Supplementary Information

Combining Two Non-Innocent Ligands in Isomeric Complexes $[Pt(pap)^mQ^n]^0$ (pap = Phenylazopyridine, Q = 3,5-Di-*tert*-butyl-benzoquinone)

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General.

All solvents were dried and distilled using common techniques unless otherwise mentioned. ^{1}H NMR spectra were recorded at 250.13 MHz on a Brucker AC250 instrument. EPR spectra in the X band were recorded with a Bruker System EMX. UV-Vis-NIR absorption spectra were recorded on a J&M TIDAS spectrophotometer. Cyclic voltammetry was carried out in 0.1 M Bu_4NPF_6 solution using a three-electrode configuration (glassy carbon working electrode, Pt counter electrode, Ag wire as psuedoreference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium (Fc/Fc^+) couple served as internal reference. Elemental Analyses was performed on a Perkin Elmer Analyser 240.

Synthesis.

1a: $Pt(pap)Cl_2$ [1, 2] (50mg, 0.139 mmol) and 3,5-di-tert-butyl catechol (30.8 mg, 0.139 mmol) were taken together in 15 ml of acetonitrile. Triethylamine (0.1 ml) was added to the solution. The reaction mixture was heated to reflux for 3 hours. The colour of the solution changed to deep green. After cooling to room temperature a green precipitate was formed. The precipitate was filtered and washed with diethylether. Yield: 45 mg (54%). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.30 (s, 9H, tert-butyl), 1.51 (s, 9H, tert-butyl), 6.62 (d, 1H, ^4J = 5.35 Hz, catecholate ring), 7.04 (d, 1H, ^4J = 5.33 Hz, catecholate ring), 7.50 (m, 4H), 7.95 (m, 1H), 8.17 (m, 1H), 8.55 (m, 1H), 8.63 (m, 1H), 9.60 (m, 1H). Anal. Calc. for $C_{25}H_{29}N_3O_2Pt$: C, 50.16; H, 4.88; N, 7.02. Found: C, 50.28; H, 4.62; N, 6.98. $\nu_{N=N}$ = 1350 cm^{-1}

1b: Pt(pap)Cl$_2$ $^{1, 2}$ (50mg, 0.139 mmol) and 3,5-di-tert-butyl catechol (30.8 mg, 0.139 mmol) were taken together in 25 ml of acetonitrile. Triethylamine (0.1 ml) was added to the solution. The reaction mixture was heated to reflux for 1 hour. The colour of the solution changed to deep green. About half of the solvent was evaporated under vacuo. The precipitate that formed was filtered and washed with diethylether. This compound corresponds to **1a**. The filtrate was purified by column chromatography on silica gel. First a green band was eluted with dichloromethane/acetonitrile (10/1). This corresponds to the compound **1b**. A second fraction was then eluted with dichloromethane/acetonitrile (10/2). This turned out to be a mixture of **1a** and **1b** and this mixture was identified by X-ray crystal structure (see main text for explaination). Yield: 15 mg (18%). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.32 (s, 9H, tert-butyl), 1.49 (s, 9H, tert-butyl), 6.65 (d, 1H, ^4J = 5.31 Hz, catecholate ring), 7.06 (d, 1H, ^4J = 5.34 Hz, catecholate ring), 7.57 (m, 4H), 7.92 (m, 1H), 8.19 (d, 1H), 8.54 (m, 1H), 8.64 (m, 1H), 9.63 (m, 1H). Anal. Calc. for $C_{25}H_{29}N_3O_2Pt$: C, 50.16; H, 4.88; N, 7.02. Found: C, 50.28; H, 4.62; N, 6.98. $\nu_{N=N}$ = 1355 cm^{-1}

Recrystallization by evaporation from their dichloromethane/n^1-hexane (1/4) solutions afforded dark green crystals of **1a**, **1b** or **1a/1b** cocrystallized.

Crystallographic details

X-ray data collection, structure solution and refinement for all compounds

Suitable crystals for the X-ray analysis of all compounds were obtained as described above. The intensity data were collected at 173(2) K on a Kappa CCD diffractometer[S-2] (graphite monochromated MoK$_\alpha$ radiation, λ = 0.71073 Å) for **1a** and **1b**; and at 150(2) K on an Oxford XCALIBUR-S CCD diffractometer (graphite monochromated MoK$_\alpha$ radiation, λ = 0.71073 Å) for **1a+1b**. Crystallographic and experimental details for the structures are summarized in Table S1. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[S-3] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined *riding* on the corresponding parent atoms. The crystals of **1b** were of poor quality. This resulted in a low maximum θ value. The thermal parameters of several atoms where then refined with restrained anisotropic parameters (Shelxl SIMU and ISOR). The structure was solved in the monoclinic system ($P2_1/a$) in order to check the correctness of the $P4_2/mbc$ assignement. A PLATON ADDSYM procedure confirmed the chosen Tetragonal space group. A MULTISCAN[4] absorption correction was applied for all compounds. Although solvent accessible voids were found, no atom was found in the difference map, the highest peak included in those coordinates bein 0.8 e/Å^3. CCDC 719277, 719278 and 719347 contain the supplementary crystallographic data for this paper that can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S-1

