Supporting Information:

Isomeric Separation in Donor-Acceptor Systems of Pd(II) and Pt(II) and a Combined Structural, Electrochemical and Spectroelectrochemical Study

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Table S1: The comparison of averaged experimental and DFT calculated selected bond lengths (Å) and angles (°) for **1b** and **2b**.

	M = Pd		M = Pt	
Bond lengths	Exp.	Calc.	Exp.	Calc.
M-O1	1.976(5)	1.990	1.994(4)	1.980
M-O2	1.955(5)	1.960	1.966(5)	1.951
M-N1	2.017(6)	2.016	1.983(5)	1.961
M-N2	1.976(6)	1.981	1.966(5)	1.959
N1-N3	1.286(9)	1.288	1.307(7)	1.297
N3-C15	1.408(10)	1.359	1.390(8)	1.352
N2-C15	1.351(10)	1.358		1.362
C1-O1	1.351(9)	1.331	1.360(7)	1.334
C2-O2	1.331(9)	1.329	1.353(7)	1.332
C1-C2	1.422(10)	1.419	1.416(8)	1.414
C2-C3	1.396(11)	1.394	1.379(9)	1.392
C3-C4	1.395(11)	1.392	1.395(8)	1.392
C4-C5	1.388(10)	1.407	1.396(9)	1.407
C5-C6	1.390(10)	1.396	1.385(9)	1.397
C6-C1	1.394(10)	1.413	1.405(5)	1.411
Bond angles				
N(1)-M-N(2)	78.3(2)	78.1	78.1(2)	78.0
N(1)-M-O(1)	103.3(2)	104.8	103.4(2)	103.6
N(2)-M-O(2)	94.7(2)	94.6	95.6(2)	96.7
O(1)-M-O(2)	83.6(2)	82.5	82.8(8)	81.7

Table S2: TD-DFT (PBE0/PCM-CH_2Cl_2) calculated lowest singlet excitation energies (eV) for **1b**^{n} with oscillator strengths larger than 0.005. Shapes of MOs involved in excitations are depicted in Figs. S3 – S5.

n	State	Main contributing excitations (%)	Transition energy[a] eV (nm)	Osc. Str.
0	b^1A	97 (HOMO → LUMO)	1.11 (1118)	0.211
	c^1A	96 (HOMO-1 → LUMO)	1.83 (678)	0.011
	d^1A	55 (HOMO → LUMO+2)	2.87 (431)	0.025
	e^1A	40 (HOMO → LUMO+1); 41 (HOMO-4 → LUMO)	2.95 (421)	0.127
	f^1A	50 (HOMO-1 → LUMO+1)	3.22 (385)	0.075
	g^1A	mixed	3.25 (381)	0.264
1	b^2A	75 (βHOMO → βLUMO)	1.39 (892)	0.007
	c^2A	90 (αHOMO → αLUMO)	1.64 (754)	0.031
	d^2A	mixed	2.88 (431)	0.023
	e^2A	mixed	2.96 (419)	0.222
	f^2A	mixed	3.05 (407)	0.092
	g^2A	mixed	3.13 (395)	0.084
	i^2A	mixed	3.26 (381)	0.045
	j^2A	mixed	3.26 (380)	0.336
-1	b^2A	98(βHOMO → βLUMO)	1.40 (833)	0.056
	c^2A	70 (βHOMO-1 → βLUMO)	2.35 (528)	0.062
	d^2A	92 (αHOMO → αLUMO)	2.44 (509)	0.027
	e^2A	80 (βHOMO-2 → βLUMO)	2.66 (466)	0.096
	f^2A	mixed	3.23 (384)	0.035
	g^2A	mixed	3.27 (379)	0.044
	j^2A	mixed	3.42 (362)	0.190

[a] Wavelength in parethesis

Table S3: TD-DFT (PBE0/PCM-CH_2Cl_2) calculated lowest singlet excitation energies (eV) for **2b**^{n} with oscillator strengths larger than 0.005. Shapes of MOs involved in excitations are depicted in Figs. S3 – S5.

