Supporting Information

Synthesis and characterization of heteroleptic rare earth double-decker complexes involving tetradiazepinoporphyrazine and phthalocyanine macrocycles

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† Dedicated to the memory of the late Professor Larisa Tomilova.

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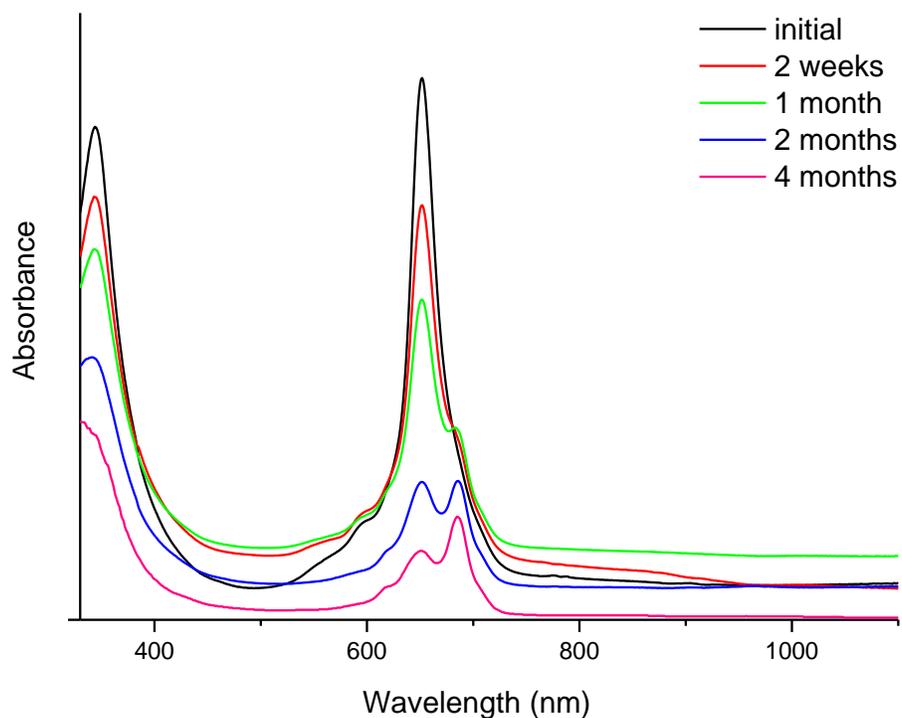
Figure S1 Stability of the reduced non-radical form of (^{Bu}Pc)$_2$La (C = 5·10^{-6} M) in Py studied by UV-Vis spectroscopy.
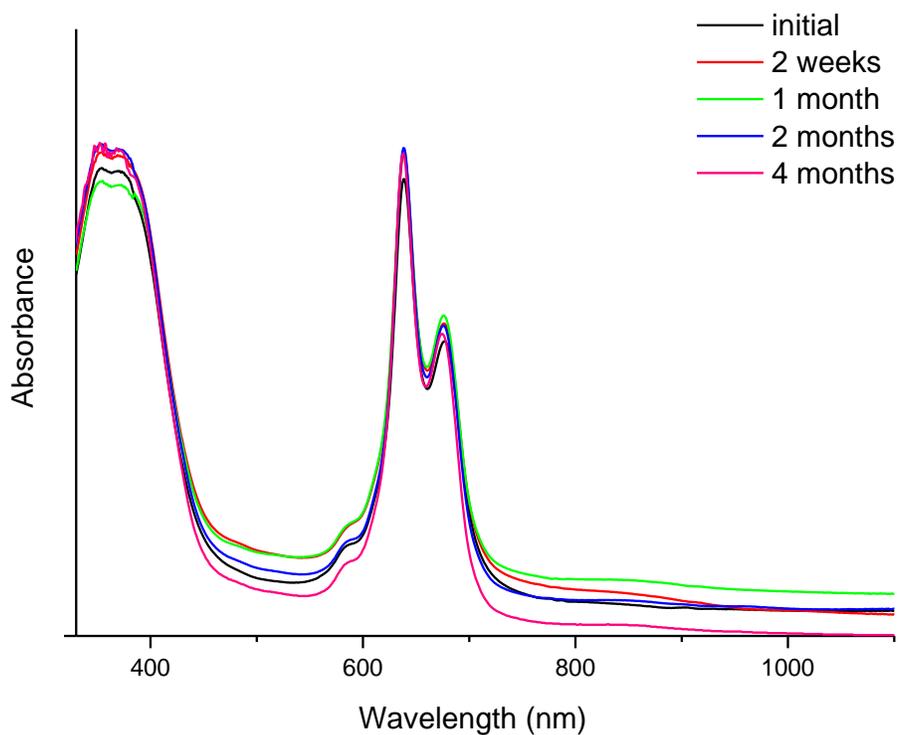
Figure S2 Stability of the reduced non-radical form of (^{tBuPh}DzPz)$_2$La (C = 5·10^{-6} M) in Py studied by UV-Vis spectroscopy.
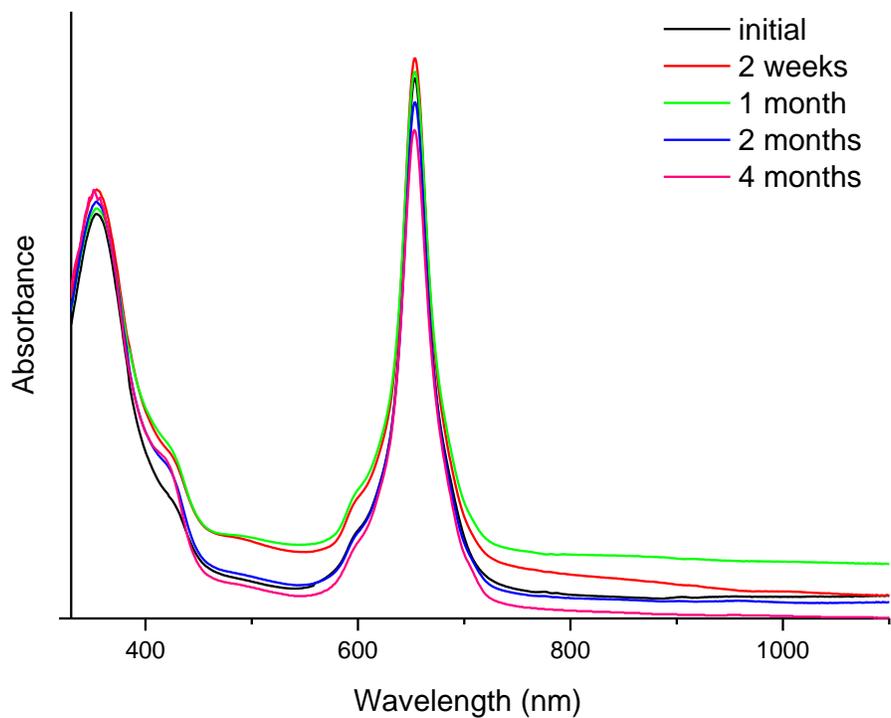
Figure S3 Stability of the reduced non-radical form of (^{tBuPh}DzPz)La(^{Bu}Pc) (C = 6·10^{-6} M) in Py studied by UV-Vis spectroscopy.

