ADVANCED FUNCTIONAL MATERIALS

Supporting Information

for

Advanced Functional Materials, adfm.200500247

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Supporting information:

1. Experimental Part

1.1 General Remarks

Compounds and Reactants

Synthesis of ligands **μ-1o** and **μ-1c** as well as the corresponding metal complexes **Ru(μ-1o)Ru, Os(μ-1o)Os, Ru(μ-1o)Os, Ru(μ-1c)Ru, Os(μ-1c)Os, and Ru(μ-1c)Os** were described in our previous work.[1] The ligand 4Bpy-Sp-NO_2 (**3**) and the metal complexes $[Ru(bpy)_2(\mathbf{3})]^{2+}$ (**4**) and $[Os(bpy)_2(\mathbf{3})]^{2+}$ (**5**) are described in literature.[2] Compound (**13**) and (**14**) are prepared by a protocol described in literature.[3] The preparation of the chiroptical ligand (**17**) is described in [4]. $[Ru(bpy)_2(\mathbf{17})]^{2+}$, $[Os(bpy)_2(\mathbf{17})]^{2+}$, and $[Re(CO)_3(\mathbf{17})Cl$ were prepared by refluxing the ligand **17** with the appropriate metal source ($Ru(bpy)_2Cl_2$, $(Os(bpy)_2Cl_2$ and $Re(CO)_5Cl$, respectively), for several hours using methoxyethanol for the ruthenium and osmium complexes and toluene for the rhenium complex formation.[5]

All reactions were carried out in oven-dried glassware under a slight positive pressure of argon. All chemicals and reagent grade products were obtained from Fluka, Aldrich and Acros Chemicals and used, unless otherwise noted, without further purification. Solvents were distilled from the appropriated drying agents following literature procedures. The palladium catalysts ($Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ and $Pd(OAc)_2$ were purchased from Stem Chemicals and were kept under argon.

Chromatography

Column chromatography was performed using silica gel, 230-400 or 400-600 mesh from *Chemie Brunschwig AG.* Preparative plates were applied by using glass sheets recoated with silica gel 60 F_{254} with layer thickness of 2 mm purchased from *Merck*. Thin layer chromatography (TLC) was performed using aluminium sheets coated with silica gel 60 F_{254} purchased from *Merck*. Metal complex purification was performed by using the described technique in [6].

Melting Point

Melting points were determined on a *Büchi 510* apparatus and were uncorrected.

NMR

All products were characterized by ^1H NMR and ^{13}C NMR, on a *Varian Gemini-300* (300.075 MHz, for ^1H NMR and 75.4 MHz for ^{13}C), on a *Bruker Advance DRX-400* (400.13 MHz, for ^1H NMR and 100.62 MHz for ^{13}C) and on a *Bruker Advance DRX-500* (500 MHz, for ^1H NMR and 125.75 MHz for ^{13}C) spectrometer. Chemical shift are given in ppm using the solvent itself as internal standard. The chemical shifts are expressed as δ values and the coupling constants (*J*) are given in Hertz. The assignments of 1H and 13C signals were performed by COSY, ROESY, and HETCOR (HMQC/HMBS) techniques. The assignment of the NMR signals is referred to the carbon numbering of molecules at the end of the synthesis description.

MS
Mass spectra were recorded either on a *Vacuum Micromass VG 70/70E* (FAB ionisation, nitrobenzylalcohol matrix of the sample) or on a *HP 5988A Quadrupol* (EI ionisation, 70 eV) mass spectrometer. ESI and high-resolution mass spectra were recorded on a *Bucker FTMS 4.7T BioAPEXII spectrometer.*

GC/MS
GC analyses were recorded on a *FISONS Instruments HRGC MEGA 2 Series* equipped with an *Optima-1701* column (0.25 μm, 25 m x 0.32 mm; Marcherey-Nagel). GC-MS analyses were recorded on a *ThermeQuest Finnigan VOYAGER GS/MS Trace GC 2000 Series* equipped with an *Optima-5-MS* column (0.25 μm, 25 m x 0.32 mm; Marcherey-Nagel).

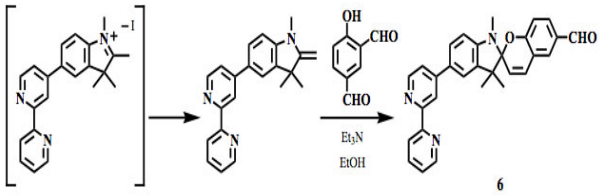
Elementary Analysis
Elementary analyses were performed at the University of Applied Sciences of Fribourg (Switzerland) using a *Carlo Erba CE Instrument, EA1110*.

