pyrazino]porphyrzinato zinc(II)

$^{Py_8}TPyzPzMg$ = Tetrakis-2,3-[5,6-di(2-pyridyl)pyrazino]porphyrzinato magnesium(II)

$^{Cl_8}TPyzPAH_2$ = Octachlorotetrapyrazinoporphyrazine

$(C_{12H_{25}})_8PyzPAH_2$ = Octadodecyltetrapyrazinoporphyrazine

Supporting references:

- [1] T.V. Dubinina, K.V. Paramonova, S.A. Trashin, N.E. Borisova, L.G. Tomilova and N.S. Zefirov, *Dalton Transactions*, 2014, 43, 2799-2809.
- [2] M. P. Donzello, D. Dini, G. D'Arcangelo, C. Ercolani, R. Zhan, Z. Ou, P. A. Stuzhin and K. M. Kadish, *Journal of the American Chemical Society*, 2003, 125, 14190-14204.
- [3] C. Bergami, M. P. Donzello, F. Monacelli, C. Ercolani and K. M. Kadish, *Inorg. Chem.*, 2005, 44, 9862-9873.
- [4] M. P. Donzello, Z. Ou, D. Dini, M. Meneghetti, C. Ercolani and K. M. Kadish, *Inorg. Chem.*, 2004, 43, 8637-8648.
- [5] M. Hamdoush, S. S. Ivanova, O. I. Koifman, M. Kos' kina, G. L. Pakhomov and P. A. Stuzhin, *Inorg. Chim. Acta*, 2016, 444, 81-86.
- [6] K. Ohta, T. Watanabe, T. Fujimoto and I. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1989, DOI: 10.1039/C39890001611, 1611-1613.
- [7] I. Noviandri, K.N. Brown, D.S. Fleming, P.T. Gulyas, P.A. Lay, A.F. Masters and L. Phillips. *The Journal of Physical Chemistry B*, 1999, 103, 6713-22.