Supporting Information:

Donor-acceptor systems of Pt(II) and redox-induced reactivity towards small molecules

Naina Deibel,[a] David Schweinfurth,[a] Stephan Hohloch,[a] Jan Fiedler[b] and Biprajit Sarkar*[a]

Experimental section

General considerations

Pt(pap)Cl_2[1] and the ligand H_2Q[1,2] were prepared according to reported procedures. All other reagents are commercially available and were used as received. All solvents were dried and distilled using common techniques unless otherwise mentioned.

Instrumentation

^{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. Simulations of EPR spectra were done using the Simfonia program. UV-vis-NIR absorption spectra were recorded on a J&M TIDAS spectrometer. 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 pseudoreference) and PAR 273 potentiostat and function generator. The ferrocene/ferrocenium (Fc/Fc^+) couple served as internal reference. Spectroelectrochemical measurements were carried out using an optically transparent thin layer electrochemical (OTTLE) cell consisting of platinum-grid working and auxiliary electrodes and a silver quasi-reference electrode sealed between optical windows. The cell was mounted on the J & M TIDAS diode-array spectrometer and the spectra were collected continuously during the potential scan within the redox steps. Elemental analysis was performed on a Perkin Elmer Analyser 240. Mass spectrometry experiments were carried out on a Bruker Daltronics Mictrotof-Q mass spectrometer.

Synthesis

Pt(pap)Cl_2 (44.9 mg, 0.1 mmol) and the ligand H_2Q^1 (29.7 mg, 0.1 mmol) were taken together under an argon atmosphere in 10 mL of dry acetonitrile. Triethylamine (0.2 mL) was added to the solution. The reaction mixture was heated to reflux for 3 hours. The color of the solution changed to deep green. After cooling to room temperature a green precipitate was formed. The compound **1a** was filtered, washed with methanol and dry on air. Yield: 27 mg (40%). The filtrate was purified by column chromatography on Al_2O_3 with dichloromethane/ acetonitrile (100/1). The complex **1b** was obtained as a deep green solid. Yield: 16 mg (24%).

1a: ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.16 (s, 9H, *tert*-butyl); 1.66 (s, 9H, *tert*-butyl); 6.72(m, 2H, catecholate); 6.91 (m, 4H); 6.99 (m, 3H); 7.22 (m, 2H); 7.36 (m, 2H); 7.53 (m,1H); 7.70 (d, 1H, $^3J_{H\text{-}H}$ = 7.7 Hz); 9.50 (d, 1H, $^3J_{H\text{-}H}$ = 6.22 Hz). Anal. Calc. for $C_{31}H_{34}N_4OPt$: C 55.27; H 5.09; N 8.32 %; found: C 55.54; H 5.27; N 8.24 %. HRMS (ESI) Calc. for $C_{31}H_{21}N_4OPt$ ($[M]^+$): m/z 673.2377; found 673.2423.

1b: ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.16 (s, 9H, *tert*-butyl); 1.43 (s, 9H, *tert*-butyl); 6.42 (s, 1H, catecholate); 6.51 (m, 1H, catecholate); 6.76 (d, 1H, $^3J_{H\text{-}H}$ = 6.23 Hz); 7.36 (m, 3H); 7.47 (m, 5H); 7.64 (m, 2H); 7.81 (d, 1H, $^3J_{H\text{-}H}$ = 8.22 Hz); 8.08 (m, 2H). Anal. Calc. for $C_{31}H_{34}N_4OPt$: C 55.27; H 5.09; N 8.32 %; found: C 55.34; H 5.40; N 8.70 %. HRMS (ESI) Calc. for $C_{31}H_{21}N_4OPt$ ($[M]^+$): m/z 673.2377; found 673.2351.