n	State	Main contributing excitations (%)	Transition energy[a] eV (nm)	Osc. Str.
0	b^1A	97 (HOMO → LUMO)	1.47 (841)	0.299
	c^1A	96 (HOMO-1 → LUMO)	2.02 (613)	0.044
	d^1A	55 (HOMO-2 → LUMO)	2.89 (427)	0.068
	e^1A	97 (HOMO → LUMO+1)	3.14 (394)	0.010
	f^1A	40 (HOMO-2 → LUMO); 41 (HOMO-4 → LUMO);	3.32 (373)	0.386
1	b^2A	95 (βHOMO → βLUMO)	1.27 (976)	0.007
	c^2A	80 (αHOMO → αLUMO)	1.67 (741)	0.043
	d^2A	mixed	1.81 (686)	0.023
	e^2A	mixed	2.70 (459)	0.155
	f^2A	mixed	2.80 (441)	0.150
	g^2A	mixed	2.93 (423)	0.082
	i^2A	mixed	3.17 (391)	0.090
	j^2A	mixed	3.22 (385)	0.182
-1	b^2A	98(βHOMO → βLUMO)	1.56 (794)	0.106
	c^2A	84 (βHOMO-1 → βLUMO)	2.14 (578)	0.036
	d^2A	92 (αHOMO → αLUMO)	2.34 (530)	0.026
	e^2A	80 (βHOMO-2 → βLUMO)	2.74 (453)	0.077
	f^2A	85 (αHOMO → αLUMO+1)	3.17 (390)	0.067
	g^2A	mixed	3.27 (378)	0.064
	h^2A	mixed	3.51 (353)	0.195

[a] Wavelength in parethesis

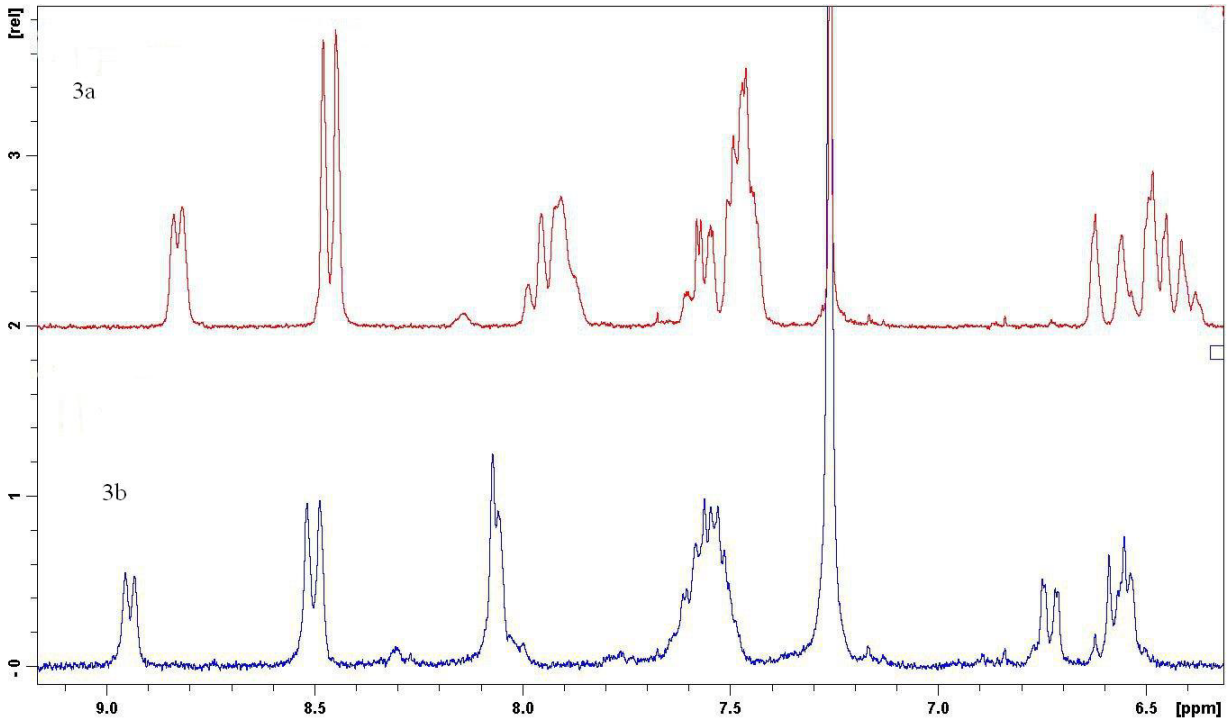

Figure S1: ^{1}H NMR spectrum (aromatic part) of the isomers **3a** and **3b** in $CDCl_3$.