High resolution mass spectra
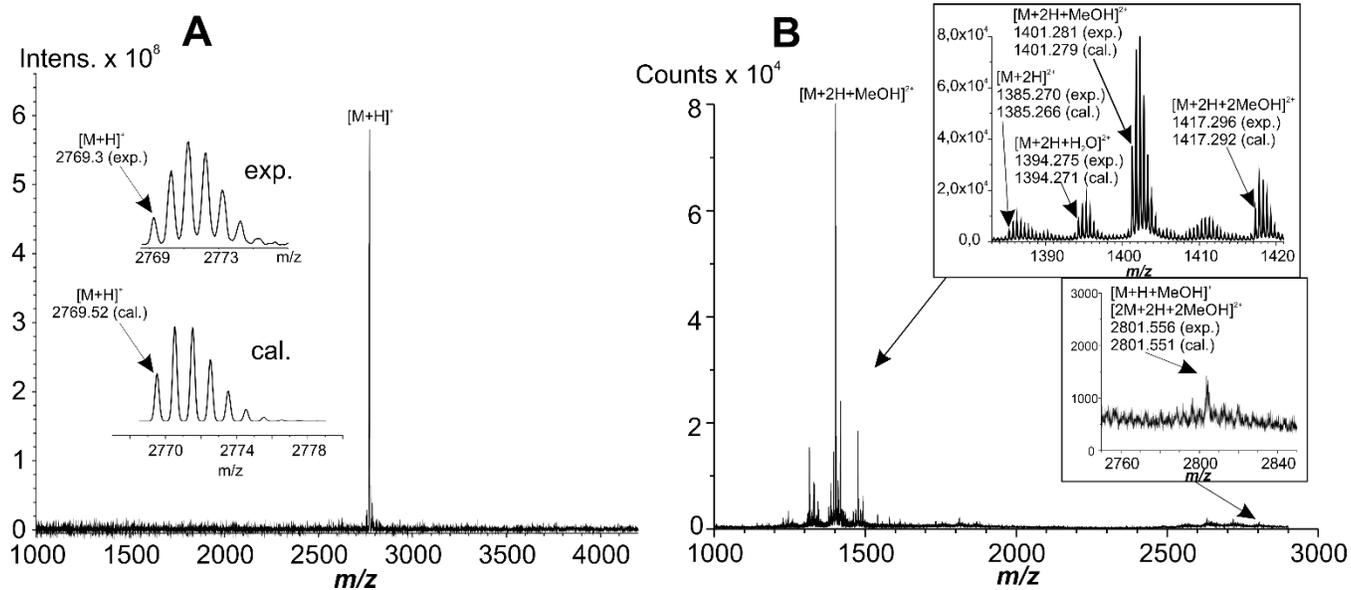
Figure S4 MALDI-TOF (**A**) and ESI-TOF (**B**) mass spectra of **3a**.
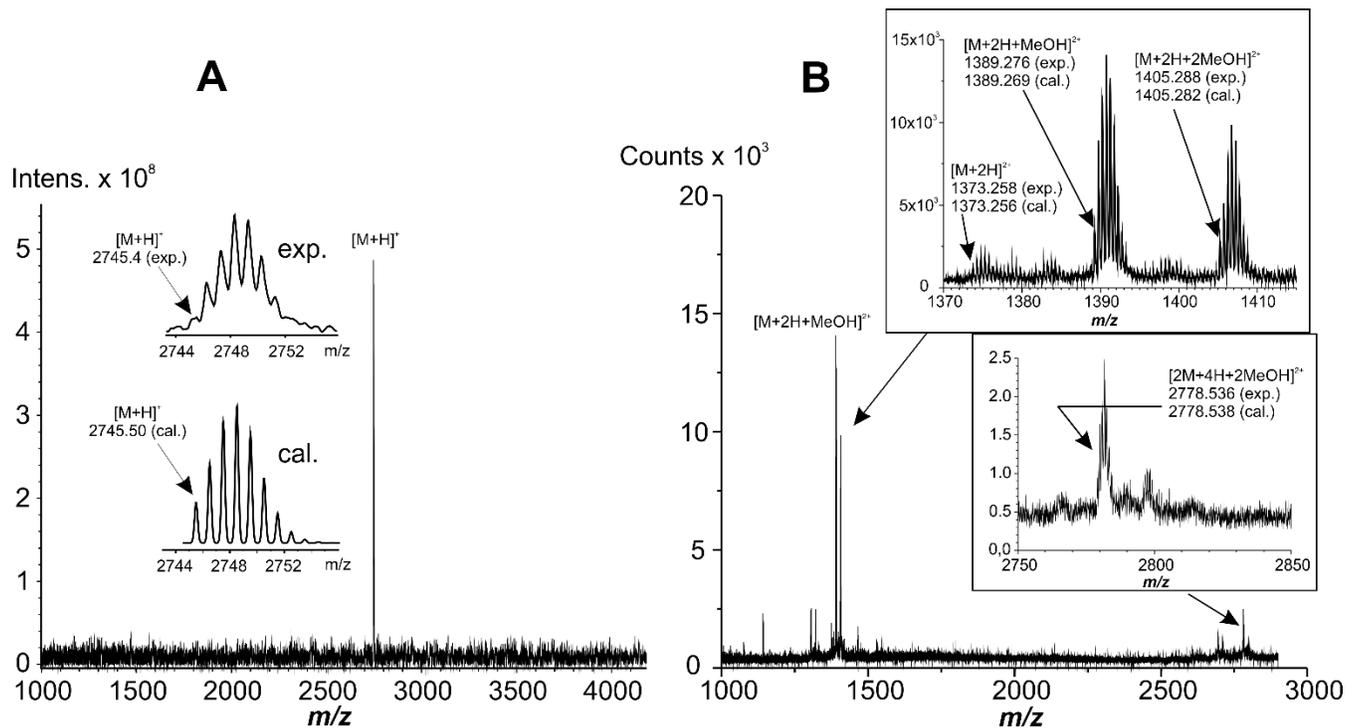
Figure S5 MALDI-TOF (**A**) and ESI-TOF (**B**) mass spectra of **3b**.
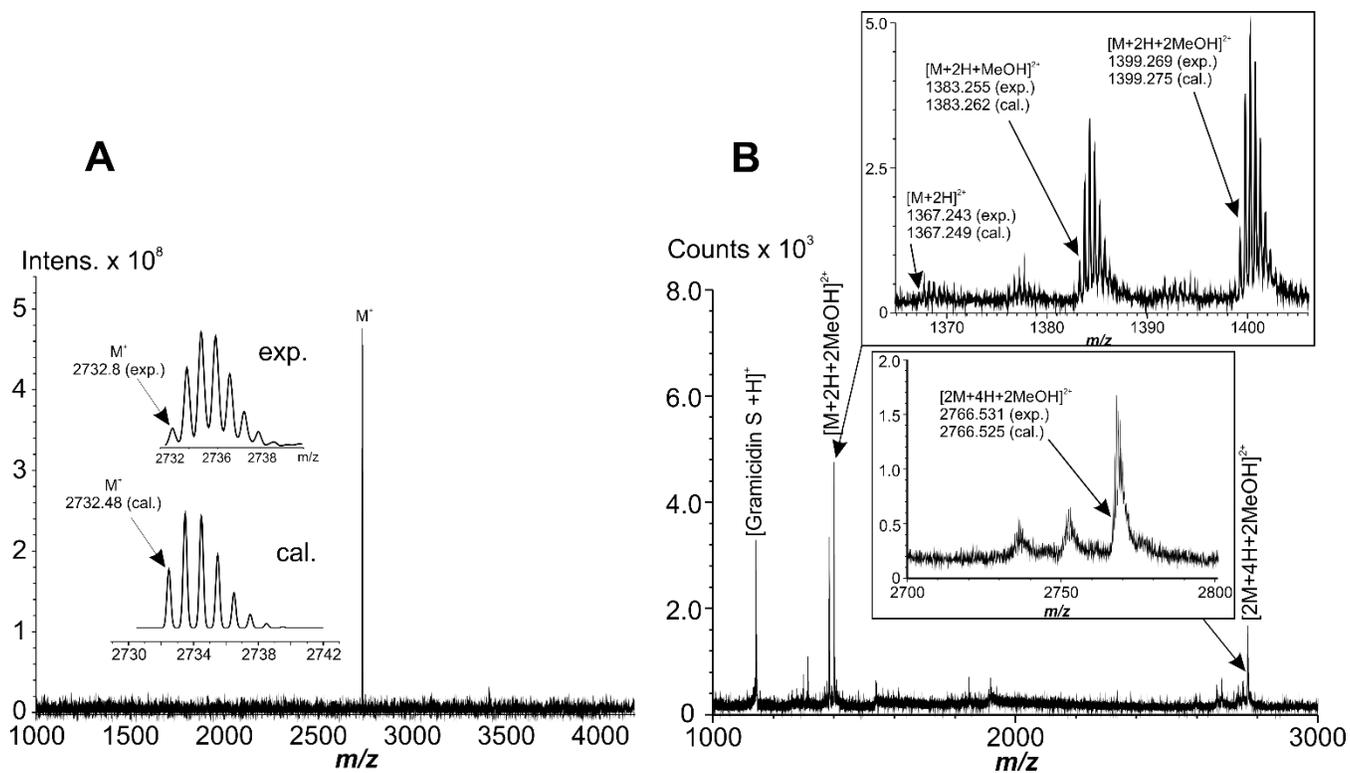
Figure S6 MALDI-TOF (**A**) and ESI-TOF (**B**) mass spectra of **3c**. Gramicidin S applied as reference.