	1a	**1b**	**1a+1b**
Chemical formula	$C_{25}H_{29}N_3O_2Pt$	$C_{25}H_{29}N_3O_2Pt$	$C_{25}H_{29}N_3O_2Pt$
M_r	598.60	598.60	598.60
Cell setting, space group	Triclinic, *P*-1	Tetragonal, $P4_2/mbc$	Triclinic, *P*-1
a, *b*, *c* (Å)	6.9677(3), 10.7867(6), 15.6342(7)	26.888(1), 26.888(1), 6.7983(3)	10.7992(3), 13.6690(4), 16.6581(6)
α, β, γ (°)	101.695(2), 95.843(3), 91.407(2)	90, 90, 90	107.050(3), 98.301(3), 101.033(2)
V (Å^3)	1143.44(2)	4915(4)	2254.2(1)
Z	2	8	4
D_x (Mg m^{-3})	1.739	1.618	1.764
μ (mm^{-1})	6.16	5.73	6.25
F(000)	588	2352	1176
Crystal size (mm)	0.13 × 0.13 × 0.10	0.18 × 0.08 × 0.08	0.21 × 0.18 × 0.15
meas., indep. and obsvd. Refl.	9059, 6626, 5701	6555, 1938, 1388	21767, 9287, 6498
R_{int}	0.031	0.045	0.046
$\theta_{\max}$ (°)	29.99	23.24	26.5
$R[I>2\sigma(I)], wR(F^2), S$	0.042, 0.097, 1.20	0.052, 0.092, 1.00	0.032, 0.049, 0.96
No. of parameters	286	186	575
$(\Delta/\sigma)_{\max}$	0.002	0.001	0.002
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å^{-3})	1.63, –2.27	0.93, –0.75	2.41, –0.94

Figure Captions:

Figure S1: ORTEP view of mixture of **1a** and **1b** in the same crystal. The ellipsoids enclose 50% of the electron density. The hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and bond angles (°): Pt(1)-N(1) 1.981(4), Pt(1)-N(2) 1.956(4), Pt(1)-O(1) 1.970(4), Pt(1)-O(2) 1.966(3), N(1)-N(3) 1.289(5), N(3)-C(15) 1.378(6), N(1)-C(20) 1.452(6), C(1)-O(1) 1.372(5), C(2)-O(2) 1.340(6), C(1)-C(2) 1.396(7), C(2)-C(3) 1.401(6), C(3)-C(4) 1.380(7), C(4)-C(5) 1.410(6), C(5)-C(6) 1.386(6), C(6)-C(1) 1.399(7); N(1)-Pt(1)-N(2)

77.9(2), N(1)-Pt(1)-O(1) 104.3(2), N(2)-Pt(1)-O(2) 95.5(2), O(1)-Pt(1)-O(2) 82.4(1); Pt(1B)-N(1B) 1.938(5), Pt(1B)-N(2B) 1.969(4), Pt(1B)-O(1B) 1.952(3), Pt(1B)-O(2B) 1.980(3), N(1B)-N(3B) 1.318(6), N(3B)-C(15B) 1.373(7), N(1B)-C(20B) 1.444(6), C(1B)-O(1B) 1.373(6), C(2B)-O(2B) 1.358(6), C(1B)-C(2B) 1.401(6), C(2B)-C(3B) 1.394(7), C(3B)-C(4B) 1.374(7), C(4B)-C(5B) 1.408(6), C(5B)-C(6B) 1.396(7), C(6B)-C(1B) 1.404(7); N(1B)-Pt(1B)-N(2B) 78.7(2), N(1B)-Pt(1B)-O(2B) 101.9(2), N(2B)-Pt(1B)-O(1B) 95.8(2), O(1B)-Pt(1B)-O(2B) 83.7(1).

Figure S2: UV/vis/NIR spectral changes during the 1st oxidation process of **1a** in CH_2Cl_2 / 0.1 M Bu_4NPF_6.

Figure S3: UV/vis/NIR spectral changes during the 1st reduction process of **1a** in CH_2Cl_2 / 0.1 M Bu_4NPF_6.