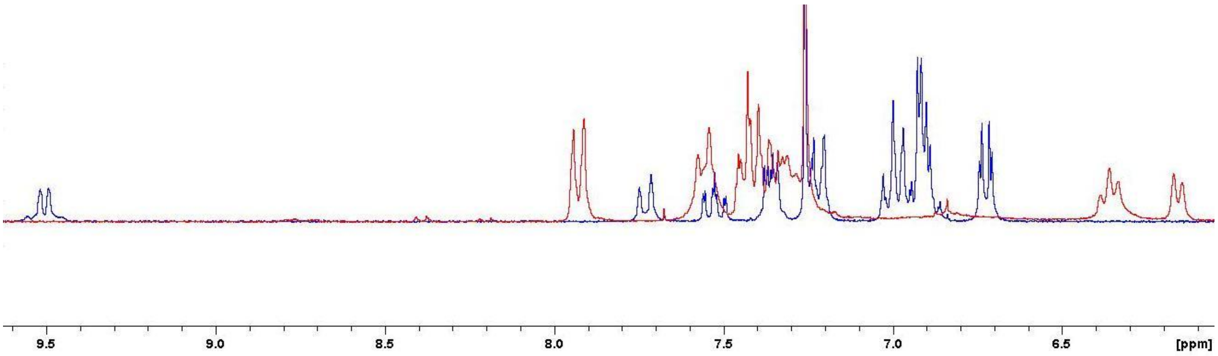


Figure S1.^{1}H-NMR spectrum of **1a** (blue) and **1b** (red) in $CDCl_3$.

Oxidation of Complexes 1a and 1b:

To a deep green solution of **1a** (75.0 mg, 0.11 mmol) in dry CH_2Cl_2 (15 mL) under an Ar atmosphere was added ferrocenium hexafluorophosphate (36.8 mg, 0.11 mmol). After the solution was stirred at room temperature for 4.5 hours, the solvent was removed by evaporation and the red solid was washed with *n*-hexane (3 x 10 mL). The red solid was recrystallized from the dichloromethane/ *n*-hexane (1:3) mixture. Yield: 65 mg (72%). Anal. Calc. for $C_{31}H_{34}F_6N_4OPPt$: C 45.48; H 4.19; N 6.84 %; found: C 45.67; H 4.34; N 6.68 %.

Cyclic voltammetry experiment in the presence of PPh_3

Under Argon atmosphere **1a** (5.4 mg, 0.008 mmol) was dissolved in degassed CH_2Cl_2/ 0.1 M Bu_4NPF_6 solution (5 mL). PPh_3 solution (2.11 mg, 0.008 mmol, 1 mL CH_2Cl_2) was added stepwise (4 x 0.25 mL) to the green solution of **1a**. After each addition of the PPh_3 solution a cyclic votammogram was recorded.

X-ray crystallography

Single crystals of **1b** were grown by layering a dichloromethane solution of **1b** with methanol (1/3) and allowing for slow diffusion at ambient temperatures. The X-ray intensity data for **1b** were collected at 100 K using a Bruker Kappa Apex II duo diffractometer. Calculations were performed with the SHELXTL PC 5.03 and SHELXL-97 program.[3] The Pt atom was found to be disordered by 92.5 / 7.5 %. This can be due to vibrations of Pt atom or simply because of low crystal quality.

Table S1: Crystallographic details for **1b**.

Chemical formula	$C_{31}H_{34}N_4OPt$
M_r	673.71g mol^{-1}
Crystal system, Space group	Monoclinic, P 21/c
a, b, c (Å)	14.1260(13), 9.7082(8), 21.2529(19)
β(°)	100.801(4)
V (Å^3)	2862.9(4)
Z	4
Densitiy (g cm^{-3})	1.563
F(000)	1336
Radiation Type	Mo K_α
μ (mm^{-1})	4.930
Crystal size	0.20 x 0.13 x 0.10
Meas. Refl.	25864
Indep. Refl.	7150
Obsvd. [$I > 2\sigma(I)$] refl.	5521
R_{int}	0.0442
R [$F^2 > 2\sigma(F^2)$], wR(F^2), S	0.0299, 0.0615, 1.009
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	3.987, -0.572

Table S2: Selected bond lengths (Å) and bond angles (°) of **1b**.