¹H NMR spectra
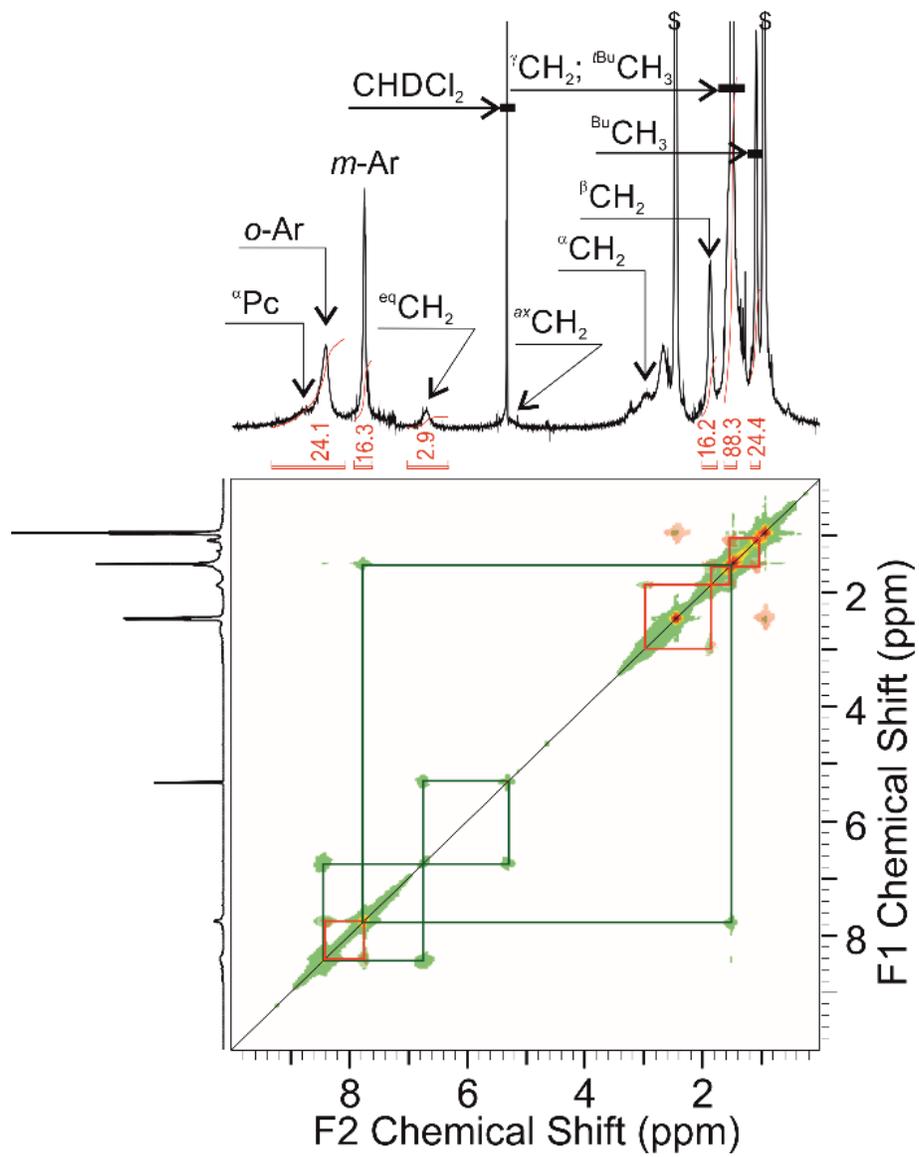
Figure S7 Superimposed ¹H-¹H COSY (red) and ¹H-¹H NOESY (green) spectra of **3a** in CD₂Cl₂. $ Signals of Et₃N.
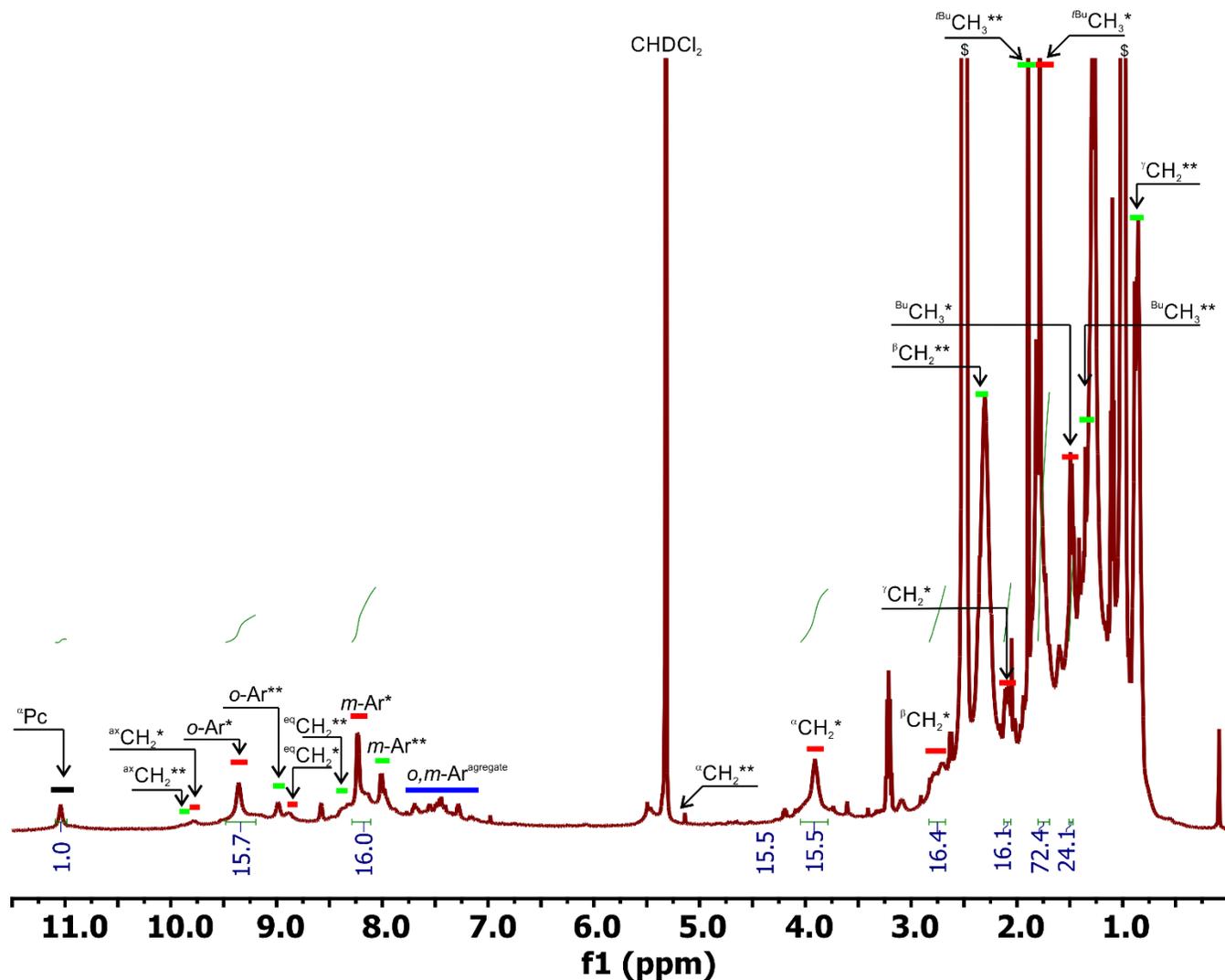
Figure S8 ^{1}H NMR spectrum of **3b** in CD$_2$Cl$_2$. Proton signals of the monomeric (*) and dimeric (**) forms. Signals of Et$_3$N ($).
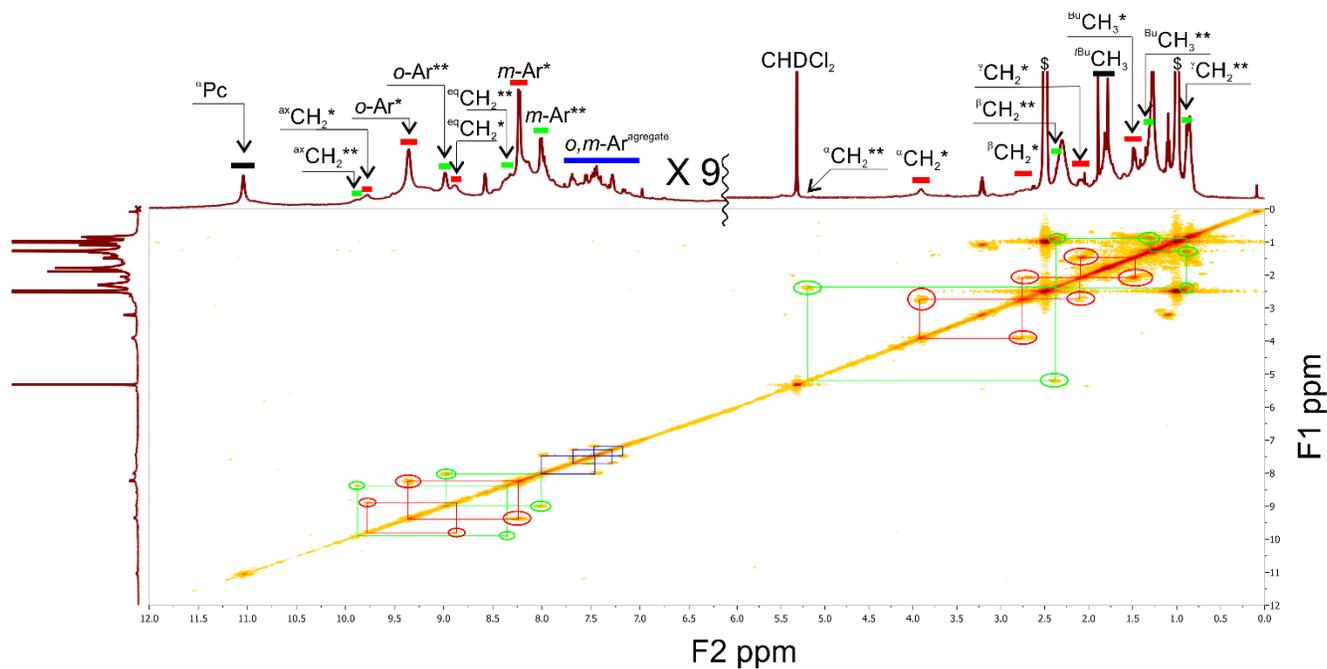
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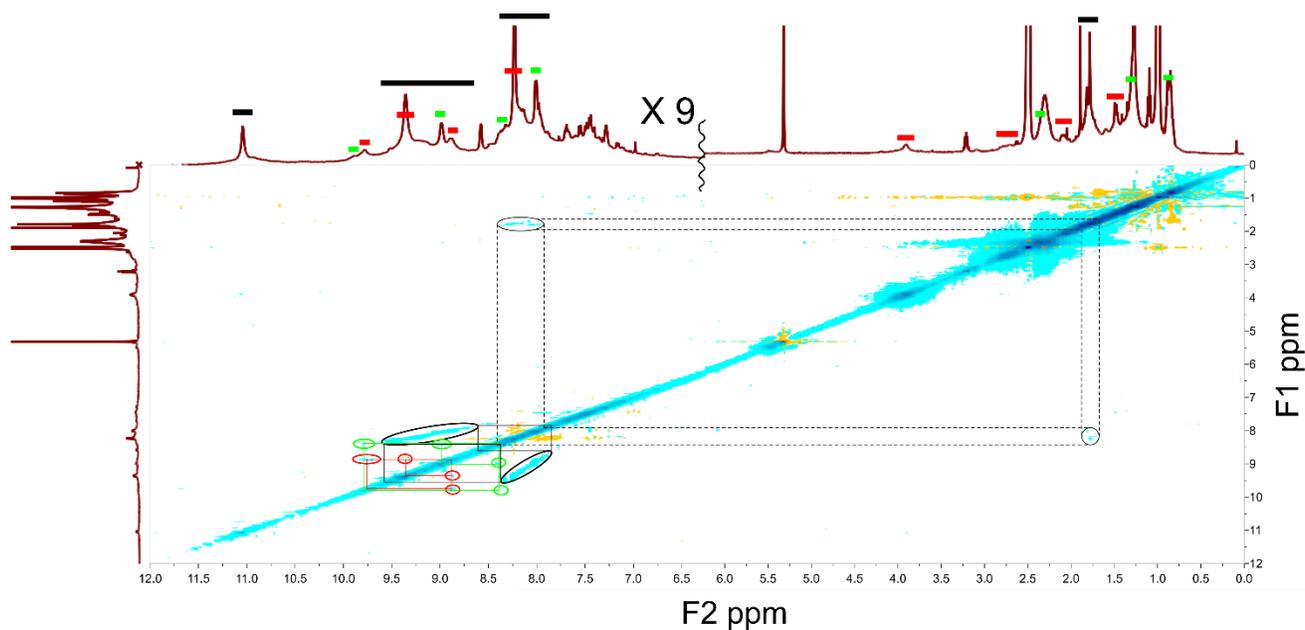
Figure S10 ^{1}H-^{1}H NOESY of **3b** in CD_2Cl_2. Proton signals of the monomeric (red line) and dimeric (green line) forms.
