

## Supporting Information

### Synthesis of discrete Re(I) di- and tricarbonyl assemblies using a [4x1] directional bonding strategy.

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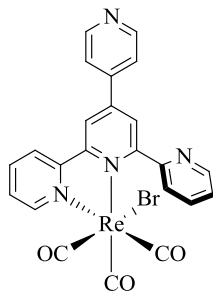
## Materials, methods and instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded in acetone-d<sub>6</sub> and DMSO-d<sub>6</sub> at room temperature (r.t.) on a Bruker AV400 (400 MHz) spectrometer for <sup>1</sup>H NMR, at 100 MHz for <sup>13</sup>C NMR and 600 MHz for DOSY experiment, respectively. Chemical shifts are reported in part per million (ppm) relative to residual solvent protons (2.05 ppm for acetone-d<sub>6</sub> and 2.50 ppm for DMSO-d<sub>6</sub>) and the carbon resonance (30.83 ppm for acetone-d<sub>6</sub> and 39.43 ppm for DMSO-d<sub>6</sub>) of the solvent.

All the photophysical measurements were carried out in deaerated acetonitrile at r.t. in septa sealed quartz cells. Absorption spectra were measured on a Cary 500i UV-Vis-NIR Spectrophotometer. For luminescence spectra a Cary Eclipse Fluorescence spectrofluorimeter was used. Accurate mass measurement were performed on a micrOTOF-Q II mass spectrometer from Bruker Daltonics, in positive electrospray mode. Appropriate [M-PF<sub>6</sub>]<sup>n+</sup> species were used for empirical formula determination, and exact masses were calculated using the Compass DataAnalysis V4.0 SP5 software package from Bruker Daltonics. Electrochemical measurements were carried out in argon-purged purified dimethylformamide at room temperature with a BAS CV50W multipurpose potentiostat. The working electrode was a glassy carbon electrode. The counter electrode was a Pt wire, and the pseudo-reference electrode was a silver wire. The reference was set using an internal 1 mM ferrocene/ferrocinium sample at 0.450 mV vs. SCE in acetonitrile. The concentration of the compounds was about 1 mM. Tetrabutylammonium hexafluorophosphate (TBAP) was used as supporting electrolyte and its concentration was 0.10 M. Cyclic voltammograms of were obtained at scan rates of 20, 50, 100, 200 and 500 mVs<sup>-1</sup>, respectively. The criteria for reversibility were the separation between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. Differential pulse voltammetry was conducted with a sweep rate of 20 mVs<sup>-1</sup> and a pulse amplitude, width and period of 50 mV, 50 ms and 200 ms, respectively. Experimental uncertainties are as follows: absorption maxima, ±2 nm; molar absorption coefficient, 10%; redox potentials, ± 10 mV, emission maxima, ±2 nm; Diffusion-ordered spectroscopy, ±10 %.

## Experimental:

### Re(4-pytpy- $\kappa^2N$ )(CO)<sub>3</sub>Br (1)



A 250 mL round-bottomed flask was charged with Re(CO)<sub>5</sub>Br (1.19 g, 2.93 mmol) and 4-pytpy ligand (1.0 g, 3.22 mmol) and to it 100 mL of toluene was added. The mixture was heated at reflux for 5 hours, after which time the solution was cooled to room temperature. The yellow suspension was filtered and washed with three portions of ether (50 mL) and dried under vacuum. No further purification procedures were needed. Yield = 1.8 g (94%), yellow solid.

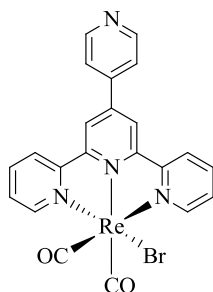
**<sup>1</sup>H-NMR** (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 9.21 (s, 1H), 9.14-9.09 (m, 2H), 8.85-8.83 (d,  $J$  = 5.8 Hz, 2H), 8.82-8.80 (d,  $J$  = 4.4 Hz, 1H), 8.43-8.33 (m, 2H), 8.22-8.20 (d,  $J$  = 5.9 Hz, 2H), 8.10-8.06 (t,  $J$  = 7.5 Hz, 1H), 7.92-7.90 (d,  $J$  = 7.7 Hz, 1H), 7.81-7.78 (t,  $J$  = 6.4 Hz, 1H), 7.66-7.63 (dd, 1H).

**<sup>13</sup>C-NMR** (DMSO-d<sub>6</sub>, 100 MHz) :  $\delta$  161.8, 157.6, 157.5, 156.0, 152.8, 150.6, 149.2, 148.0, 141.9, 139.9, 137.0, 127.6, 125.6, 125.0, 124.8, 121.8, 121.0.

**ESI-MS**: Calcd. for [M+H]<sup>+</sup>: 660.98625, Found: 660.98716, Diff.: 1.39 ppm.

**Elemental Analysis**: Calcd. for C<sub>23</sub>H<sub>14</sub>N<sub>4</sub>ReO<sub>3</sub>Br : C, 41.82; H, 2.14; N, 8.48. Found : C, 41.80; H, 2.11; N, 8.37.

### Re(4-pytpy- $\kappa^3N$ )(CO)<sub>2</sub>Br (2)



A 20 mL Biotage® microwave vial was loaded with finely grinded powder of precursor **1** (200 mg, 0.3 mmol). The vial was sealed and three cycles of N<sub>2</sub>/vacuum were applied in order to remove the oxygen. The vial was heated to 280°C in a sand bath for 8 hours. After this time, the solid was cooled to room temperature. The solid was dispersed in ether and filter over paper. No further purification procedure needed. Yield = 119 mg (60%), burgundy solid.