Electronic Absorption and Luminescence Measurements
Absorption spectra were recorded on a *Perkin-Elmer Lambda 40* spectrometer and Hewlett Packard 8543 diode array spectrophotometer with spectral range of 190-1100 nm and a 2 nm spectral resolution. Wavelengths are given in nm and molar absorption coefficients (ε) in $M^{-1}cm^{-1}$.
Emission spectra were recorded on a Perkin-Elmer Luminescence LS 50B spectrometer. Continuous-wave (CW) emission spectra were recorded on a SPEX Fluorolog III equipped with a Xe arc light source and containing two double monochromators (excitation and emission). The detector is a Peltier-cooler R928 (Hamamatsu) photomultiplier tube. The electronic absorption and emission measurements were performed in spectroscopic grade acetonitrile and THF (Fluka) as received. Deaerated solutions were prepared by freeze-pump-thaw technique on a vacuum line.

Irradiation

Irradiation experiments were carried using a 50-500 W mercury arc lamp source from *Thermo Oriel*.

1.1 Synthesis of 5'-(2,2'-bipyrid-4-yl)-1',3'-dihidro-6-formyl-1',3',3'-trimethylspiro [2H-1-benzopyran-2,2'-(2H)-indole]; 4bpy-Sp-CHO (6)



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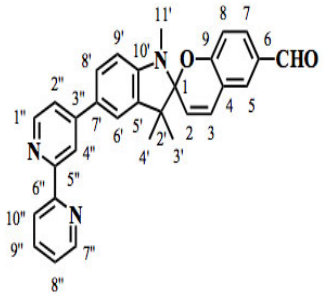
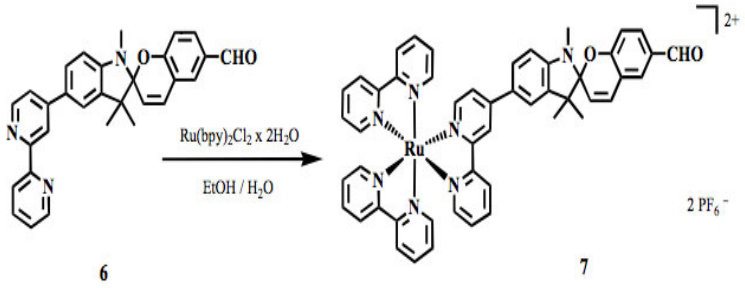
1,3,3-Trimethyl-2-methylene-5-(2,2'-pyridin-4-yl)indoline[6] (250 mg, 0.55 mmol) and 5-salicylaldehyde (83 mg, 0.55 mmol), were dissolved in 10 ml of freshly distilled ethanol and heated at 80°C under argon. To the boiling solution, Et_3N (0.1 ml) was added through a septum and the refluxing was maintained until TLC (SiO_2, CH_2Cl_2/MeOH/Et_3N, 99/1/0.5) did not show further changes (20 hours). After this period the solvent was removed under vacuum and the crude mixture was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 99/1) to yield the compound 4bpy-Sp-CHO (**6**) (150 mg, 59 %).

^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): 1.17 (s, 3H, H-C(3')), 1.30 (s, 3H, H-C(4')), 2.74 (s, 3H, H-C(11')), 5.73 (d, 1H, ^{3}J=9.9, H-C(2')), 6.57 (d, 1H, ^{3}J=8.2, H-C(8)), 6.76 (d, 1H, ^{3}J=8.2, H-C(9')), 6.88 (d, 1H, ^{3}J=10.5, H-C(3)), 7.26 (ddd, 1H, ^{3}J=5.0, ^{4}J=1.4, H-C(8'')),7.46 (d, 1H, ^{4}J=1.8 H-C(6')), 7.49 (dd, 1H, ^{3}J=5.5, ^{4}J=1.8, H-C(2'')), 7.57 (m, 3H, H-C(5), H-C(7) and H-C(8')), 7.77 (td, 1H, ^{3}J=7.7, ^{4}J=1.8, H-C(9'')), 8.43 (d, 1H, ^{3}J=8.2, H-C(10'')), 8.60 (m, 3H, H-C(1'') and H-C(4'') and H-C(7'')), 9.77 (s, 1H, H-CO).
^{13}C-NMR (100 MHz, $CDCl_3$, δ in ppm): 20.4, 26.3, 29.3, 31.2, 52.5, 53.8, 106.1, 107.7, 116.1, 118.7, 119.3, 120.5, 120.9, 121.3, 122.0, 124.3, 127.9, 128.8, 129.4, 129.5, 130.1, 132.9, 137.5, 137.9, 149.5, 149.6, 159.9, 190.8.
MS (ESI): m/z 460.20 $[M+H]^+$.