Bond lengths

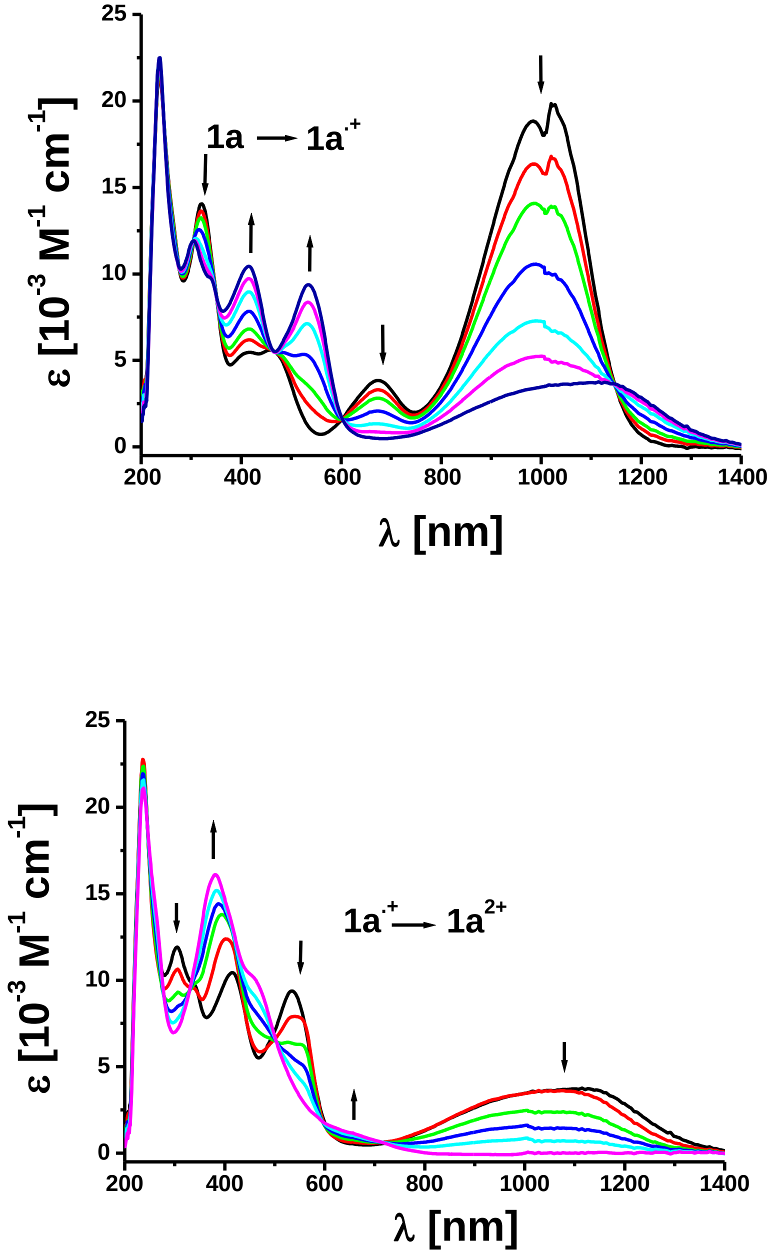
Pt1-N1	1.978(3)
Pt1-N2	1.962(3)
Pt1-N4	1.974(3)
Pt1-O1	1.964(3)
C1-O1	1.329(4)
C2-N1	1.386(5)
C1-C2	1.422(5)
C2-C3	1.407(5)
C3-C4	1.379(5)
C4-C5	1.408(5)
C5-C6	1.388(5)
C6-C1	1.403(5)

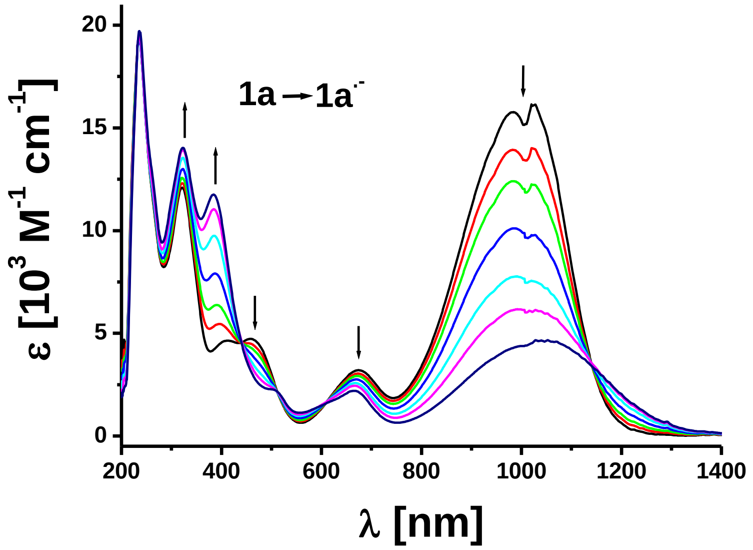
N2-N3	1.321(4)
N3-C21	1.362(5)

Bond angles

N1-Pt1-N2	108.1(1)
N2-Pt1-N4	77.6(1)
N4-Pt1-O1	93.7(2)
N1-Pt1-O1	80.9(1)

Figure S2: Changes in the UV-vis-NIR spectra of **1a** in CH_2Cl_2 / 0.1 M Bu_4NPF_6 during the various redox processes from spectroelectrochemistry in the OTTLE cell.