Figure S1:

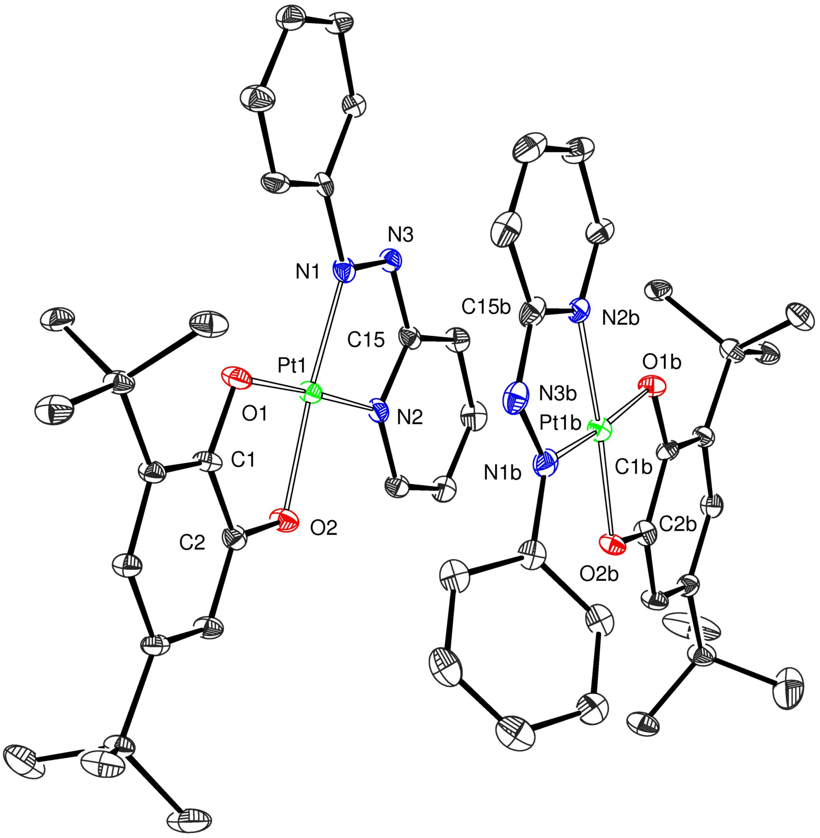


Figure S2

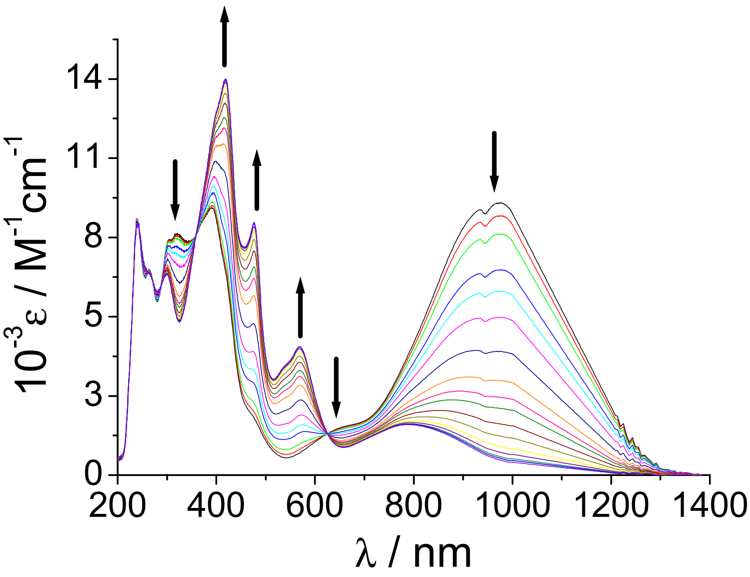
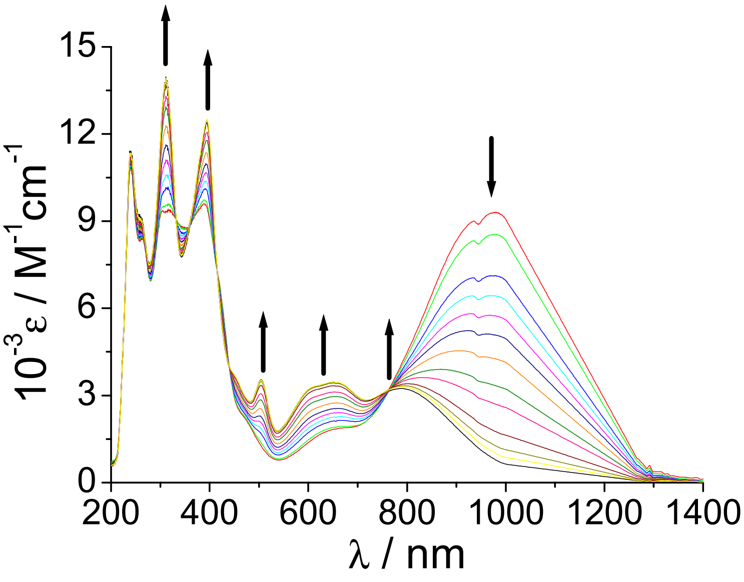


Figure S3



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