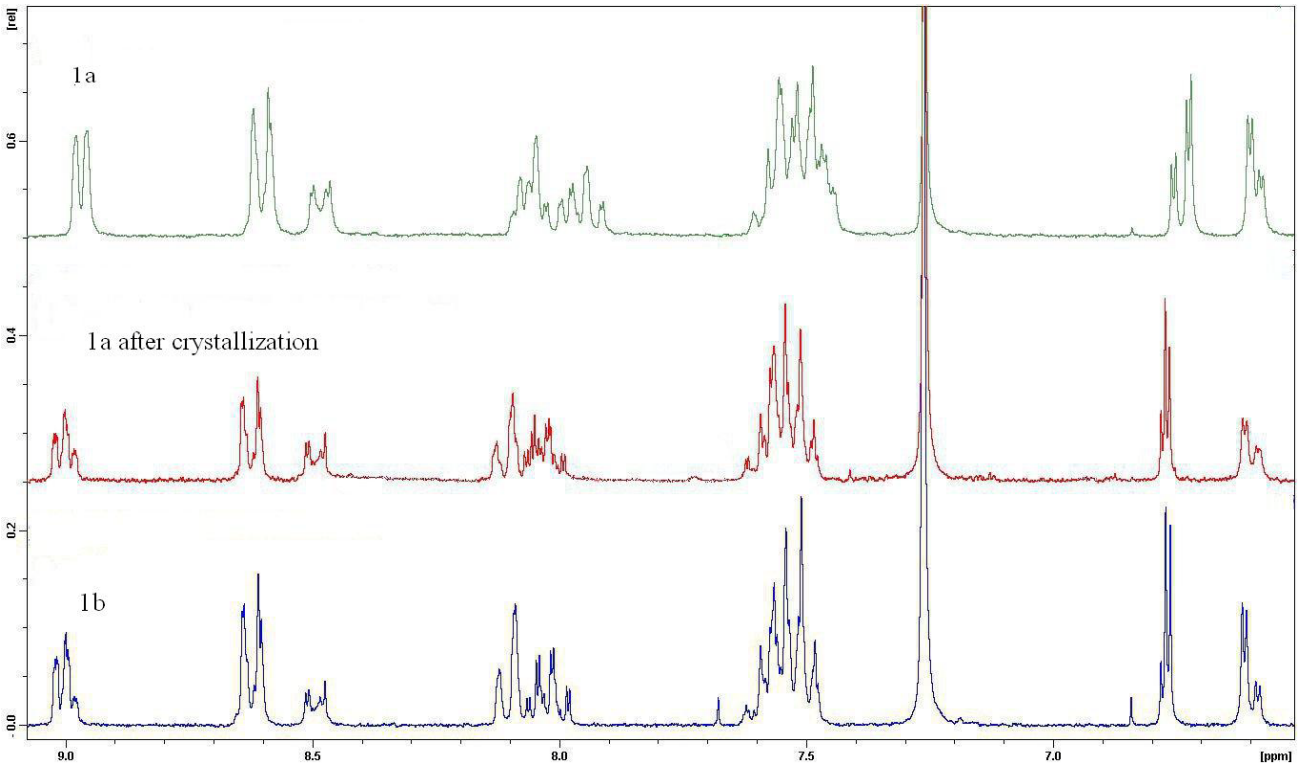

Figure S2: ^{1}H NMR spectrum (aromatic part) of the isomers **1a** and **1b** in $CDCl_3$ showing their interconversion during crystallization.