1a → 1a·-
ε [10³ M⁻¹ cm⁻¹]
0
5
10
15
20
200
400
600
800
1000
1200
1400
λ [nm]

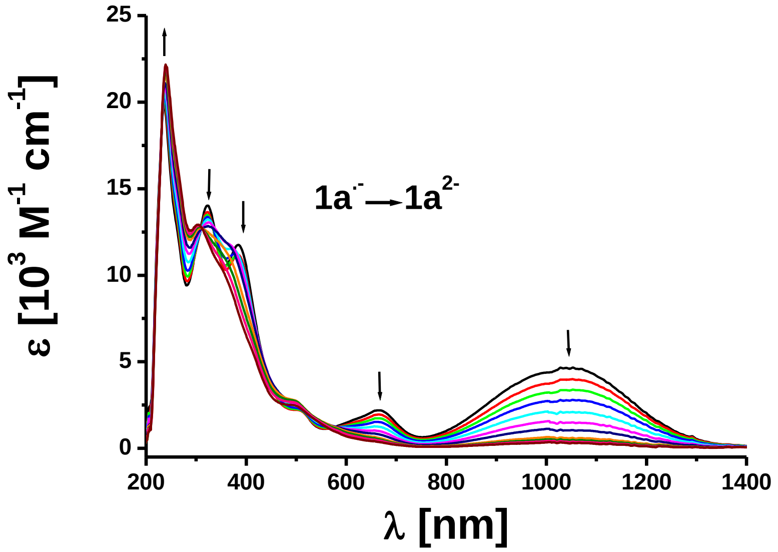

1a·- → 1a²⁻
ε [10³ M⁻¹ cm⁻¹]
0
5
10
15
20
25
200
400
600
800
1000
1200
1400
λ [nm]

Table S3: UV-vis-NIR data of **1a**$^{\mathbf{n}}$.[a]

	λ [nm] (ε [10^3 M^{-1}·cm^{-1}])
1a	241 (17.6); 326 (12.1); 392 (5.4); 457 (4.6); 679 sh (2.0); 897 (20.9)
1a^{+}	238 (22.5); 305 (11.9); 338 (9.8) sh; 415 (10.5); 535 (9.4); 1114 (3.8)
1a^{2+}	238 (21.1); 381 (16.1); 456 (10.3) sh; 632 (1.4) sh
1a^{-}	236 (19.8); 323 (14.1); 385 (11.8); 505 (2.3) sh; 665 (2.2); 1042 (4.7)
1a^{2-}	239 (22.2); 304 (12.9); 349 (10.5) sh; 487 (2.5) sh

[a] From OTTLE spectroelectrochemistry in CH_2Cl_2 /0.1 M Bu_4NPF_6.

Figure S3: X-band EPR spectrum of 1a$^{\cdot-}$ in CH_2Cl_2 at 295 K together with simulation.