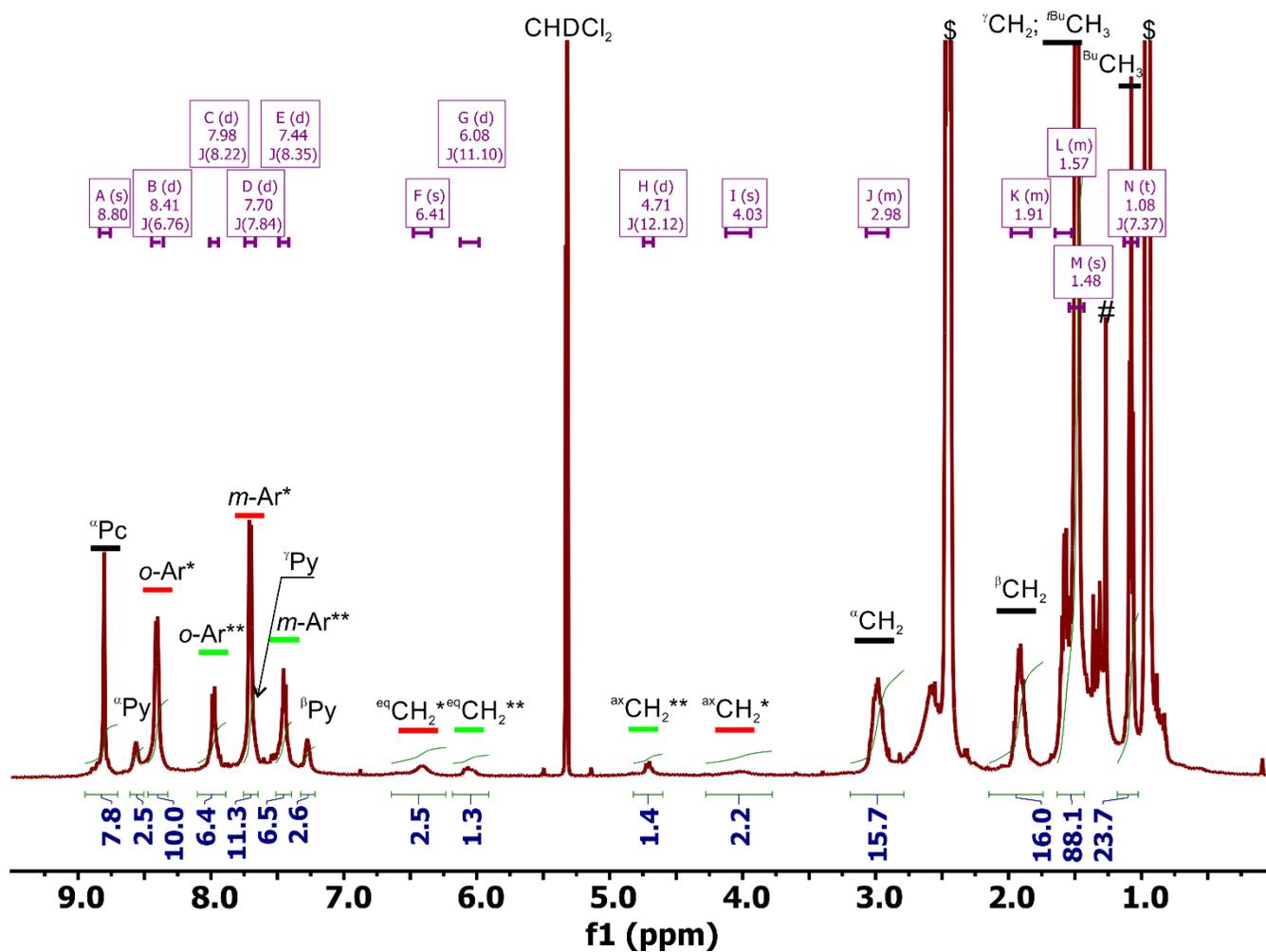
Figure S11 ^{1}H NMR spectrum of **3c** in CD_2Cl_2. Proton signals of the monomeric (*) and dimeric (**) forms. Signals of Et$_3$N ($).
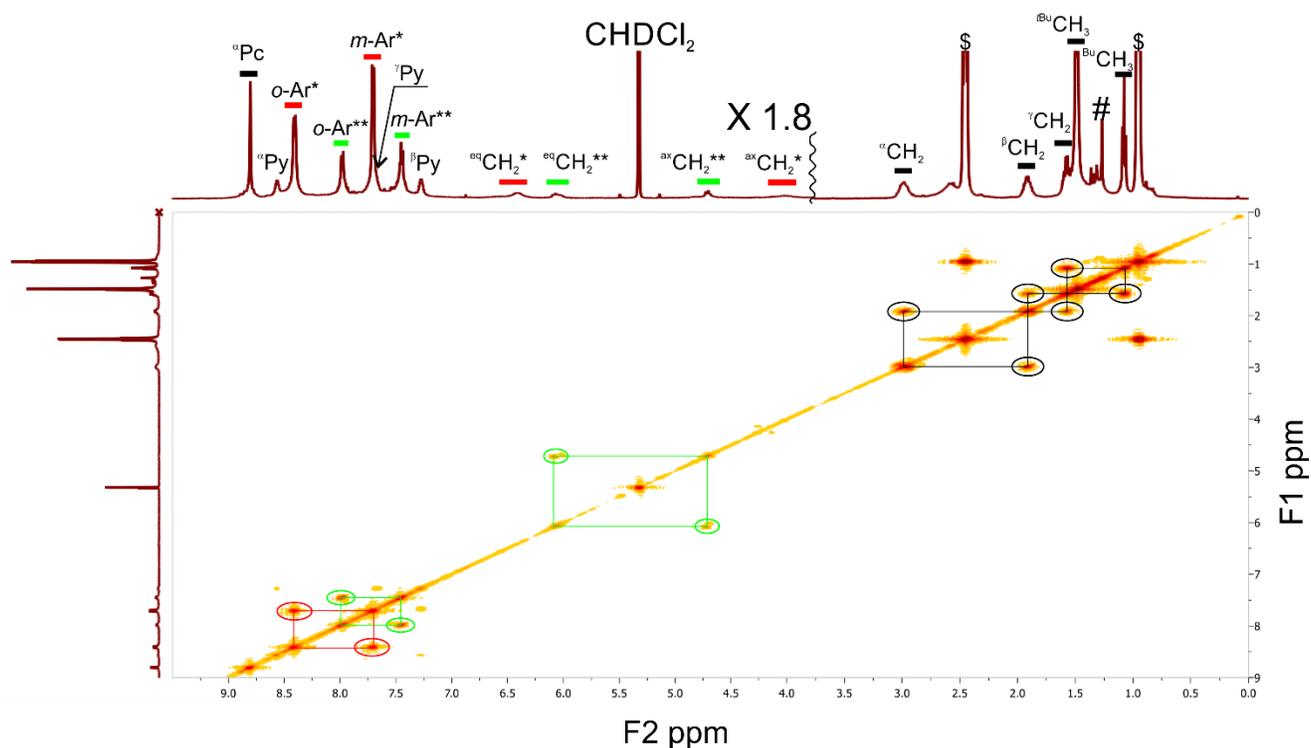
Figure S12 ^{1}H-^{1}H COSY of **3c** in CD_2Cl_2 Proton signals of the monomeric (*) and dimeric (**) forms. Signals of Et_3N ($).
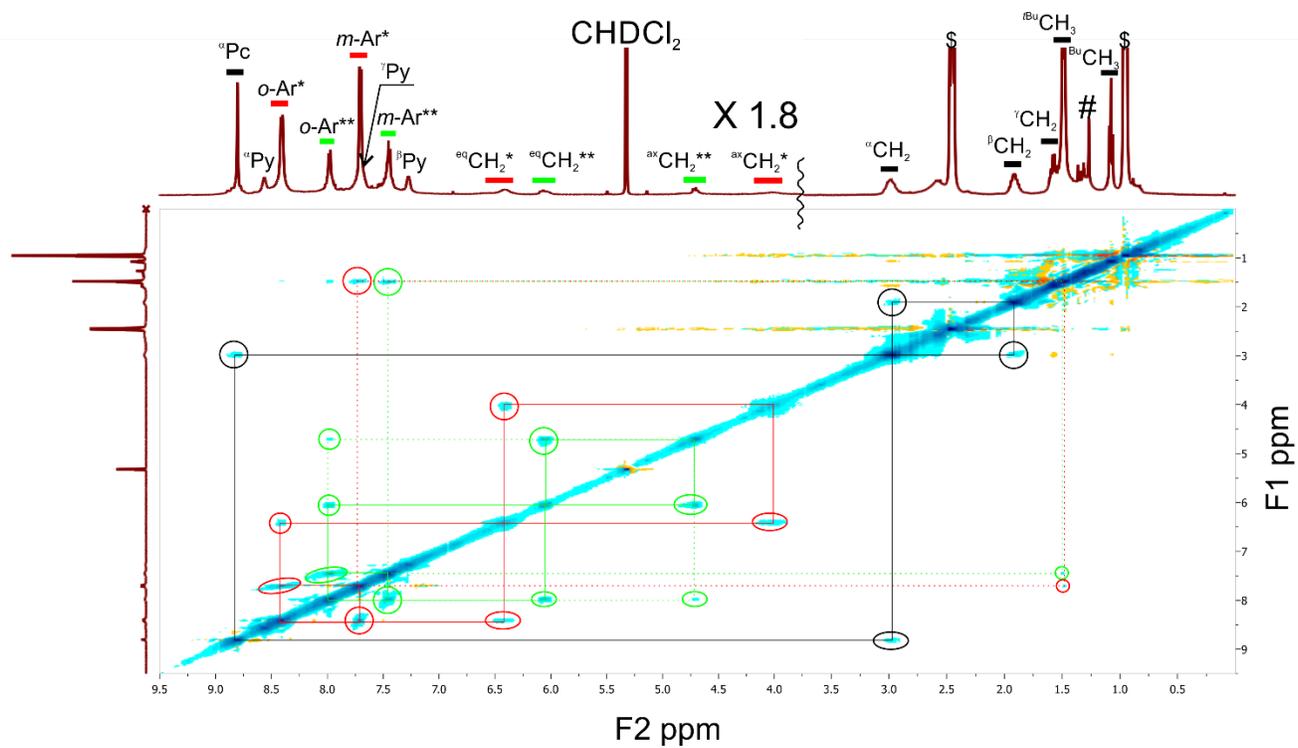
Figure S13 ^{1}H-^{1}H NOESY of **3c** in CD_2Cl_2. Proton signals of the monomeric (*) and dimeric (**) forms. Signals of Et_3N ($).