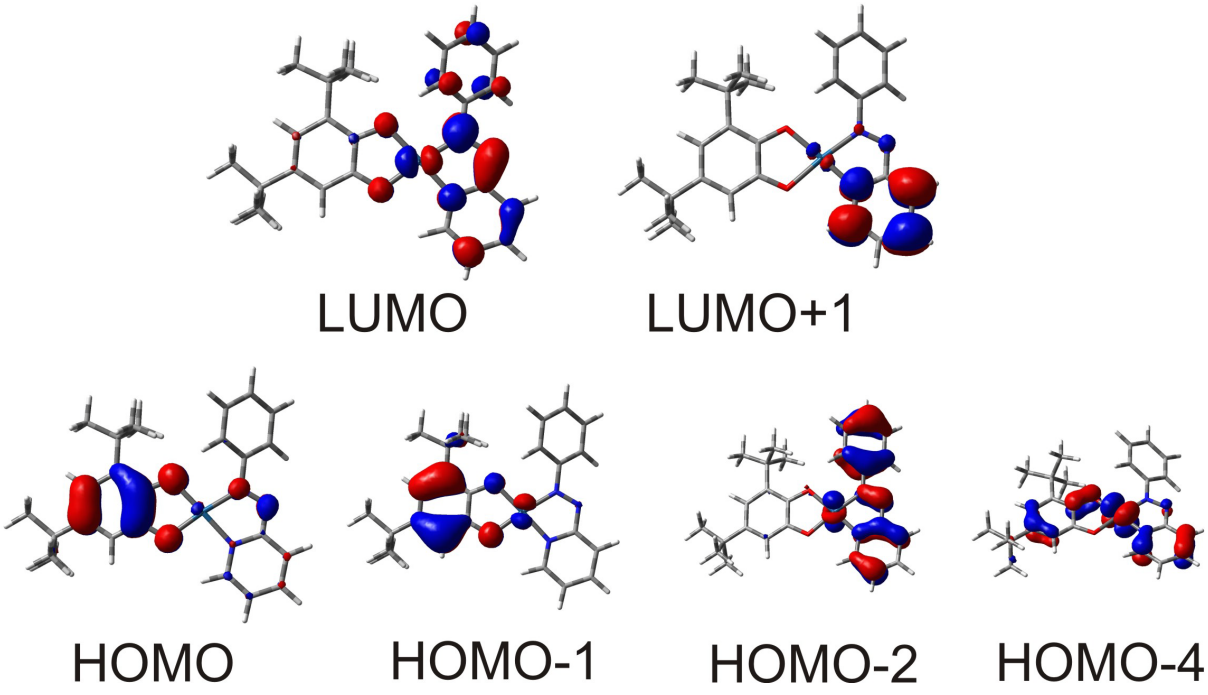

Figure S3. Frontier molecular orbitals involved in TD DFT calculated lowest singlet transitions of **2b** presented in Table S3. PBE0/PCM-CH_2Cl_2 calculation. Corresponding FMO's of the complex **1b** have similar shapes.

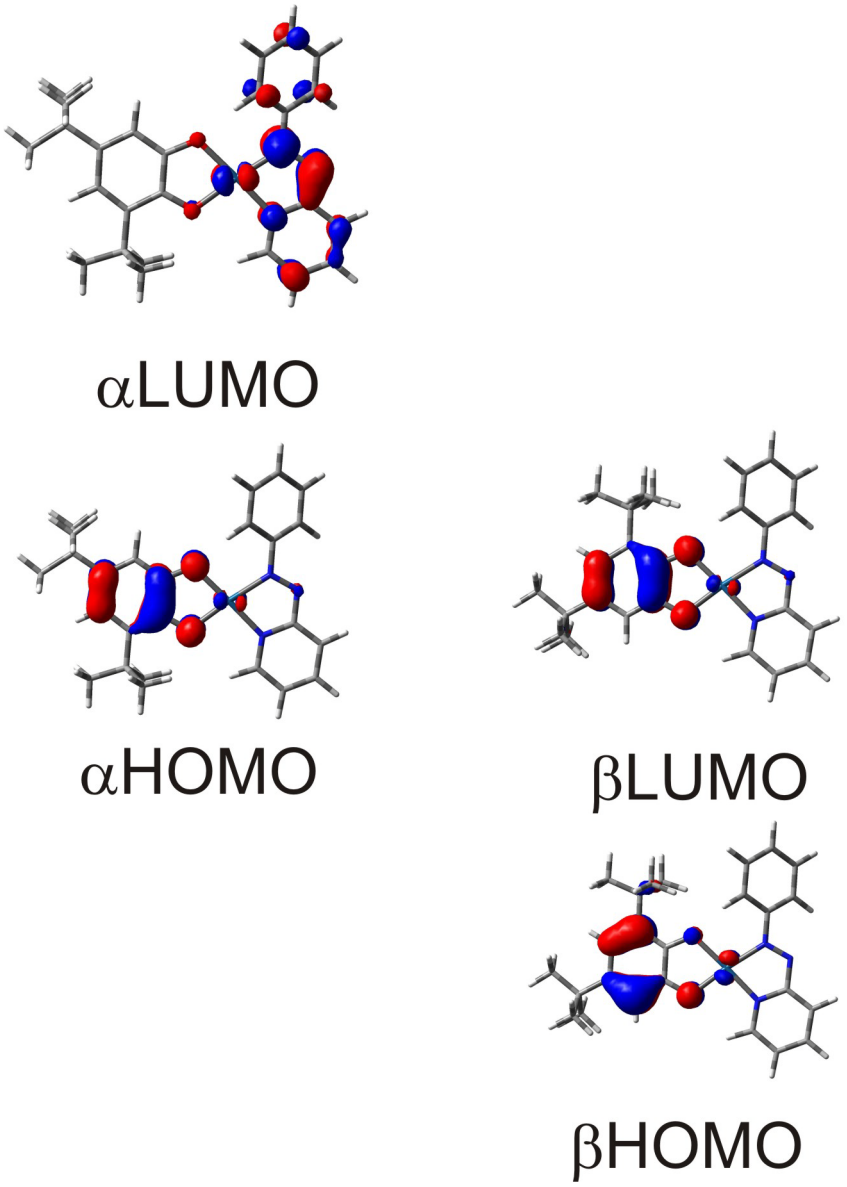

Figure S4. Frontier molecular orbitals involved in TD DFT calculated lowest singlet transitions of **2b**$^{+}$ presented in Table S3. PBE0/PCM-CH_2Cl_2 calculation. Corresponding FMO's of the complex **1b**$^{+}$ have similar shapes.