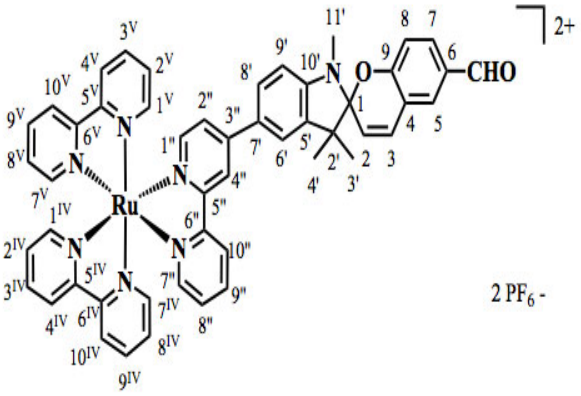


1.2 Synthesis of $[Ru(bpy)_2(6)] (PF_6)_2$ (7)



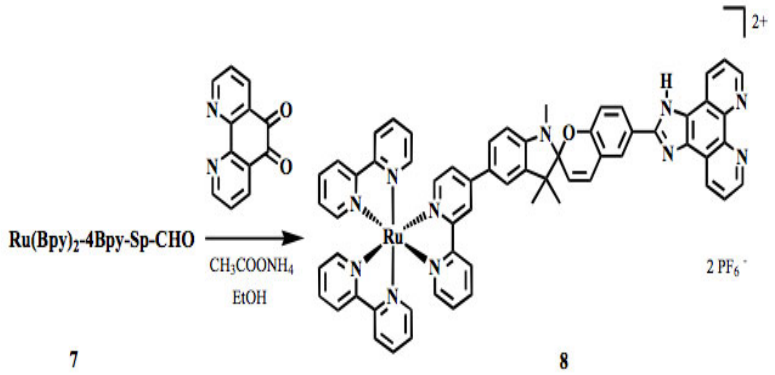
$Ru(bpy)_2Cl_2 \cdot H_2O$ (358 mg, 0.690 mmol), 4bpy-Sp-CHO (**6**) (288 mg, 0.627 mmol) and $EtOH/H_2O$ (6 ml; 3:1, v/v) were heated at 90°C under argon atmosphere during 20 h. The solvent was removed under reduced pressure, the residue was dissolved in water, NH_4PF_6 (1 g) was added and the resulting orange precipitate was isolated by suction filtration. The crude product was dissolved in acetone (3 ml), and purified on a column of neutral aluminium oxide with acetone/water, 99/1 as eluant. The orange band was isolated and the solvent removed under reduced pressure getting an orange solid. The product was further purified by plate chromatography (SiO_2) using a mixture of $ACN/H_2O/MeOH/KNO_3$, 40/10/10/1 as eluant. The main orange red band was scratched out and isolated by solution of 1% NH_4PF_6 in acetone. After adding water, the organic solvent was removed and an orange red powder was recovered by filtration. The solid compound was washed by water and dried by diethyl ether to yield $[Ru(bpy)_2$-4bpy-Sp-CHO$] (PF_6)_4$ (**7**) (580 mg, 80 %) as a orange red solid.

^{1}H-NMR (500 MHz, CD_3CN, δ in ppm): 1.22 (s, 3H, H-C(3')), 1.35 (s, 3H, H-C(4')), 2.81 (s, 3H, H-C(11')), 5.89 (d, 1H, ^{3}J=10.4, H-C(2)), 6.74 (dd, 1H, ^{3}J=8.2, ^{4}J=3.0, H-C(8) and H-C(9')), 7.09 (d, 2H, ^{3}J=10.4, H-C(3)), 7.37 – 7.42 (m, 5H, H-C(2'''), H-C(8'') - H-C(8^{IV}) and H-C(2^{IV})), 7.59 – 7.62 (m, 2H, H-C(2'') and H-C(4'')), 7.66 – 7.68 (m, 2H, H-C(7) and H-C(6')), 7.71 – 7.81 (m, 7H, H-C(3'''), H-C(3^{IV}), H-C(5), H-C(9'') - H-C(9^{IV}) and H-C(8')), 8.02 – 8.05 (m, 5H, H-C(4'''), H-C(10'') - H-C(10^{IV}) and H-C(4^{IV})), 8.48 – 8.51 (m, 4H, H-C(1'''), H-C(1^{IV}), H-C(7''') and H-C(7^{IV})), 8.69 – 8.70 (m, 2H, H-C(1'') and H-C(7'')), 9.82 (s, 1H, H-CO).
^{13}C-NMR (125 MHz, CD_3CN, δ in ppm): 20.1, 26.1, 29.1, 52.9, 106.8, 108.4, 116.3, 119.5, 120.2, 120.8, 121.6, 121.8, 124.5, 125.2, 127.2, 128.4, 128.5, 129.0, 129.6, 130.1, 131.2, 132.9, 138.6, 138.7, 139.1, 150.7, 151.4, 152.1, 152.6, 152.6, 157.9, 158.0, 158.3, 159.9, 191.7.
MS (ESI): m/z 1018.24 $[M\text{-}PF_6]^+$, 436.62 $[(M\text{-}2PF_6)/2]^{2+}$.