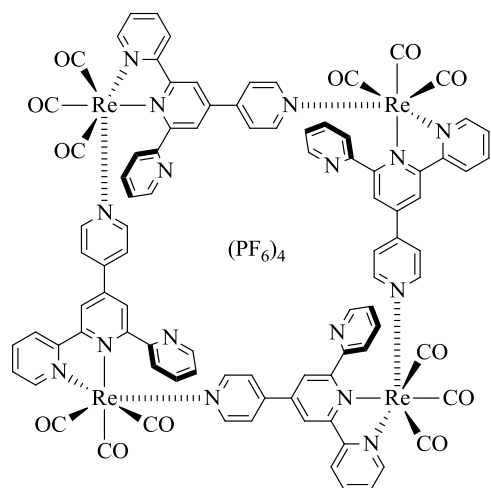
**<sup>1</sup>H-NMR** (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 9.03 (s, 2H), 8.93-8.92 (d,  $J$  = 5.4 Hz, 2H), 8.90-8.88 (d,  $J$  = 5.8 Hz, 2H), 8.82-8.80 (d,  $J$  = 8.1 Hz, 2H), 8.20-8.19 (d,  $J$  = 5.9 Hz, 2H), 8.10-8.11 (t,  $J$  = 7.1 Hz, 2H), 7.50-7.49 (t,  $J$  = 6.4 Hz, 2H).

$^{13}\text{C-NMR}$  (DMSO- $d_6$ , 100 MHz):  $\delta$  157.1, 156.6, 150.4, 138.9, 138.5, 137.5, 128.5, 124.8, 122.0, 119.7

**ESI-MS:** Calcd. for  $[\text{M}]^+$ : 631.98528, Found: 631.98263, Diff.: 4.19 ppm

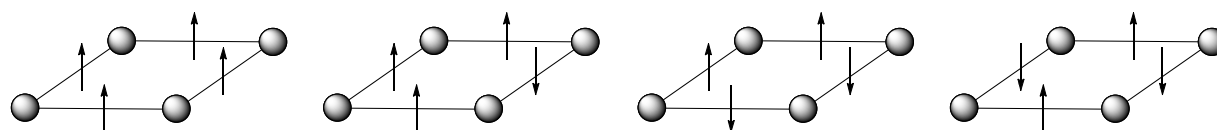
**Elemental Analysis:** Calcd. for  $\text{C}_{22}\text{H}_{14}\text{N}_4\text{ReO}_2\text{Br}\cdot\text{H}_2\text{O}$  : C, 40.49; H, 2.78; N, 8.59. Found : C, 40.39; H, 2.09; N, 8.44.

**$[\text{Re}(\text{4-pytpy}-\kappa^2\text{N})(\text{CO})_3]_4[(\text{PF}_6)]_4$  (**5**)**



A 250 mL round-bottomed flask was charged with **1** (100 mg, 0.151 mmol), silver triflate (43 mg, 0.166 mmol) and 100 mL of acetonitrile. The solution was heated at reflux under inert atmosphere for 5 hours in the dark. After this time, the AgBr precipitate was removed by filtration. The filtrate was evaporated to dryness under vacuum and 100 mL of a solvent combination of acetone:toluene (1:1) was added to the flask. The solution was heated to reflux for another 12 hours. The solvent was evaporated to dryness under vacuum. The precipitate was carefully dissolved in a minimum amount of acetonitrile and metathesis of the counter-anions was achieved by the addition of an aqueous  $\text{KPF}_6$  solution (10 equivalents), leading to the precipitation of a bright yellow compound. Purification was achieved by eluting the compound on Sephadex LH-20 column with a solvent combination of MeOH:MeCN:H $_2$ O (45:45:10). The first band to elute is the desired product. A second metathesis was achieved by the addition of an aqueous solution of  $\text{KPF}_6$ . The precipitate was isolated by filtration and dried under vacuum. Yield = 155 mg (46%), bright yellow solid.

Due to the 4 possible isomers (**Fig. S1**; the arrow indicate the position of the free pyridyl rings), all of the peaks are multiplets and exact  $^1\text{H}$  NMR assignments are not useful, however, the correct number of protons are present for the title compound.



**Figure**

**S1.** Representation of the four different isomers of molecular square **5**.

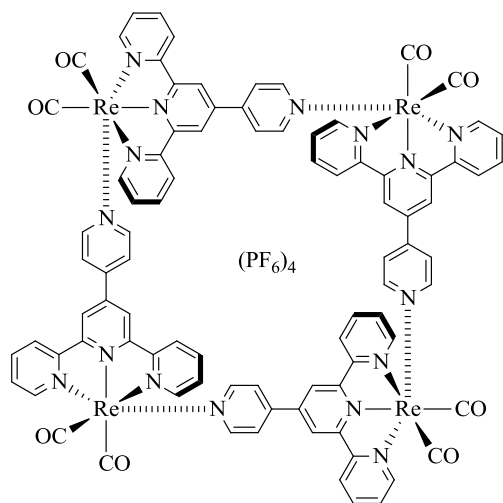
**<sup>1</sup>H-NMR** (400 MHz, acetone-*d*<sub>6</sub>): δ = 9.55-9.52 (m, 4H), 9.01-8.87 (m, 8H), 8.76-8.73 (dd, 2H), 8.59-8.31 (m, 12H), 8.26-7.89 (m, 26H), 7.80-7.74 (m, 4H).

**<sup>13</sup>C-NMR** (DMSO-*d*<sub>6</sub>, 100 MHz) : δ 164.1, 163.9, 163.8, 163.7, 159.0, 158.9, 158.7, 157.6, 157.53, 157.47, 155.7, 155.6, 155.5, 154.2, 154.1, 154.0, 151.80, 151.76, 151.7, 151.6, 149.9, 149.7, 148.1, 147.9, 147.8, 147.6, 146.2, 145.7, 143.1, 142.9, 142.7, 142.6, 139.4, 139.2, 130.7, 130.60, 130.57, 130.3, 129.6, 128.6, 128.5, 128.2, 128.1, 127.94, 127.91, 127.8, 127.6, 127.53, 127.51, 127.4, 127.3, 127.2, 126.8, 126.7, 126.6, 126.5, 126.32, 126.25, 124.4, 124.3, 123.2, 122.5.