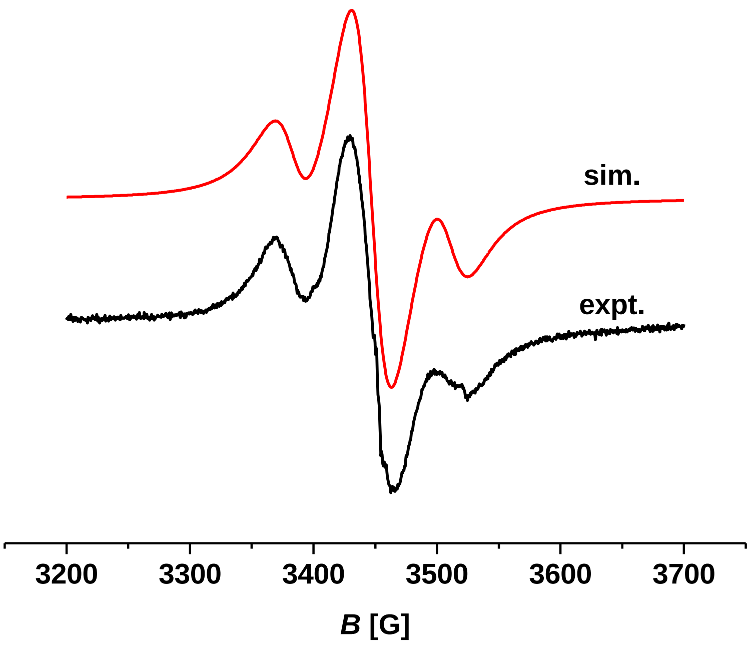
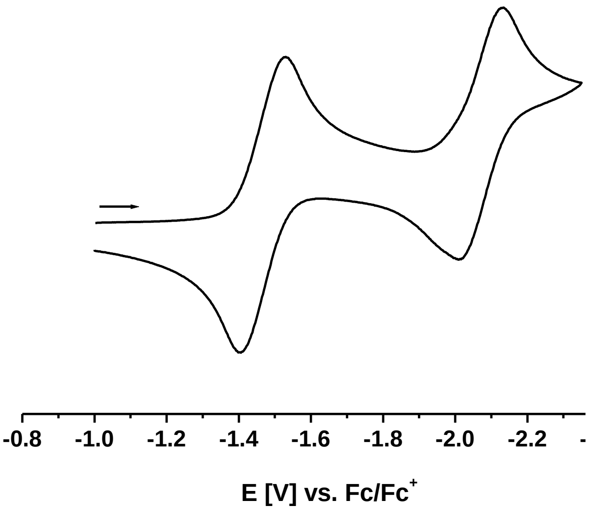
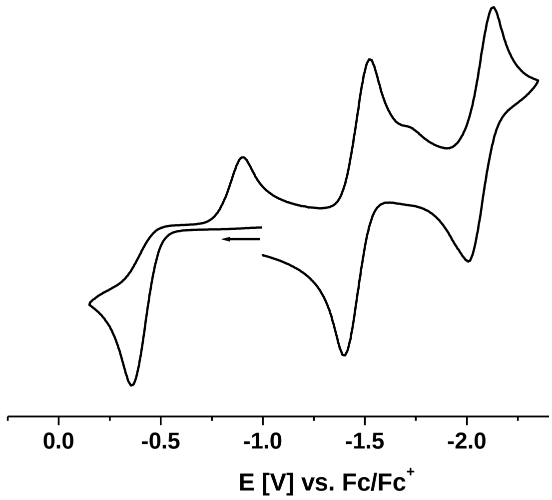

sim.
expt.
3200
3300
3400
3500
3600
3700
B [G]

Figure S4: Regional scans of the cyclic voltammgram of **1a** in the presence of one equivalent of PPh_3 in dichloromethane at 100 mV / s.





ESI Mass Spectrometry

Under an argon atmosphere **[1a]PF$_6$** (1.6 mg, 0.002 mmol) was dissolved in degassed dichlomethane (2 mL). A PPh_3 solution (0.5 mg, 0.002 mmol, 0.1 mL CH_2Cl_2) was added to the red solution of **[1a]PF$_6$**. The deep red solution was immediately injected (0.1 mL) in the mass spectrometer. The compound **[1a$^{\cdot+}$ + PPh$_3$]** was observed in the mass spectrum.

[1a]PF$_6$ (5.0 mg, 0.006 mmol) and KO*t*Bu (2.7 mg, 0.025 mmol) were dissolved in 5 mL degassed dichloromethane. The sample with the red solution was bubbled with H_2 at room temperature. After 10 minutes the solution was frozen in liquid nitrogen to slow down the reaction. The sample was injected (0.1 mL) in the mass spectrometer. The compound **[1a$^{\cdot+}$ + H^{-}]** was observed in the mass spectrum.

Figure S5: Reaction of **[1a]PF$_6$** + PPh$_3$ followed by ESI mass spectrometry. HRMS (ESI) Calc. for $C_{49}H_{49}N_4OPPt$ ([M+PPh$_3$]$^+$): m/z 935.3290; found 935.3263.