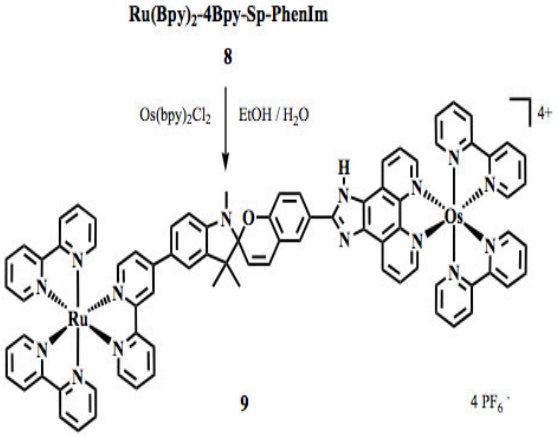


1.3 Synthesis of [Ru(bpy)$_2$-4bpy-Sp-PhenIm-(bpy)$_2$Os] (PF$_6$)$_4$ (9)

a) Synthesis of [Ru(bpy)$_2$-4bpy-Sp-PhenIm] (PF$_6$)$_2$ (**8**)[7]



A stirred mixture of Ru(bpy)$_2$-4bpy-Sp-CHO (**7**) (500 mg, 0.430 mmol), 1,10-phenanthroline-5,6-dion[8,9] (993 mg, 4.7 mmol) and ammonium acetate (662 mg) in 140 ml of EtOH was heated at 90^{o}C under argon. The refluxing was maintained until TLC (SiO_2, CH_2Cl_2/MeOH/Et_3N, 96/4/0.25) did not show further changes (20 hours). After this period the precipitated product was filtered off and vacuum dried. This crude mixture was dissolved in acetone and a saturated aqueous solution of NH_4PF_6 was added. The acetone was removed under reduced pressure from the water phase and the precipitated solid was filtered off, washed with water and diethyl ether. The crude product [Ru(bpy)$_2$-4bpy-Sp-PhenIm] $(PF_6)_2$ (**8**) was used without further purification.



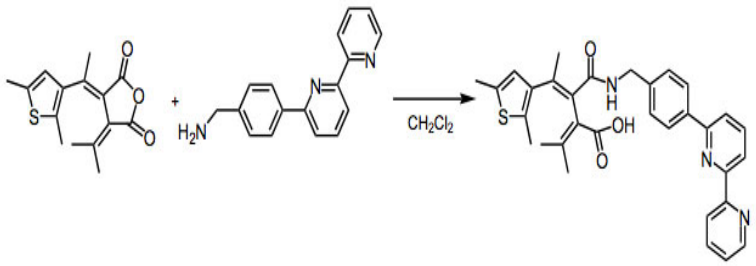
b) Synthesis of [Ru(bpy)$_2$-4bpy-Sp-PhenIm-Os(bpy)$_2$] $(PF_6)_4$ (**9**)

Os(bpy)$_2$Cl$_2$ (247 mg, 0.400 mmol), 4bpy-Sp-PhenIm (**8**) (430 mg, 0.400 mmol) and EtOH/H$_2$O (6 ml; 3:1, v/v) were heated at 90^{o}C under argon atmosphere during 20 h. The solvent was removed under reduced pressure, the residue was dissolved in acetone/water, NH_4PF_6 (1 g) was added and the resulting orange precipitate was isolated by suction filtration. The crude product was dissolved in acetone (3 ml), and purified by column chromatography (SiO_2, ACN/H$_2$O/MeOH/KNO_3, 40/10/10/1). The green/brown fraction was isolated and the solvent was removed under reduced pressure giving a green/brown solid. The product was further purified by plate chromatography (SiO_2) using a mixture of ACN/H$_2$O/MeOH/KNO_3, 40/10/10/1 as eluant. The main green/brown band was scratched out and isolated by solution of 1% NH_4PF_6 in acetone. After adding water, the organic solvent was removed and a green/brown precipitate was recovered by filtration. The solid was washed by water and dried by diethyl ether to yield the compound [Ru(bpy)$_2$-4bpy-Sp-PhenIm-Os(bpy)$_2$] $(PF_6)_4$ (**9**) (300 mg, 35 %).

^{1}H-NMR (500 MHz, CD_3CN, δ in ppm): 1.26 (s, 3H), 1.41 (s, 3H), 2.86 (s, 3H), 5.97 (d, 1H, ^{3}J=10.3), 6.77 (d, 1H, ^{3}J=8.4), 6.89 (d, 1H, ^{3}J=8.6), 7.09 – 7.13 (m, 2H), 7.21 (d, 1H, ^{3}J=10.3), 7.36 – 7.48 (m, 10H), 7.60 – 7.64 (m, 2H), 7.69 – 6.70 (m, 1H), 7.73 – 7.83 (m, 12H), 7.89 – 7.92 (m, 2H), 8.02 – 8.09 (m, 7H), 8.19 (dd, 1H, ^{3}J=8.6, ^{4}J=2.1), 8.26 (d, 1H, ^{4}J=2.1), 8.47 – 8.53 (m, 8H), 8.66 (dd, 1H, ^{3}J=4.4, ^{4}J=1.1), 8.70 – 8.71 (m, 2H), 8.76 (dd, 1H, ^{3}J=8.2, ^{4}J=1.3).