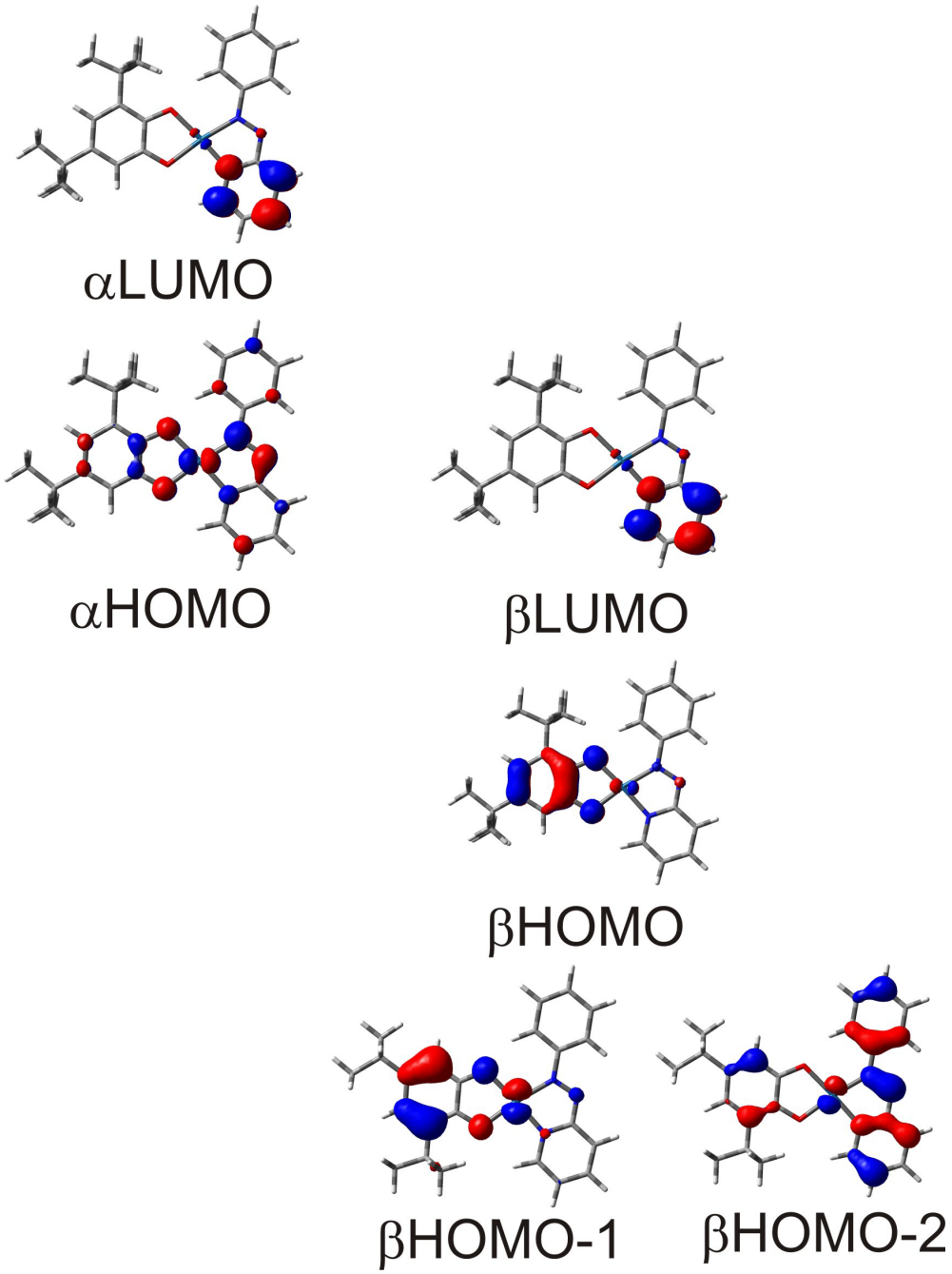

Figure S5: Frontier molecular orbitals involved in TD DFT calculated lowest singlet transitions of **2b**$^-$ presented in Table S3. PBE0/PCM-CH_2Cl_2 calculation. Corresponding FMO's of the complex **1b**$^-$ have similar shapes.