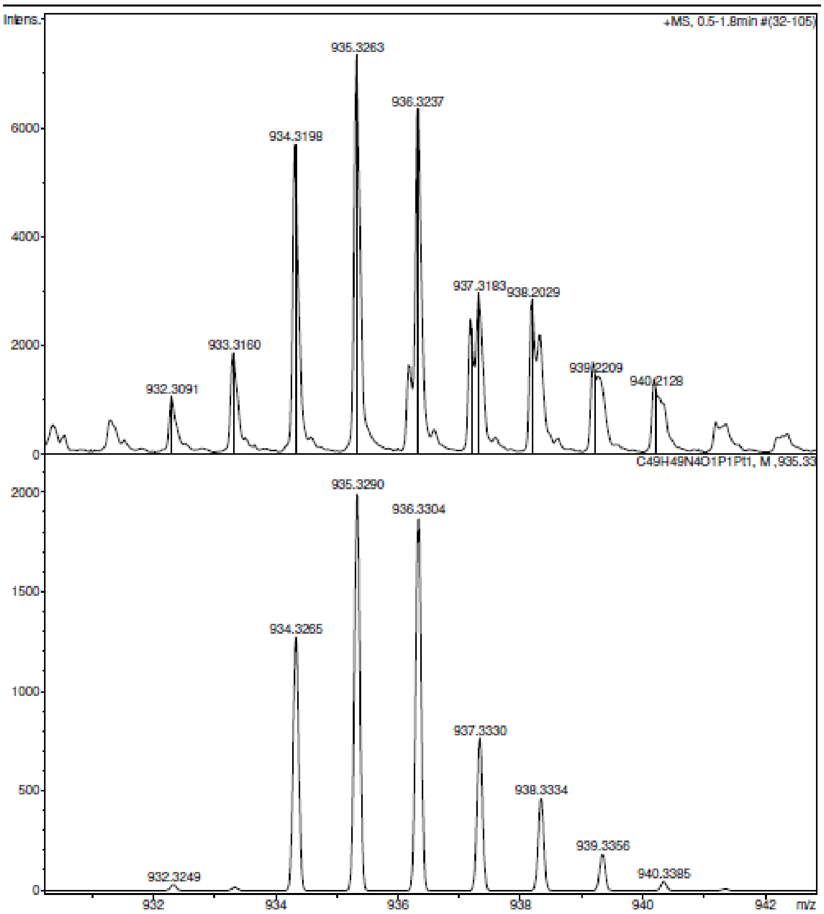


Figure S6: Reaction of **[1a]PF$_6$** + H_2 (in presence of KO^{t}Bu) monitored by UV-vis-NIR spectroscopy.