^{13}C-NMR (125 MHz, CD_3CN, δ in ppm): 20.1, 20.1, 20.2, 25.9, 26.2, 29.1, 29.2, 32.4, 52.9, 106.7, 108.5, 116.8, 117.4, 117.7, 119.8, 119.9, 120.0, 120.7, 121.2, 121.3, 121.6, 121.8, 124.5, 125.1, 125.2, 125.3, 125.4, 125.5, 125.5, 126.1, 126.6, 126.8, 127.2, 127.6, 127.8, 127.8, 128.4, 128.5, 128.6, 128.8, 128.9, 128.9, 129.0, 129.0, 129.1, 129.7, 130.1, 130.5, 131.8, 137.6, 137.9, 138.1, 138.2, 138.4, 138.6, 138.7, 138.8, 130.1, 145.1, 149.2, 149.8, 150.7, 151.4, 151.9, 152.1, 152.2, 152.4, 152.6, 152.7, 152.7, 157.9, 158.0, 158.0, 158.1, 158.3, 158.5, 159.8, 159.9, 159.9, 160.0, 160.1, 166.6.
MS (ESI): m/z 929.15 $[(M-2PF_6)/2]^{2+}$, 571.11 $[(M-3PF_6)/3]^{3+}$, 392.09 $[(M-4PF_6)/4]^{4+}$.
HRMS (ESI): m/z $[(M-2PF_6)/2]^{2+}$ calcd for $C_{85}H_{71}F_{12}N_{15}OOs(190)P_2Ru(102)$: 928.16677 found 928.16677 and calcd for $C_{85}H_{71}F_{12}N_{15}OOs(192)P_2Ru(102)$: 929.16788 found 929.16788; $[(M-3PF_6)/3]^{3+}$ calcd for $C_{85}H_{71}F_{18}N_{15}OOs(192)P_3Ru(102)$: 571.12489 found 571.12489 and calcd for $C_{85}H_{71}F_{18}N_{15}OOs(190)P_3Ru(102)$: 570.45724 found 570.45724; $[(M-4PF_6)/4]^{4+}$ calcd for $C_{85}H_{71}N_{15}OOs(192)Ru(102)$: 392.10193 found 392.10193 and calcd for $C_{85}H_{71}N_{15}OOs(190)Ru(102)$: 391.60136 found 391.60136.

1.4 Synthesis of (3E)-1-[4-(2,2'-bipyridine-6yl)benzyl]-3-[1-(2,5-dimethylthien-3-yl) ethylidene]-4-(1-methylethylidene)pyrrolidine-2,5-dione ((E)-12o)

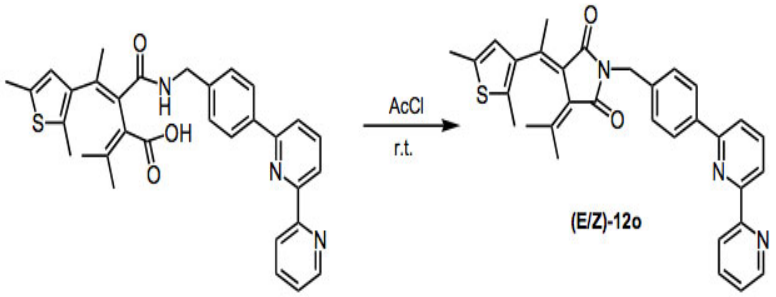


Step a)

The (Z)-2-(1-(2,5-dimethylthiophen-3-yl)ethylidene)-3-(propan-2-ylidene)succinic anhydride (0.7 g, 2.54 mmol) and 4-(4-aminophenyl)-2,2'-bipyridine (0.66 g, 2.53 mmol) were dissolved in 50 ml of dichloromethane, and treated at 40°C during 3 hours. The solvent was

then evaporated, and the crude product was purified by column chromatography on silica gel (CH_2Cl_2 / MeOH 9:1) to yield 1.22 g (89%) of the monoamidated product.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 1.8 (s, 3 H), 1.9 (s, 3 H), 2.1 (s, 3 H), 2.2 (s, 3 H), 2.3 (s, 3 H), 4.3 (s, 2 H), 5.8 (s, 1 H), 6.4 (s, 1 H), 7.1 (d, *J*=8.1 Hz, 2 H), 7.3 (m, 1 H), 7.5 (dd, *J*=3.5 Hz, 1 H), 7.7 (d, *J*=7.6 Hz, 2 H), 7.8 (m, 1 H), 8.4 (d, *J*=8.1 Hz, 1 H), 8.6 (s, 1 H), 8.7 (m, 2 H).
^{13}C NMR (101 MHz, $CDCl_3$, δ in ppm): 13.3, 15.1, 21.8, 30.9, 44.0, 118.8, 121.3, 121.5, 123.9, 124.4, 126.2, 127.5, 128.5, 133.1, 136.6, 137.0, 137.5, 137.9, 138.3, 148.6, 149.2, 149.7, 156.0, 156.7, 171.4.
MS (EI): m/z 538.21 [M+H$^+$].