DFT optimized structure of dimeric sandwich complex

A Upfield shifting of δ_H signals of Alkyl**H**

B Upfield shifting of δ_H signals of Ar**H** and Alkyl**H**

C Upfield shifting of δ_H signals of Ar**H**

Dimerization similarly to the free base

DFT-optimized structures of the ligand dimer
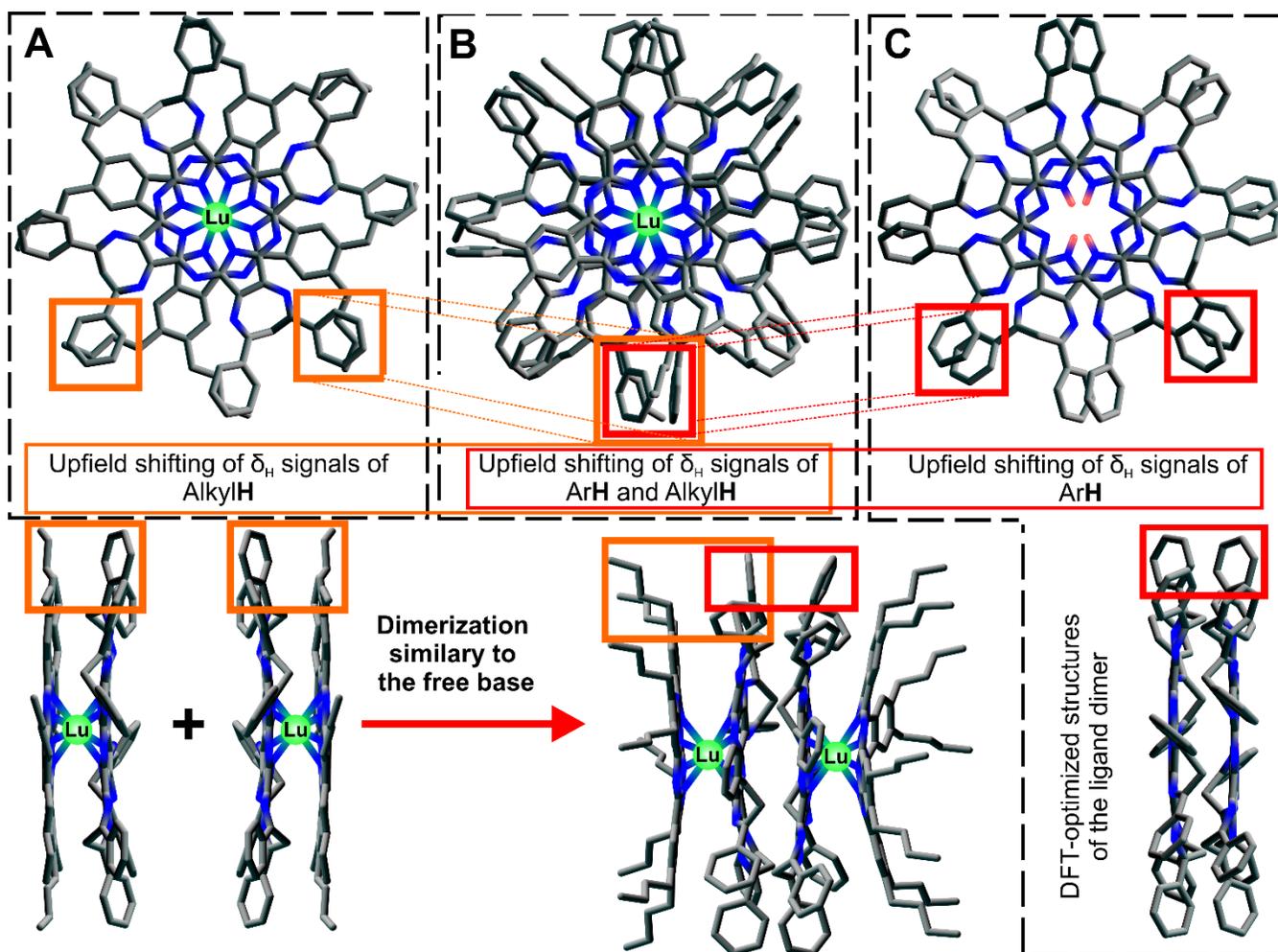
Figure S14 Calculated structures of (^{Ph}DzPz)Lu(^{Bu}Pc) (**A**), dimer {(^{Ph}DzPz)Lu(^{Bu}Pc)}$_2$ (**B**) and dimeric free base {^{Ph}DzPzH$_2$}$_2$ (**C**)[1].