**ESI-MS**: Calcd. for [M+K]<sup>+</sup>: 2941.06736, Found: 2941.06302, Diff.: -1.48 ppm, calcd. for [M-2PF<sub>6</sub>]<sup>+2</sup>: 1306.0875, Found: 1306.08541, Diff.: -1.60 ppm, calcd. for [M-3PF<sub>6</sub>]<sup>+3</sup>: 822.40342, Found: 822.40391, Diff.: 0.60 ppm

**Elemental Analysis**: Calcd. for C<sub>92</sub>H<sub>56</sub>N<sub>16</sub>Re<sub>4</sub>O<sub>12</sub>P<sub>4</sub>F<sub>24</sub>.H<sub>2</sub>O : C, 37.84; H, 2.00; N, 7.67. Found : C, 37.60; H, 1.77; N, 7.45.

**[Re(4-pytpy-κ<sup>3</sup>N)(CO)<sub>2</sub>]<sub>4</sub>[(PF<sub>6</sub>)<sub>4</sub>] (6)**



A 250 mL round-bottomed flask was charged with **2** (200 mg, 0.32 mmol), silver triflate (120 mg, 0.47 mmol) and 100 mL of acetonitrile. The solution was heated at reflux under inert atmosphere over 5 hours in the dark. After this time, the AgBr precipitate was removed by filtration. The filtrate was evaporated to dryness under vacuum and 100 mL of a solvent combination of acetone:toluene (1:1) was added to the flask. The solution was heated at reflux for another 10 hours. The solvent was evaporated to dryness under vacuum. The precipitate was carefully dissolved in a minimum amount of acetonitrile and metathesis of the counter-anions was achieved by the addition of an aqueous KPF<sub>6</sub> solution (10 equivalents), leading to the precipitation of a bright yellow compound. Purification was achieved by eluting the compound on Sephadex LH-20 column with a solvent combination of MeOH:MeCN:H<sub>2</sub>O (45:45:10). The first band to elute is the desired product. A second metathesis was achieved by the addition of an aqueous solution of KPF<sub>6</sub>. The precipitate was isolated by filtration and dried under vacuum. Yield = 183 mg (83%), brown solid.

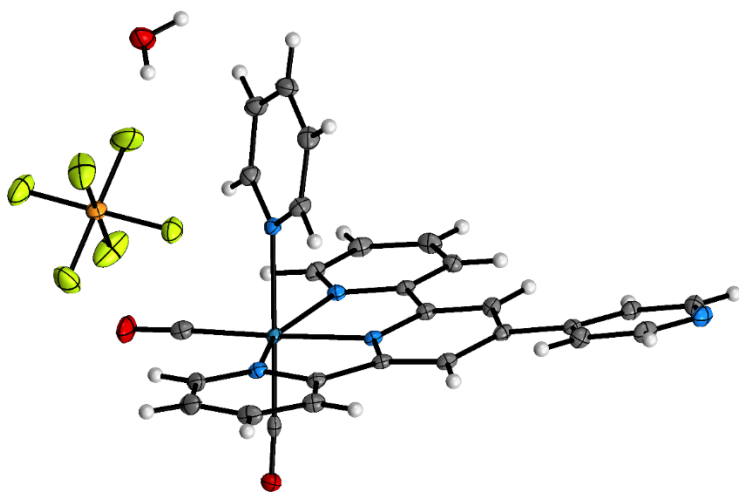
**<sup>1</sup>H-NMR** (400 MHz, acetone-*d*<sub>6</sub>): δ = 9.20-9.18 (d, *J* = 5.2 Hz, 8H), 8.80 (s, 8H), 8.72-8.70 (d, *J* = 8.1 Hz, 8H), 8.34-8.32 (d, *J* = 6.6 Hz, 8H), 8.22-8.18 (t, *J* = 8.1 Hz, 8H), 7.87-7.85 (d, *J* = 6.7 Hz, 8H), 7.78-7.74 (t, *J* = 6.5 Hz, 8H).

**<sup>13</sup>C-NMR** (DMSO-*d*<sub>6</sub>, 100 MHz) : δ 168.8, 168.6, 167.6, 167.4, 167.0, 161.8, 161.5, 156.9, 156.4, 149.5, 147.6, 140.7, 140.6, 139.0, 139.8, 136.2, 135.4, 135.3, 134.9, 132.4, 131.8, 131.7, 129.7.