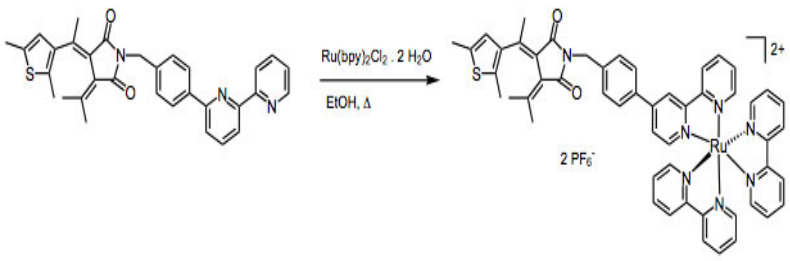
Step b)

The monoamide (1.18 g, 2.19 mmol) was then treated by acetyl chloride (10 ml) at room temperature during 1 hour. The remaining solvent, but also the resulting acetic acid were then removed under vacuum and the residue was neutralized by a mixture of ice and saturated solution of $NaHCO_3$; then, the organic product was extracted with CH_2Cl_2 in a separating funnel, dried with magnesium sulfate and the solvent was evaporated. The crude product was purified by a Flash-column chromatography on silica gel, using a mixture of ethyl acetate/methanol in a ratio 9:1 to give 950 mg **(E/Z)-12o** (1.84 mmol), which corresponds to 84% yield. The **(E/Z)-12o**-mixture was transformed by irradiation at 313 nm into **12c** (the closed form) and reopened by irradiation with white light (450 nm cut-off filter) to form the

pure **(E)-12o** ligand.

^{1}H NMR (400 MHz, CD_2Cl_2, δ in ppm): 1.2 (s, 3 H), 2.1 (s, 3 H), 2.3 (s, 3 H), 2.4 (s, 3 H), 2.6 (s, 3 H), 4.8 (s, 2 H), 6.5 (s, 1 H), 7.3 (m, 2 H), 7.5 (d, 1 H),7.5 (d, *J*=8.1 Hz, 2 H), 7.6 (d, *J*=7.1 Hz, 2 H), 7.7 (d, *J*=8.6 Hz, 2 H), 8.5 (d, *J*=8.1 Hz, 2 H).
^{13}C NMR (101 MHz, CD_2Cl_2, δ in ppm): 15.1, 15.5, 22.0, 26.6, 27.3, 41.4, 119.2, 121.6, 122.1, 124.4, 124.6, 125.7, 127.8, 127.9, 129.5, 129.8, 134.3, 135.9, 137.8, 138.1, 138.8, 141.1, 148.9, 149.3, 149.8, 150.3, 155.4, 156.7, 157.3, 166.1, 168.7, 169.1.
MS (EI): m/z 520.2 [M+H$^+$].

1.5 Synthesis of the metal complex [Ru(bpy)$_2$((E)-12o)](PF$_6$)$_2$

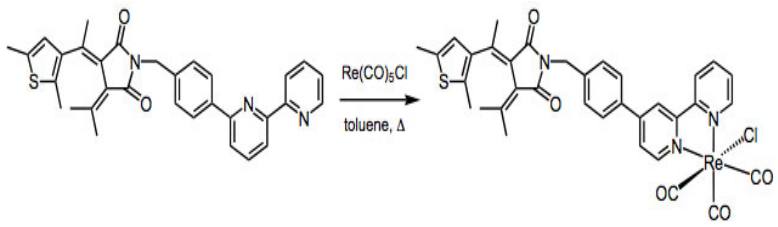


In a two-necked 50 mL flask, under argon atmosphere, **(E)-12o** (60 mg, 0.11 mmol) and $Ru(bpy)_2Cl_2$ (61 mg, 0.13 mmol) were suspended in deareated ethanol (30 ml). The mixture was brought to reflux during 3 hours. Then, the heating was stopped, and ethanol was evaporated. The remaining product was solubilized in water, and washed with CH_2Cl_2. Adding NH_4PF_6 then precipitated the complex in the water-phase, and the resulting solid was isolated by filtration under reduced pressure (149 mg). This solid was then air-dried overnight, and purified by column-chromatography (SiO_2) using a mixture of acetonitrile/ methanol/saturated solution of KNO_3 in a ratio 40:10:10 to give the ruthenium complex of

(E)-12o (109 mg, 0.09 mmol) in 78% yield.

^{1}H NMR (400 MHz, CD_3CN, δ ppm): 1.2 (s, 3 H), 2.0 (s, 6 H), 2.1 (s, 3 H), 2.4 (d, *J*=1.0 Hz, 3 H), 4.7 (d, *J*=48.0 Hz, 2 H), 6.6 (d, *J*=1.0 Hz, 1 H),7.5 (d, *J*=8.3 Hz, 1 H), 7.5 (m, 1 H), 7.6 (m, 1 H), 7.7 (m, 1 H), 7.8 (m, 2 H), 7.8 (t, *J*=2.0 Hz, 1 H), 7.8 (d, *J*=1.8 Hz, 1 H), 8.6 (dd, *J*=7.5, 3.4 Hz, 1 H), 8.7 (dd, *J*=6.8, 1.8 Hz, 2 H).
^{13}C NMR (101 MHz, CD_3CN, δ ppm): 14.1, 14.7, 14.9, 15.0, 25.5, 118.2, 122.8, 125.2, 125.3, 125.7, 126.3, 126.8, 128.5, 128.6, 129.5, 129.7, 134.5, 135.7, 136.0, 138.1, 138.6, 138.7, 140.9, 141.3, 150.2, 152.5, 152.6, 157.9, 158.2, 168.8, 168.9, 169.3.
MS(ESI): m/z 1078.2 $[M\text{-}PF_6^-]^+$.