UV-Vis/NIR, MCD spectroscopy
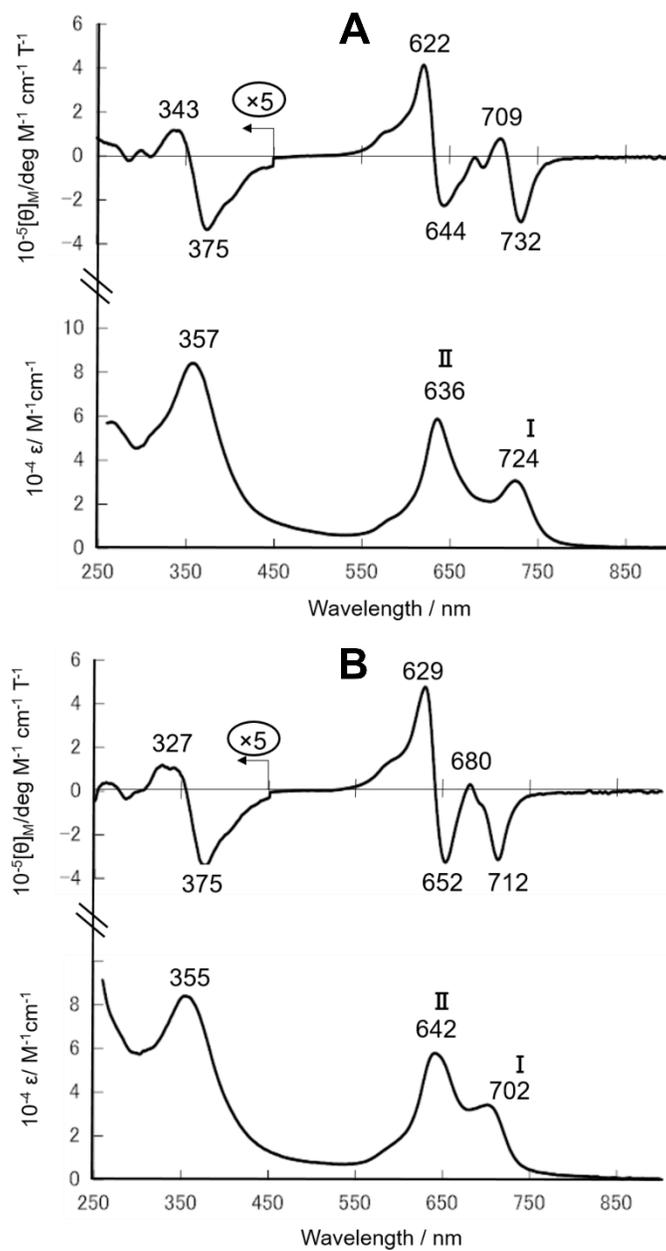
Figure S15 Electronic absorption and MCD spectra of the reduced non-radical forms of **3a** $(1.7 \cdot 10^{-5}$ M) (**A**) and **3b** $(1.2 \cdot 10^{-5}$ M) (**B**) in DCM.

Table S1 UV-Vis/NIR data for homoleptic $(^{Bu}Pc)_2Ln$ and $(^{tBuPh}DzPz)_2Ln$, and heteroleptic $(^{Ph}DzPz)Ln(^{Bu}Pc)$ complexes in DCM solution

Compd	λ_{max}, nm (log ε)							Ref.
	Reduced state			Neutral state				
	B(Soret)	Q_1	Q_2	B(Soret)	Q	RV	IV[a]	
$(^{Bu}Pc)_2Lu^b$	345	637	711	351	675	930	-	[2]
$(^{tBuPh}DzPz)Lu(^{Bu}Pc)$	357(5.06)	636(4.96)	724(4.67)	365(5.06)	668(4.98)	897(3.8)	1214sh, 1306	tw
$(^{tBuPh}DzPz)_2Lu$	369(5.09)	620(4.86)	722(4.78)	377	653(5.00)	865(3.91)	1216sh, 1305	[1]
$(^{Bu}Pc)_2Eu^b$	347	651	698	357	691	-	-	[2]
$(^{tBuPh}DzPz)Eu(^{Bu}Pc)$	355(5.19)	642(5.06)	702(4.83)	356(5.20)	676(4.99)	879(3.73)	1347sh 1473	tw
$(^{tBuPh}DzPz)_2Eu$	368(5.20)	631(5.03)	699(4.89)	380	660(5.13)	853	1195sh, 1376sh, 1476	[1]
$(^{Bu}Pc)_2La$		652	-	-	-	-	-	tw
$(^{tBuPh}DzPz)La(^{Bu}Pc)$	354(5.09)	654(5.20)	-	-	-	-	-	tw
$(^{tBuPh}DzPz)_2La$	373(5.25)	638(5.31)	674(5.02)	365	671(5.25)	839	1780	[1]

[a]The spectra were recorded in CCl$_4$. [b]The spectra were recorded in *o*-DCB.

Electrochemistry
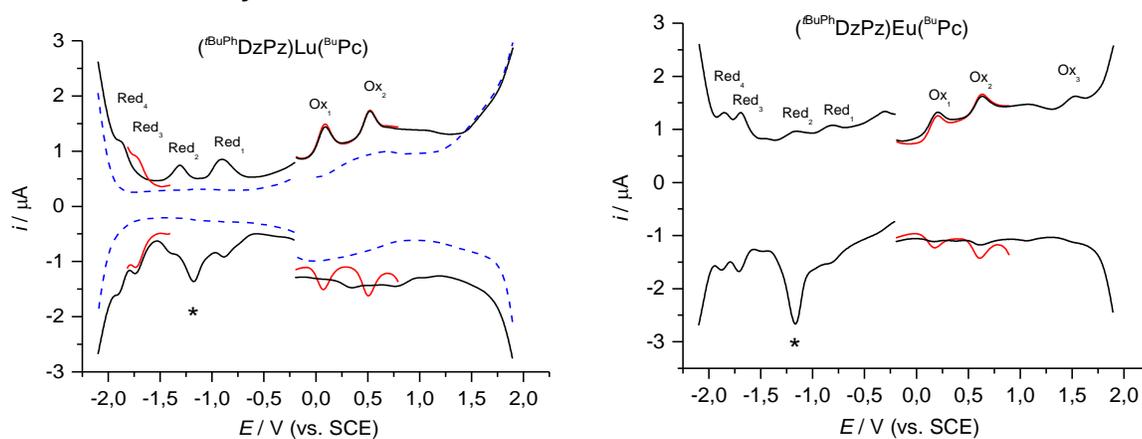
Figure S16 SWVA of (^{tBuPh}DzPz)Ln(^{Bu}Pc) (0.24 mM (Ln = Lu) or 0.36 mM (Ln = Eu), o-DCB, 0.1 M TBABF$_4$, frequency of 10 Hz; amplitude of 50 mV; step potential of 5 mV). E$_{1/2}$(Fc$^+$/Fc) = 0.548 V. * - irregular irreversible peak, probably, owing to traces of contaminants in the samples.
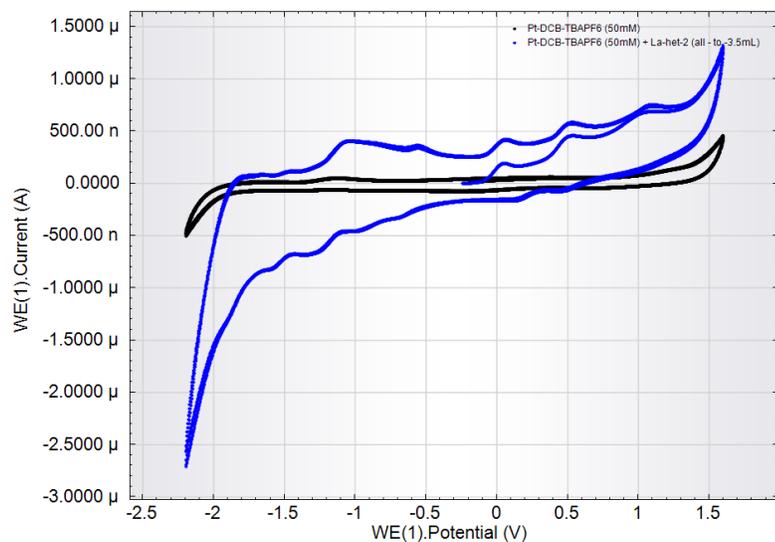
Figure S17 CV of Pt 1 mm electrode in DCB+TBAPF$_6$ soln (3.5 mL+68 mg ~ 50 mM = BG) – black points. The blue curve was measured after complete dissolution of (^{tBuPh}DzPz)La(^{Bu}Pc) portion in 3.5 mL BG soln. under argon. Potentials are given vs Ag/Ag$^+$(10 mM, AN), E$_{1/2}$(Fc/Fc$^+$) vs Ag/Ag$^+$ ~ 0.27V.
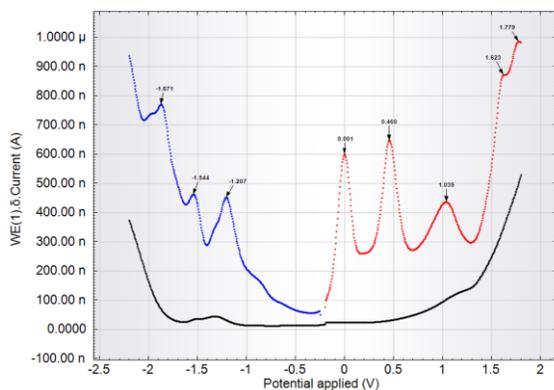
Figure S18 SWV of Pt 1mm electrode in DCB+TBAPF$_6$ soln (3.5 mL+68 mg ~ 50 mM = BG) – black points. Blue/Red curves (from open circuit potential to cathodic and anodic direction) were measured after the CV test (Figure S16). Potentials are given vs Ag/Ag$^+$(10 mM, AN).
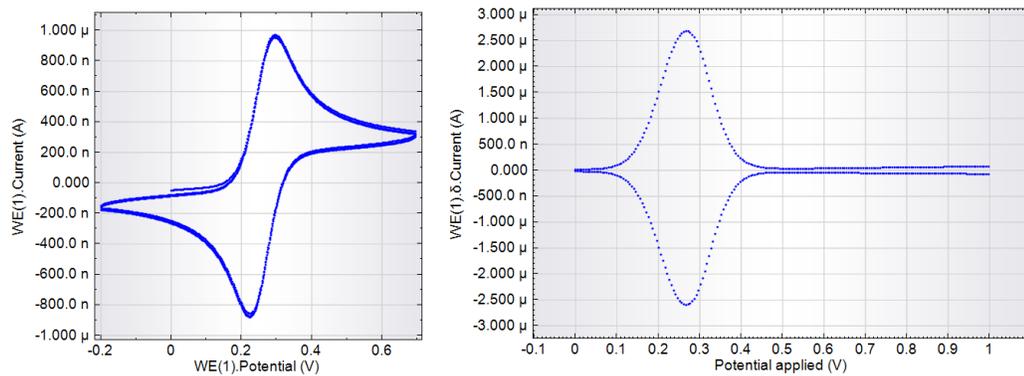
Figure S19 CV (left) and SWV (right) of Fc/Fc$^+$ (~1 mM) couple in 0.1 M TBAPF$_6$ DCB solution. Measured vs Ag/Ag$^+$ (0.01 M AN) RE, WE = 1 mm diam. Pt. E$_{1/2}$(Fc/Fc$^+$) vs Ag/Ag$^+$ ~ 0.27V.
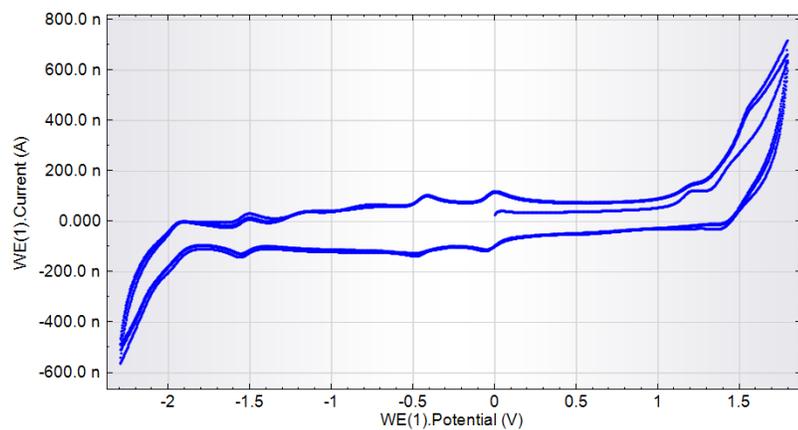
Figure S20 CV of (^{Bu}Pc)$_2$Lu sample (2.1 mg in 10 mL DCB) in 0.1 M TBAPF$_6$ DCB solution. Measured vs Ag/Ag$^+$ (0.01 M AN) RE, WE = 1mm diam. Pt
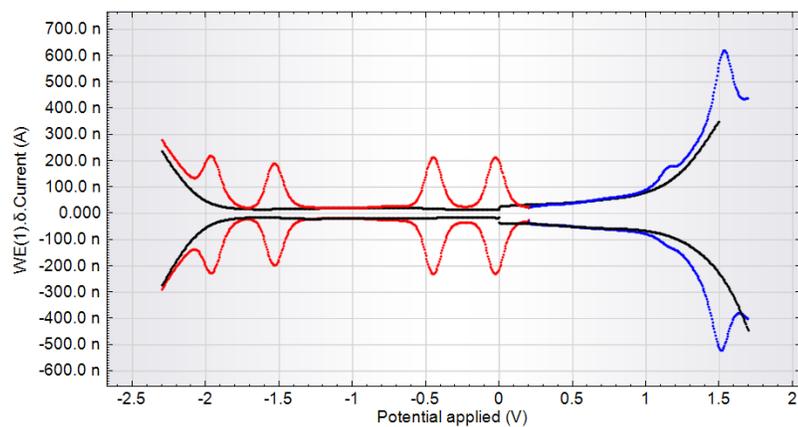
Figure S21 SWV of (^{Bu}Pc)$_2$Lu sample (2.1 mg in 10 mL DCB) in 0.1 M TBAPF$_6$ DCB solution. Measured vs Ag/Ag$^+$ (0.01 M AN) RE, WE = 1 mm diam. Pt