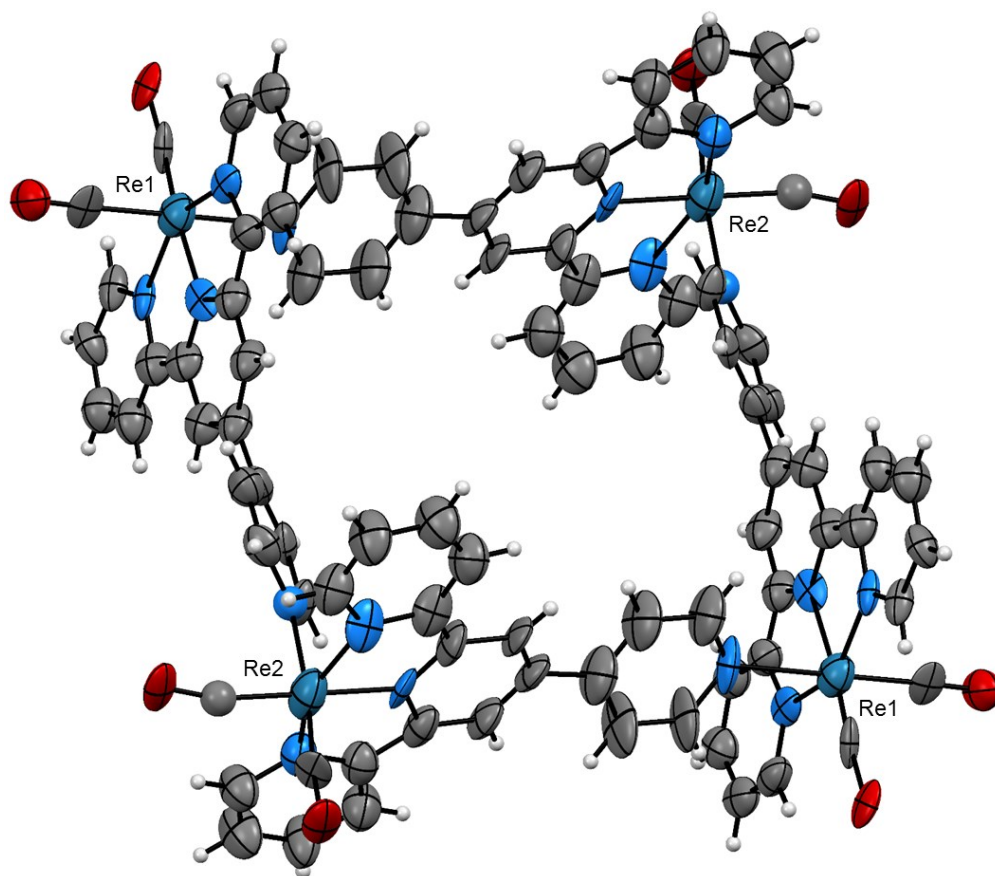
**ESI-MS**: Calcd. for [M-2PF<sub>6</sub>]<sup>+2</sup>: 1250.09763, Found: 1250.10666, Diff.: 7.2 ppm, calcd. for [M-3PF<sub>6</sub>]<sup>+3</sup>: 785.07684, Found: 785.08305, Diff.: 7.2 ppm

**Elemental Analysis**: Calcd. for C<sub>88</sub>H<sub>56</sub>N<sub>16</sub>Re<sub>4</sub>O<sub>8</sub>P<sub>4</sub>F<sub>24</sub>·2H<sub>2</sub>O : C, 37.40; H, 2.14; N, 7.93. Found : C, 37.05; H, 1.93.; N, 7.71.

#### Crystallographic measurements:



**Figure S2.** X-ray structure of complex 4. Thermal ellipsoid are shown with a 50% probability.



**Figure S3.** X-ray structure of complex **6**. Thermal ellipsoid are shown with a 50% probability. Counter-anions (4 PF<sub>6</sub>) were omitted for clarity.

**Table S1** Crystallographic data for complexes **4** and **6**.

Compound	<b>4</b>	<b>6</b>
CCDC Number	1017263	1017619
Formula	[C <sub>27</sub> H <sub>19</sub> N <sub>5</sub> O <sub>2</sub> Re][PF <sub>6</sub> ](H <sub>2</sub> O)	[C <sub>88</sub> H <sub>56</sub> N <sub>16</sub> O <sub>8</sub> Re <sub>4</sub> ][PF <sub>6</sub> ] <sub>4</sub>
M <sub>w</sub> (g/mol); F(000)	776.64; 1544	2790.21; 5344
T (K); Wavelength	100 ; 1.54178	100 ; 1.54178
Crystal System	Monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /n	C2/c
Unit cell : (Å)	<i>a</i> 13.9820(2)	27.917(16)
<i>b</i> (Å)	8.17950(10)	12.514(7)
<i>c</i> (Å)	24.0881(4)	32.083(17)
$\alpha$ (°)	90	90
$\beta$ (°)	104.4190(10)	94.010(9)
$\gamma$ (°)	90	90

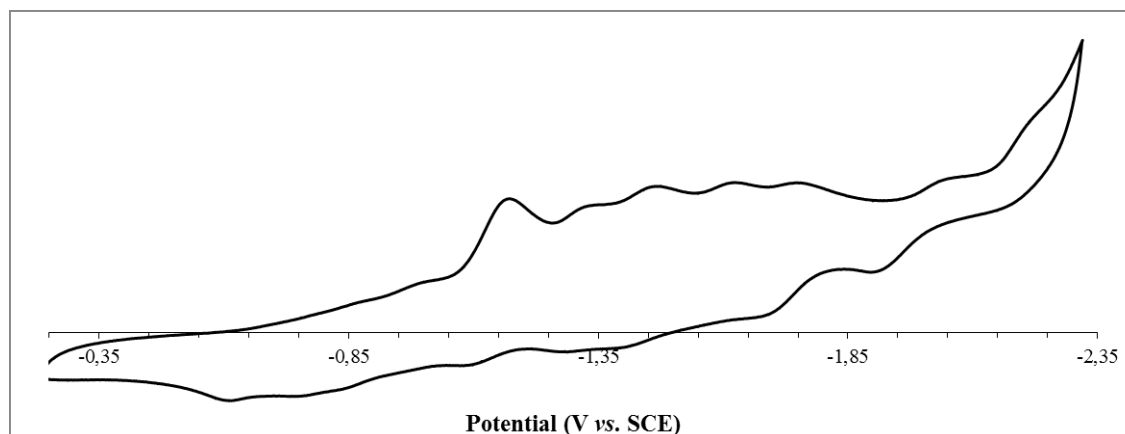
**Table S1 (next)** Crystallographic data for complexes **4** and **6**.