1.6 Synthesis of the metal complex [$Re(CO)_3Cl$(E-12o)]

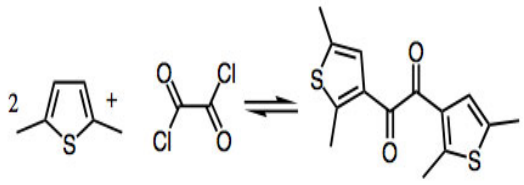


In a two-necked 20 ml flask, under argon atmosphere, **(Z)-12o** (60 mg, 0.11 mmol) and $Re(CO)_5Cl$ (45 mg, 0.12 mmol) were mixed in deareated toluene (6 ml). The mixture was brought to reflux, TLC followed the progress of the reaction, and heating was stopped after 22 hours. The solvent was evaporated; the neutral complex was isolated without any further work-up, and purified by silica-gel column chromatography using CH_2Cl_2/MeOH (9:1) as eluant. The rhenium complex was finally obtained (68 mg, 0.08 mmol) in 68% yield.

^{1}H NMR (400 MHz, CD_2Cl_2, δ in ppm): 1.3 (s, 3 H), 2.0 (s, 3 H), 2.1 (s, 3 H), 2.3 (s, 3 H), 2.4 (s, 3 H), 4.7 (s, 2 H), 6.5 (s, 1 H), 7.5 (d, *J*=8.1 Hz, 3 H), 7.5 (d, *J*=8.3 Hz, 1 H), 7.6 (dd,

J=5.8, 1.8 Hz, 1 H), 7.6 (m, 2 H), 7.7 (d, *J*=8.3 Hz, 1 H), 8.0 (m, 1 H), 8.3 (d, *J*=8.3 Hz, 1 H), 8.9 (m, 2 H).
^{13}C NMR (101 MHz, CD_2Cl_2, δ in ppm): 14.3, 14.9, 15.2, 21.8, 25.6, 121.1, 123.4, 123.9, 124.2, 124.5, 124.8, 124.9, 125.4, 125.9, 126.1, 127.4, 127.8, 127.9, 134.1, 135.6, 137.0, 137.5, 139.5, 140.8, 150.2, 151.3, 153.3, 156.0, 156.3, 168.2, 168.4, 168.8.
MS (ESI): m/z 790.14 $[M\text{-}CO]^+$.

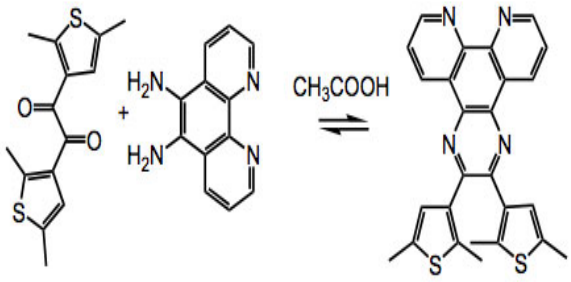
1.7 Synthesis of 1,2-Bis(2,5-dimethylthien-3-yl)ethanedione[10]



Oxalyl chloride (3.7 ml, 43.9 mmol, 1eq) in 1,2-dichloroethane (20 ml) was added under stirring and cooling to a suspension of $AlCl_3$ (14 g, 105 mmol, 2,4 eq) in 1,2-dichloroethane (30 ml) under argon. The resulting solution was cooled between –20 to –30°C and 2,5-dimethylthiophene (10 ml, 88 mmol. 2 eq) was added drop wise. The reaction mixture was maintained at this temperature for 30 min and then 1,2-dichloroethane (30 ml) and anhydrous pyridine (40 ml) were added. During that step, a precipitation of $Al(OH)_3$ was observed. The mixture was stirred during 1 h and warmed up to room temperature. Cold water (10 ml) was carefully added to the reaction mixture and acidic water (HCl, 2N, 20 ml) was added to remove the solid $Al(OH)_3$. The water layer was extracted with 1,2-dichloroethane (3x50 ml). The combined organic phase was washed twice with water (2x50 ml), dried (Na_2SO_4), filtered and the solvent was evaporated in vacuum to yield a black oil. The crude product was purified by column chromatography (hexane/AcOEt 9:1, rf: 0.5) yielding (1.2 g, 10 %).

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.38 (6H, s, CH_3), 2.73 (6H, s, CH_3), 6.92 (2H, s, H_{het}).
^{13}C NMR (101 MHz, $CDCl_3$, δ ppm): 14.9, 16.0, 126.9, 131.8, 136.3, 151.7, 189.2.
MS (EI+): 278.1 (278.0 for M^+).