S13
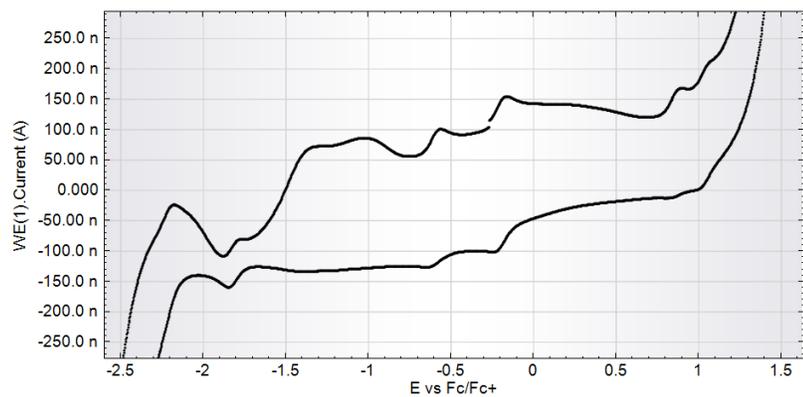
Figure S22 SWV of (^{Bu}Pc)$_2$Eu sample (1.54 mg in 10 mL DCB) in 0.1 M TBAPF$_6$ DCB solution. Measured vs Ag/Ag$^+$ (0.01M AN) RE, converted to Fc/Fc$^+$ scale. WE: Pt 1mm diam.
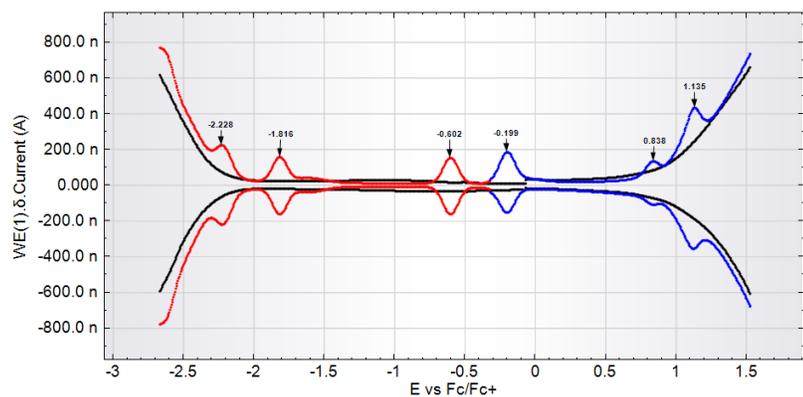
Figure S23 SWV of (^{Bu}Pc)$_2$Eu sample (1.54 mg in 10 mL DCB) in 0.1M TBAPF$_6$ DCB solution. Measured vs Ag/Ag$^+$ (0.01M AN) RE, converted to Fc/Fc$^+$ scale. WE: Pt 1 mm diam.

DFT calculation details

Table S2 Optimized geometry of (****PhDzPz)Lu(BuPc)

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CARTESIAN COORDINATES (ANGSTROEM)


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H	5.921147000	9.564892000	−1.134572000	H	9.221702000	−2.062039000	−3.105388000
H	−5.794892000	−7.189720000	−0.460462000	H	10.611336000	−4.058883000	−2.460659000
H	−5.921131000	−9.565060000	−1.134213000	H	9.564954000	−5.921188000	−1.135153000
H	−4.059623000	−10.611132000	−2.461087000	H	7.189489000	−5.795320000	−0.461794000
H	−2.063192000	−9.221330000	−3.106735000	H	5.335008000	−5.504943000	0.269968000
H	−1.959658000	−6.791284000	−2.440834000	H	4.096339000	−4.226220000	0.575589000
H	−6.982571000	−1.621637000	−1.961796000	H	5.894628000	−7.053577000	−1.254756000
H	−9.401518000	−1.706363000	−2.676056000	H	5.995022000	−9.429669000	−1.968495000
H	−10.627862000	−3.903004000	−2.678054000	H	3.902910000	−10.627895000	−2.678515000
H	−9.430007000	−5.994933000	−1.966791000	H	1.706074000	−9.401915000	−2.675468000
H	−7.053967000	−5.894588000	−1.253144000	N	4.766530000	−2.637769000	−1.407920000
H	−7.189540000	5.795178000	−0.462083000	N	2.533490000	−4.811604000	−1.444468000
H	−9.564939000	5.921068000	−1.135686000	Lu	−0.000024000	−0.000033000	0.374799000
H	−10.611229000	4.058708000	−2.461191000	C	−0.721536000	6.610014000	1.723599000
H	−9.221571000	2.061796000	−3.105661000	C	0.712953000	6.613388000	1.716576000
N	1.408194000	1.381302000	−0.962233000	C	−1.418312000	5.387931000	1.833919000
N	0.034793000	3.377911000	−1.183851000	C	1.419829000	5.395237000	1.818109000
N	1.381348000	−1.408282000	−0.962173000	C	−1.487568000	7.911382000	1.569890000
N	3.377963000	−0.034865000	−1.183797000	C	−3.004412000	7.832163000	1.770367000
N	−1.408193000	−1.381441000	−0.962233000	C	−3.715614000	9.169506000	1.528811000
N	−3.377969000	0.034704000	−1.183786000	C	−5.226491000	9.088666000	1.771634000
N	−0.034791000	−3.378067000	−1.183797000	C	1.466762000	7.920303000	1.559800000