V (Å <sup>3</sup> ); Z; d <sub>calcd.</sub> (g/cm <sup>3</sup> )	2668.08(7); 4; 1.978	11181(11); 1.658
θ range (°); completeness	3.34-70.60; 0.973	1.27-16.11; 0.948
Collected reflection; R <sub>σ</sub>	99183; 0.0091	9905; 0.1580
Unique reflections; R <sub>int</sub>	5025; 0.0274	2641; 0.1522
μ (mm <sup>-1</sup> ); Abs. Corr.	10.237; multi-scan	9.638; multi-scan
R1(F); wR(F <sup>2</sup> ) (I > 2σ(I))	0.0263; 0.0654	0.0916; 0.2344
R1(F); wR(F <sup>2</sup> ) (all data)	0.0263; 0.0654	0.1474; 0.2646
GoF(F <sup>2</sup> )	1.080	0.949
Residual electron density	1.453; -1.267 e <sup>-</sup> /Å <sup>3</sup>	1.110; -0.580 e <sup>-</sup> /Å <sup>3</sup>

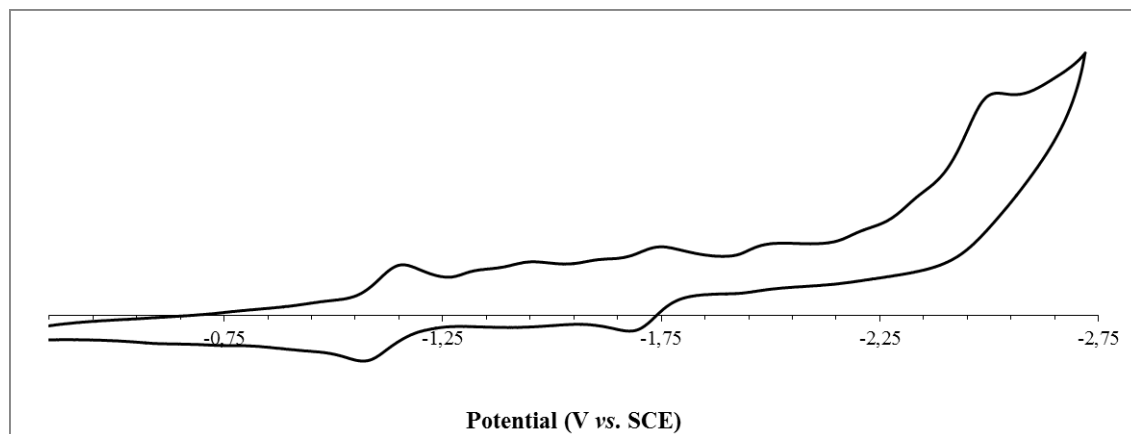
**Cyclic voltammetry:****Table S2** Electrochemical data for the tpy-κ<sup>2</sup>N and tpy-κ<sup>3</sup>N complexes. Values in parenthesis indicate the difference between the anodic and cathodic peak in mV.

Cmpd	$E_{1/2}^{Ox}$ <sup>a</sup>			$E_{1/2}^{Red}$ <sup>a</sup>									
	1	1.41 <sup>b</sup>	0.76 (119)	-	-0.88 <sup>b</sup>	-0.97 (45)	-1.13 <sup>c</sup>	-1.30 (49)	-1.43 (69)	-1.63 <sup>b</sup>	-1.72 <sup>c</sup>	-1.98 <sup>c</sup>	-2.22 <sup>b</sup>
2	-	0.71 (70)	0.53 (64)	-0.85 (112)	-1.15 <sup>b</sup>	-1.21 (87)	-1.74 <sup>b</sup>	-2.15	-	-	-	-	-
5	-	-	-	-0.69 (43)	-0.78 (52)	-0.86 (56)	-1.31 (67)	-1.43 (75)	-1.58 (82)	-1.70 <sup>b</sup>	-	-	-
6	0.87 (104) <sup>c</sup>	0.71 (60)	0.53 (60)	-0.81 <sup>b</sup>	-0.85 (153)	-1.11 <sup>b</sup>	-1.20 (149)	-2.15 <sup>c</sup>	-	-	-	-	-

<sup>a</sup> Potentials are in volt vs SCE. Cyclic voltammetry was performed in DMF/t-Bu<sub>4</sub>N(PF<sub>6</sub>) (0.1M), recorded at 25 ± 1°C with a sweep rate of 50mV s<sup>-1</sup>. All potentials are corrected vs Fc/Fc<sup>+</sup>. <sup>b</sup> Irreversible; potential is given for the cathodic wave. <sup>c</sup> Quasi-reversible process.

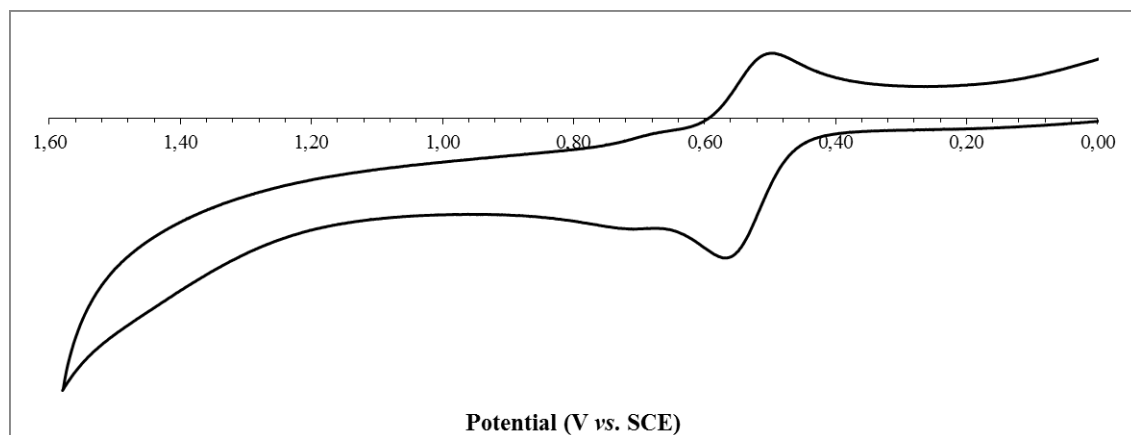
**Compound 1:****Figure S4.** Cyclic voltammogram of complex **1**, with emphasis on the reversibility of the fourth and fifth reduction waves.**Figure S5.** Cyclic voltammogram of complex **1** showing the first nine reduction waves. Upon reduction at high potential (-1.6 and over), degradation related process are observed.