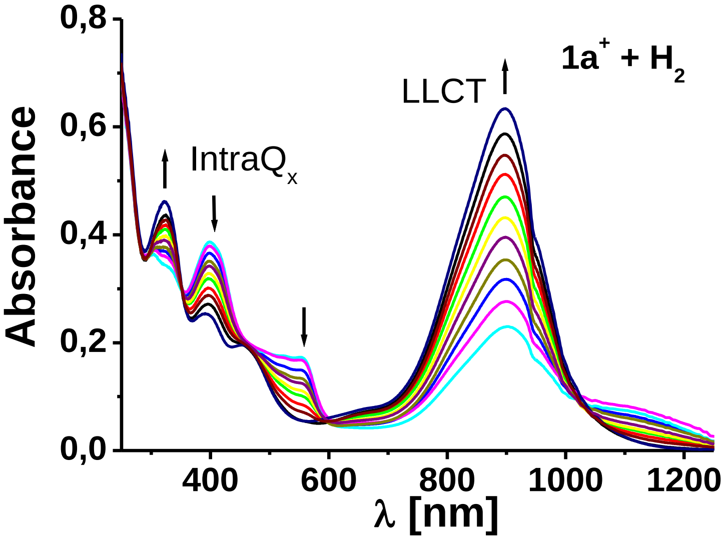
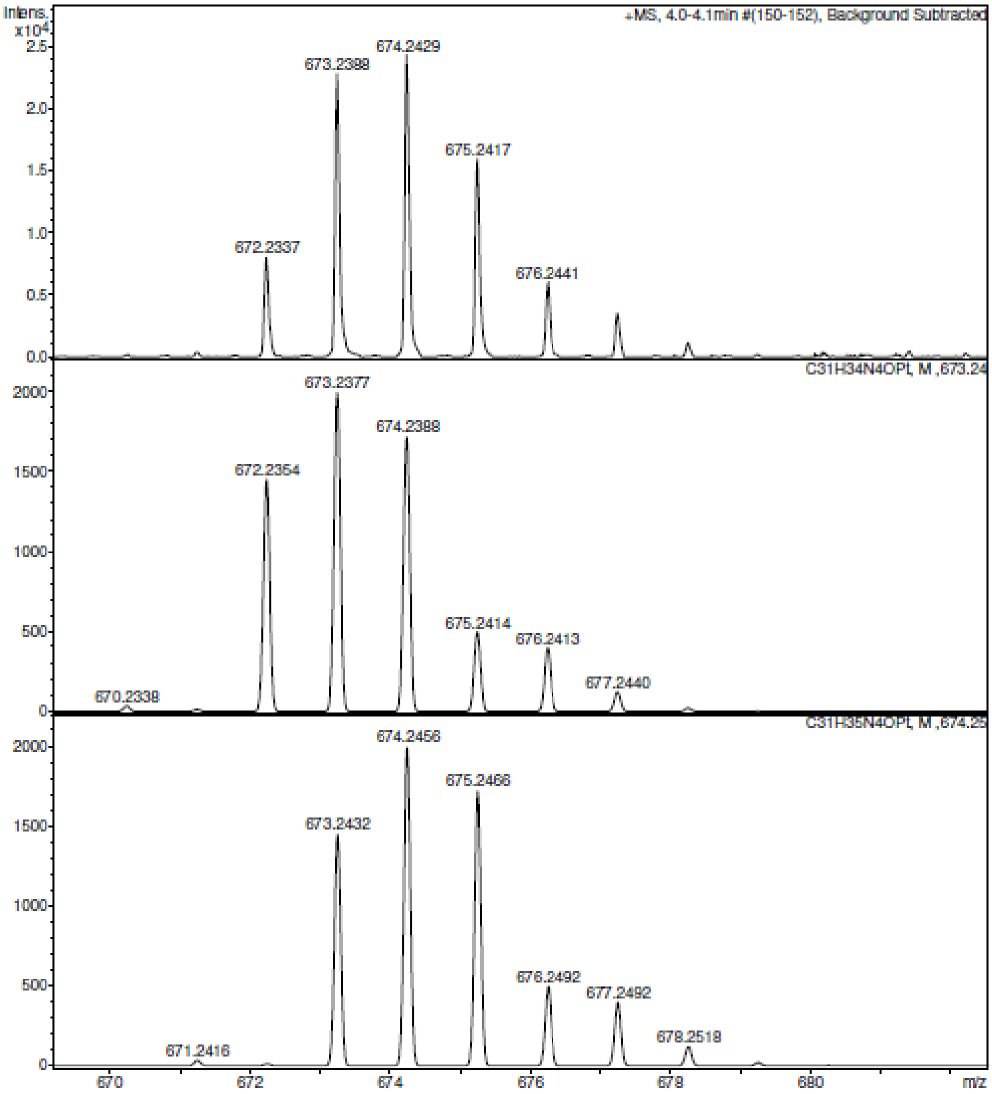


Figure S7: Reaction of **[1a]PF$_6$** + H_2 observed by ESI mass spectrum. HRMS (ESI) Calc. for $C_{31}H_{35}N_4OPt$ ([M+H$^-$]$^+$): m/z 674.2459; found: 674.2429.



Reduction of [1a]PF_6 with H_2.

In a UV-vis reaction cell **1a** (5.3 mg, 0.008 mmol) and KO*t*Bu (1.8 mg, 0.016 mmol) were dissolved in 10 mL degassed dichloromethane. An initial UV-vis spectrum was recorded. To the green solution ferrocenium hexafluorophosphate (2.6 mg; 0.008 mmol) was added. The sample with the red solution was bubbled with H_2 at room temperature. The reaction was observed by UV-vis spectrometer. The sample was stirred for the duration of the experiment (~20 min). The end of the reaction was determined by the appearance of the band at 898 nm. The reaction was repeated 15 times.

Figure S8: Plot of number of cycles performed versus % of catalyst recovered.