C	2.951554000	7.899185000	1.942336000	H	8.262669000	-1.370480000	0.499852000
C	3.609353000	9.281405000	1.838208000	H	8.710555000	-0.962352000	2.162482000
C	5.082330000	9.279228000	2.260456000	H	7.508022000	-3.060105000	2.982134000
H	-2.516086000	5.359958000	1.848854000	H	7.193700000	-3.505253000	1.283089000
H	2.518759000	5.376257000	1.817166000	H	9.643338000	-3.521560000	0.788113000
H	-1.076128000	8.669513000	2.277349000	H	10.008696000	-3.043279000	2.467392000
H	-1.279724000	8.327554000	0.553966000	H	8.570699000	-5.676726000	1.639460000
H	-3.436614000	7.081153000	1.073557000	H	10.286457000	-5.542055000	2.153160000
H	-3.224431000	7.466256000	2.801324000	H	8.965276000	-5.199630000	3.322807000
H	-3.270863000	9.954418000	2.185865000	C	0.721576000	-6.609963000	1.723864000
H	-3.523991000	9.493457000	0.479849000	C	-0.712918000	-6.613386000	1.716987000
H	-5.691128000	8.315751000	1.118172000	C	1.418304000	-5.387849000	1.834066000
H	-5.454741000	8.816787000	2.827521000	C	-1.419836000	-5.395256000	1.818462000
H	-5.730284000	10.056430000	1.553611000	C	1.487650000	-7.911318000	1.570250000
H	1.370549000	8.262510000	0.499286000	C	3.004520000	-7.831954000	1.770461000
H	0.962189000	8.710713000	2.161768000	C	3.715819000	-9.169251000	1.528950000
H	3.059860000	7.508307000	2.981915000	C	5.226723000	-9.088218000	1.771547000
H	3.505289000	7.193872000	1.282963000	C	-1.466676000	-7.920344000	1.560349000
H	3.521521000	9.643435000	0.787752000	C	-2.951439000	-7.899266000	1.942969000
H	3.042839000	10.008952000	2.466876000	C	-3.609236000	-9.281483000	1.838806000
H	5.676633000	8.571128000	1.639745000	C	-5.082184000	-9.279331000	2.261162000
H	5.541647000	10.286950000	2.153140000	H	2.516077000	-5.359796000	1.848950000
H	5.199107000	8.965919000	3.322915000	H	-2.518769000	-5.376344000	1.817572000
C	6.609976000	0.721491000	1.723915000	H	1.076368000	-8.669352000	2.277907000
C	6.613328000	-0.713002000	1.716908000	H	1.279657000	-8.327677000	0.554434000
C	5.387898000	1.418285000	1.834165000	H	3.436531000	-7.080990000	1.073483000
C	5.395158000	-1.419858000	1.818313000	H	3.224677000	-7.465897000	2.801335000
C	7.911387000	1.487494000	1.570424000	H	3.271247000	-9.954140000	2.186155000
C	7.832142000	3.004336000	1.770905000	H	3.524085000	-9.493340000	0.480051000
C	9.169483000	3.715585000	1.529480000	H	5.691170000	-8.315308000	1.117945000
C	9.088566000	5.226441000	1.772422000	H	5.455096000	-8.816226000	2.827378000
C	7.920252000	-1.466828000	1.560284000	H	5.730598000	-10.055939000	1.553526000
C	7.899000000	-2.951671000	1.942605000	H	-1.370499000	-8.262628000	0.499857000
C	9.281169000	-3.609577000	1.838506000	H	-0.962019000	-8.710681000	2.162345000
C	9.278770000	-5.082651000	2.260424000	H	-3.059704000	-7.508448000	2.982576000
H	5.359920000	2.516057000	1.849074000	H	-3.505211000	-7.193913000	1.283668000
H	5.376163000	-2.518789000	1.817329000	H	-3.521482000	-9.643460000	0.788325000
H	8.669391000	1.076019000	2.278001000	H	-3.042676000	-10.009065000	2.467393000
H	8.327718000	1.279651000	0.554566000	H	-5.676527000	-8.571200000	1.640526000
H	7.081187000	3.436517000	1.074021000	H	-5.541509000	-10.287047000	2.153827000
H	7.466139000	3.224345000	2.801829000	H	-5.198880000	-8.966073000	3.323645000
H	9.954370000	3.270802000	2.186544000	C	-6.610067000	-0.721308000	1.723846000
H	9.493506000	3.524069000	0.480521000	C	-6.613378000	0.713187000	1.716960000
H	8.315676000	5.691085000	1.118937000	C	-5.388026000	-1.418167000	1.834095000
H	8.816607000	5.454589000	2.828311000	C	-5.395165000	1.419972000	1.818360000
H	10.056318000	5.730298000	1.554500000	C	-7.911493000	-1.487272000	1.570404000

C	−7.832393000	−3.004069000	1.771304000	H	−9.494007000	−3.523807000	0.481247000
C	−9.169874000	−3.715169000	1.530201000	H	−8.316498000	−5.690913000	1.119925000
C	−9.089196000	−5.225987000	1.773434000	H	−8.817103000	−5.453967000	2.829326000
C	−7.920238000	1.467104000	1.560273000	H	−10.057084000	−5.729701000	1.555787000
C	−7.898898000	2.951935000	1.942625000	H	−8.262608000	1.370793000	0.499823000
C	−9.281008000	3.609952000	1.838448000	H	−8.710612000	0.962673000	2.162417000
C	−9.278513000	5.083024000	2.260375000	H	−7.507987000	3.060331000	2.982182000
H	−5.360150000	−2.515947000	1.848942000	H	−7.193504000	3.505472000	1.283171000
H	−5.376093000	2.518902000	1.817516000	H	−9.643135000	3.521967000	0.788038000
H	−8.669566000	−1.075587000	2.277779000	H	−10.008619000	3.043709000	2.467287000
H	−8.327695000	−1.279670000	0.554438000	H	−8.570375000	5.677052000	1.639443000
H	−7.081560000	−3.436576000	1.074487000	H	−10.286161000	5.542507000	2.153075000
H	−7.466331000	−3.223821000	2.802263000	H	−8.965052000	5.199974000	3.322771000
H	−9.954596000	−3.270117000	2.187282000				

Table S3 Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis for **(PhDzPz)Lu(BuPc)**

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    Threshold for printing:   0.25 kcal/mol
    (Intermolecular threshold: 0.03 kcal/mol)
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		E(2)	E(j)-E(i)	F(i,j)
Donor NBO (i)	Acceptor NBO (j)	kcal/mol	a.u.	a.u.

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=============================================================================================
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from unit 1(BuPc) to unit 2(PhDzPz)

π-π donor interaction

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
BD (2) C 4 - N 18	/***. BD*(2) C 27 - N 127	0.50	0.26	0.015
BD (2) C 7 - N 17	/***. BD*(2) C 29 - N 123	0.38	0.25	0.013
BD (2) C 8 - N 20	/***. BD*(2) C 32 - N 122	0.32	0.24	0.012
BD (2) C 11 - N 19	/***. BD*(2) C 34 - N 125	0.38	0.25	0.013
BD (2) C 12 - N 23	/***. BD*(2) C 38 - N 124	0.32	0.24	0.012
BD (2) C 15 - N 21	/***. BD*(2) C 40 - N 128	0.38	0.25	0.013
LP*(1) C 16	/***. BD*(2) C 44 - N 126	1.79	0.09	0.019
BD*(2) C 7 - N 17	/***. BD*(2) C 29 - N 123	2.80	0.02	0.015
BD*(2) C 11 - N 19	/***. BD*(2) C 34 - N 125	2.80	0.02	0.015
BD*(2) C 15 - N 21	/***. BD*(2) C 40 - N 128	2.80	0.02	0.015

hydrogen bonds between N_{meso} to C–H_{ax}

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
LP (1) N 18	/***. BD*(1) C 58 - H 103	0.53	0.63	0.023
LP (1) N 20	/***. BD*(1) C 63 - H 105	0.53	0.63	0.023
LP (1) N 22	/***. BD*(1) C 53 - H 101	0.53	0.63	0.023
LP (1) N 23	/***. BD*(1) C 143 - H 158	0.52	0.63	0.023

from unit 2(PhDzPz) to unit 1(BuPc)

π-π donor interaction

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
BD (2) C 27 - N 127	/***. BD*(2) C 1 - C 265	0.13	0.30	0.008
BD (2) C 27 - N 127	/***. BD*(2) C 4 - N 18	0.52	0.25	0.015
BD (2) C 34 - N 125	/***. BD*(2) C 10 - C 200	0.13	0.30	0.008
BD (2) C 34 - N 125	/***. BD*(2) C 11 - N 19	0.35	0.23	0.012
BD (2) C 38 - N 124	/***. BD*(2) C 12 - N 23	0.43	0.25	0.013
BD (2) C 40 - N 128	/***. BD*(2) C 14 - C 232	0.13	0.30	0.008
BD (2) C 40 - N 128	/***. BD*(2) C 15 - N 21	0.35	0.23	0.012
BD (2) C 44 - N 126	/558. LP*(1) C 16	1.18	0.15	0.019
LP*(1) C 46	/***. BD*(2) C 3 - N 22	1.52	0.10	0.020
BD*(2) C 32 - N 122	/***. BD*(2) C 8 - N 20	3.63	0.02	0.015
BD*(2) C 38 - N 124	/***. BD*(2) C 12 - N 23	3.63	0.02	0.015