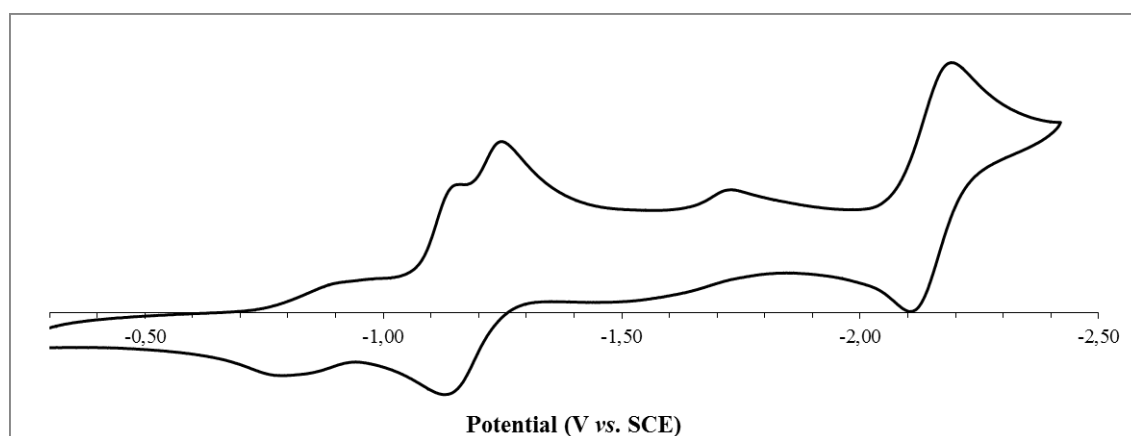


**Figure S6.** Cyclic voltammogram of complex **1** with emphasis on the last irreversible process.

**Compound 2:**

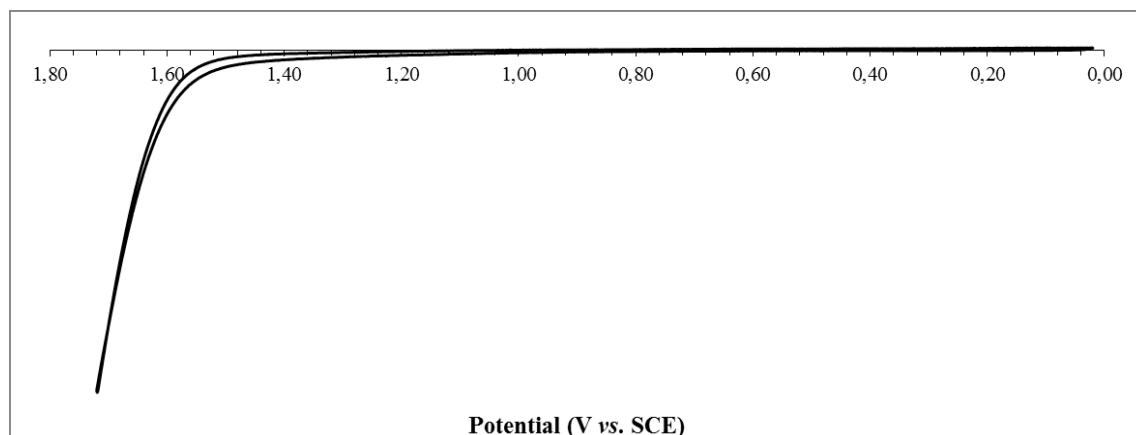


**Figure S7.** Cyclic voltammogram of complex **2** displaying the metal-based oxidation potential.

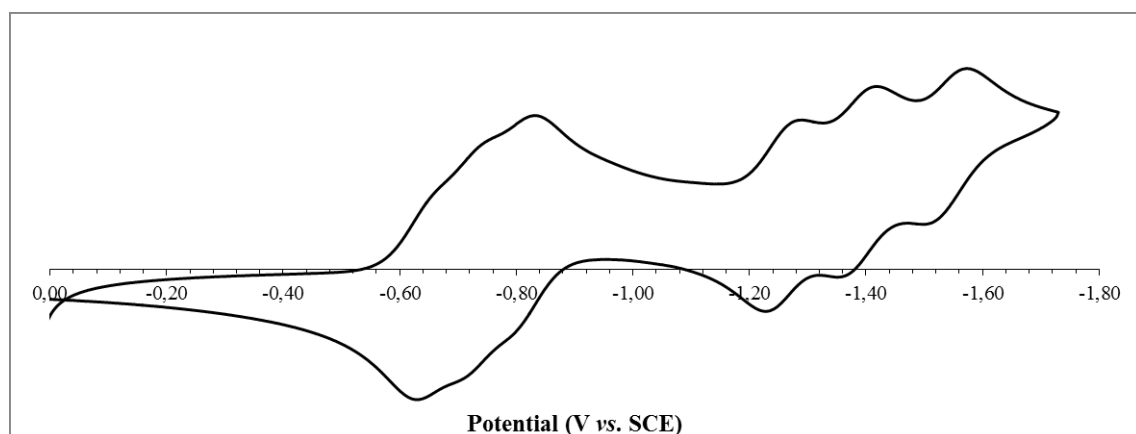


**Figure S8.** Cyclic voltammogram of complex **2** displaying the ligand-based reductions.

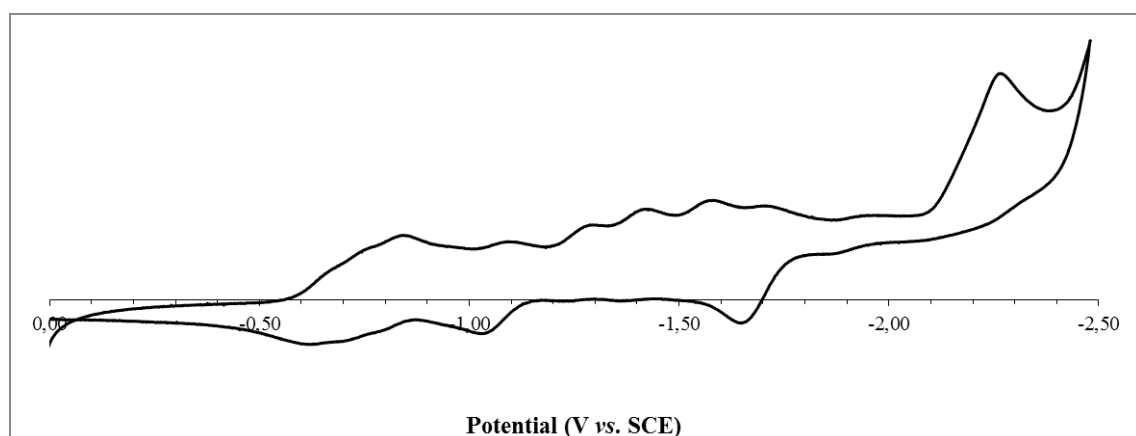