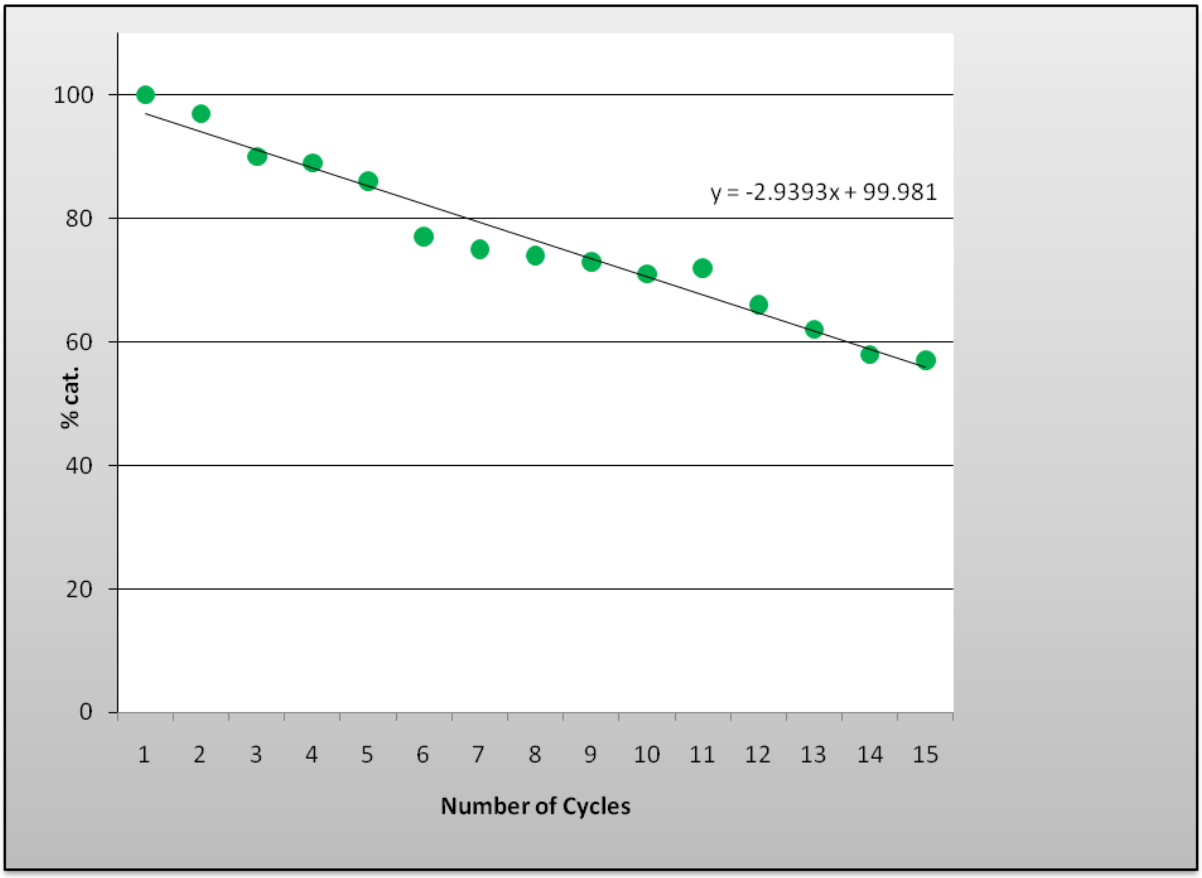
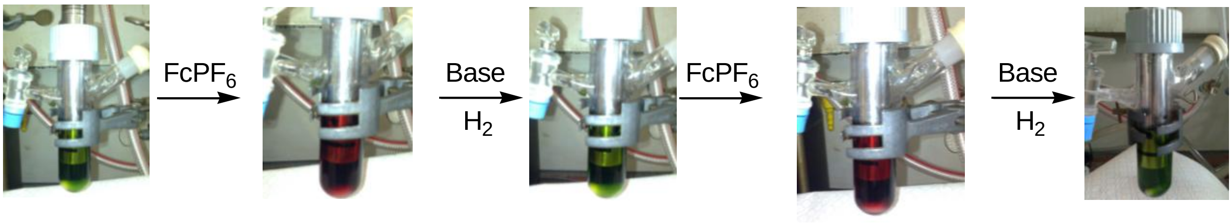


Figure S9: Catalytic (step-wise) reaction of ferreocenium hexafluorophosphate with H_2 in the presence of **1a**$^{\cdot+}$ as catalyst.

$$\mathbf{1a} \xrightarrow{FcPF_6} \mathbf{1a}^{\cdot+} \xrightarrow[H_2]{Base} \mathbf{1a} \xrightarrow{FcPF_6} \mathbf{1a}^{\cdot+} \xrightarrow[H_2]{Base} \mathbf{1a}$$



References:

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2 P. Chaudhuri, C.N. Verani, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt *J. Am. Chem. Soc.*, 2001, **123**, 2213.

3 G. M. Sheldrick, SHELXL-97, *Program for refinement of crystal structures*, University of Göttingen, Göttingen, Germany, 1997.