**Compound 5:**



**Figure S9.** Cyclic voltammogram of complex **5**. No evidence of metal-based oxidation at potential lower than the solvent oxidation was found.

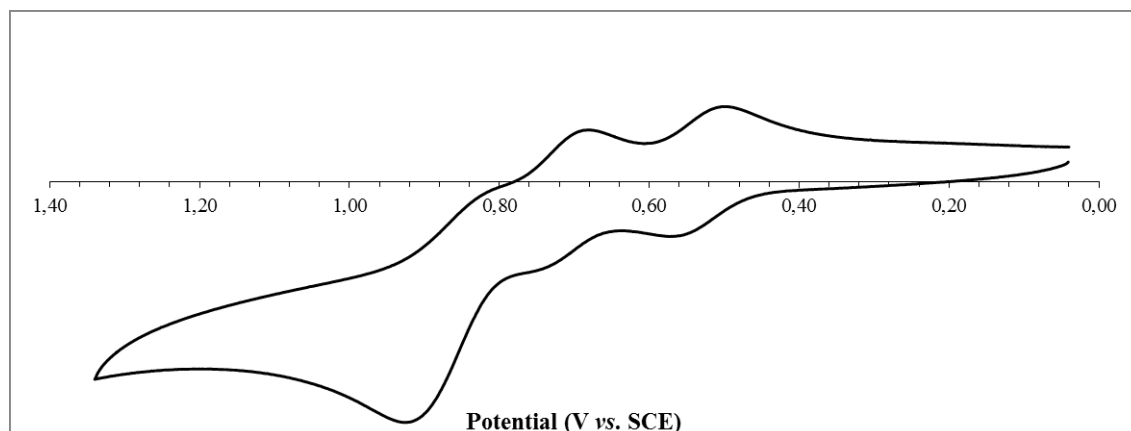


**Figure S10.** Cyclic voltammogram of complex **5** showing the six fully reversible reduction processes.

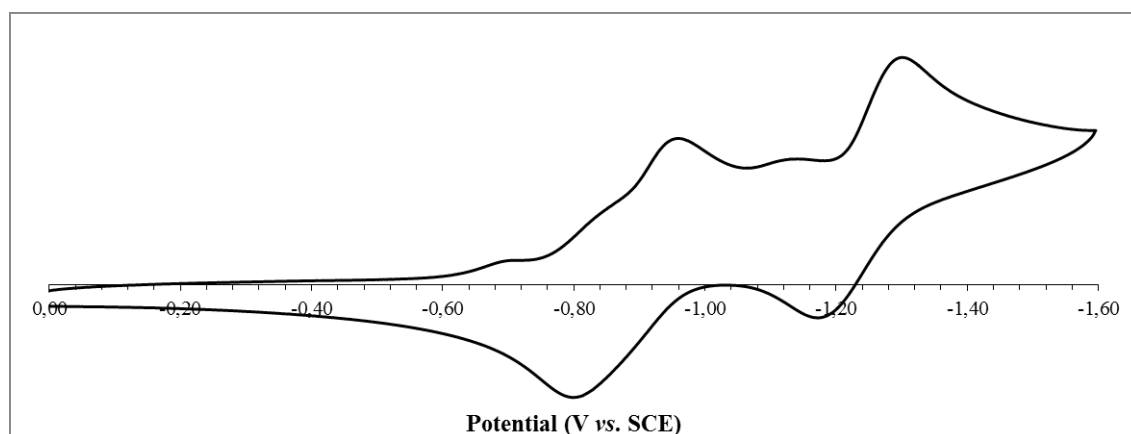


**Figure S11.** Cyclic voltammogram of complex **5**. Upon reduction at high potential (-2.0 and over), degradation related processes are observed.

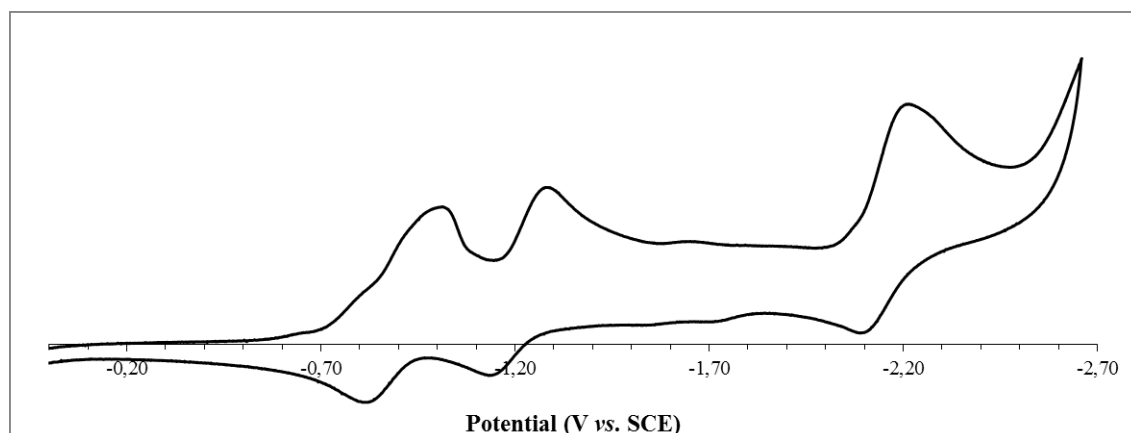
**Compound 6:**



**Figure S12.** Cyclic voltammogram of complex **6** displaying three metal-based oxidation waves. The first two waves are fully reversible while the last one is quasi-reversible.



**Figure S13.** Cyclic voltammogram of complex **6** the ligand-based reduction. The peak at -0.65 V is due to the presence of trace amounts of water.



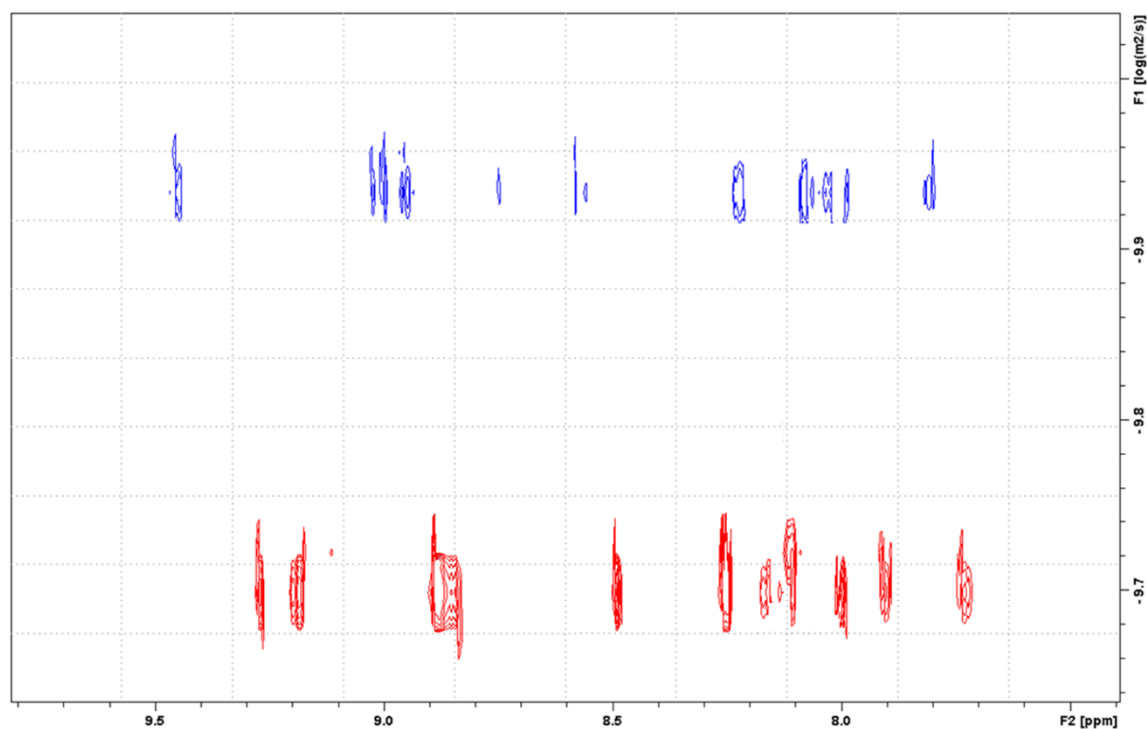
**Figure S14.** Cyclic voltammogram of complex **6** the ligand-based reduction. Upon reduction at high potential (-2.0 and over), degradation related processes are observed.

## Infrared spectroscopy :

**Table S3** Experimental C≡O infrared frequencies

Cmpd	$\nu$ (CO)
1	2019, 1936, 1883
2	1889, 1806
3	1903, 1856, 1833
4	1905, 1834
5	2030, 1909
6	1906, 1833
[Re(py)(CO) <sub>3</sub> (2,2'-bpy)][PF <sub>6</sub> ]	2040, 1950
[Re(py)(CO) <sub>2</sub> (tpy- $\kappa^3$ N)][OTf]	1912, 1841
[Re(CH <sub>3</sub> CN)(CO) <sub>2</sub> (tpy- $\kappa^3$ N)][OTf]	1921, 1848
Re(CO) <sub>2</sub> (tpy- $\kappa^3$ N)Cl	1891, 1798
Re(CO) <sub>3</sub> (tpy- $\kappa^2$ N)Cl	2011, 1924, 1902

## Diffusion-Ordered Spectroscopy :



**Figure S15.** Representative Diffusion-ordered spectroscopy experiment for complexes **1** (red) and **5** (blue) showing the slower diffusion in solution (dmsO-d<sub>6</sub>) of the supramolecular square compared to its precursor.

**Table S4** Experimental DOSY values.

Cmpd	Log D (m <sup>2</sup> /s)	D (m <sup>2</sup> /s)
<b>1</b>	-9.701	1.99x10 <sup>-10</sup>
<b>2</b>	-9.732	1.85x10 <sup>-10</sup>
<b>5</b>	-9.941	1.14x10 <sup>-10</sup>
<b>6</b>	-10.013	9.71x10 <sup>-11</sup>