1.8 Synthesis of 6,7-bis(2,5-dimethylthien-3-yl)pyrazino[2,3-f]-[1,10]phenanthroline[11]

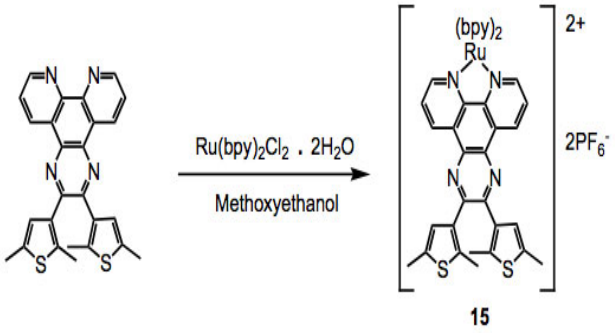


To a deaerated solution of 1,2-diketone (140 mg, 0.5 mmol, 1eq.) in acetic acid (15 ml) was added phenanthroline-5,6-diamin[13] (106mg, 0.5mmol, 1eq) in one portion. The reaction mixture was stirred for one hour at 60°C. Water (15 ml) was added and the solution was neutralized with Na_2CO_3. The product was then extracted with CH_2Cl_2 (3x50 ml). The collected organic phase was dried with Na_2SO_4, filtered and the solvent removed. The crude product was purified by chromatographic column (CH_2Cl_2/TEA 95:5, then CH_2Cl_2/MeOH/TEA 30:1:1) to yield 70 mg (31%) of product.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.34 (6H, s, CH_3), 2.40 (6H, s, CH_3), 6.61 (2H, s, $H_{thiophene}$), 7.73 (2H, dd, $^3J_1$=4.5 Hz, $^3J_2$=8.2 Hz, $H_{phenanthroline}$), 9.23 (2H, dd, $^3J_1$=4.3 Hz, $^4J_3$=1.6 Hz, $H_{phenanthroline}$), 9.44 (2H, dd, $^4J_3$=1.4 Hz, $^3J_2$=8.2 Hz, $H_{phenanthroline}$).

^{13}C NMR (101 MHz, $CDCl_3$, δ ppm): 14.3, 15.2, 123.9, 127.2, 127.2, 133.2, 135.4, 135.8, 137.3, 138.0, 147.5, 149.6, 151.9.
MS (ESI): *m/z* 453.12 (M+1 : 453.11).
HRMS (ESI) calcd for $C_{26}H_{21}N_4S_2$: M+1, 453.1202; found : *m/z* 453.1199.

1.9 [Ru(bpy)$_2$(6,7-Di(2,5-dimethylthien-3-yl)pyrazino [2,3-f] [1,10]phenanthroline)](PF$_6$)$_2$ (15)[3]



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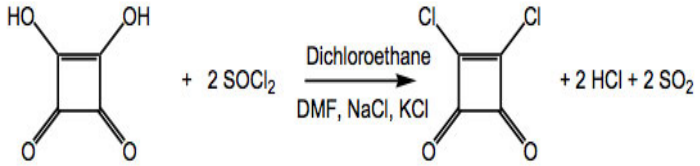
In a 50ml, one necked, round-bottem flask were added the ligand (40 mg, $8.84 \cdot 10^{-2}$ mmol, 1 eq), $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (50 mg, $9.72 \cdot 10^{-2}$ mmol, 1.1 eq) and methoxyethanol (20 ml). The solution was refluxed under argon during 7 h. The solvent was removed under vacuum and the residue was taken up with a solution of NH_4PF_6 (5 ml, 10 g/150 ml). The precipitate was collected by filtration and purified on silica gel plate (acetonitrile/methanol/water/aqueous solution of potassium nitrate 100:10:10:1) yielding the final product (80 mg, 78 %) as a red powder.

^{1}H NMR (400 MHz, CD_3CN, δ in ppm): 2.39 (6H, s, CH_3), 2.41 (6H, s, CH_3), 6.63 (2H, s, $H_{thiophene}$), 7.26 (2H, dd, J_1=6.4 Hz, J_2=6.4 Hz), 7.47 (2H, dd, J_3=6.4 Hz, J_4=6.4 Hz,), 7.69 (2H, d, J_5=5.0 Hz), 7.85 (2H, d, J_6=5.5 Hz), 7.87 (2H, d, J_7=5.5 Hz), 8.01 (2H, dd, J_8=7.7 Hz, J_9=7.7 Hz), 8.12 (J_{10}=7.9 Hz, J_{11}=7.9 Hz), 8.17 (2H, d, J_{12}=5.0 Hz), 8.52 (2H, d, J_{13}=8.2 Hz), 8.56 (2H, d, J_{14}=8.2 Hz), 9.51 (2H, d, J_{15}=8.2 Hz).
MS (EI+): 1011.12 (1011.12 for M^+-PF_6).

1.10 Synthesis of 3,4-dichloro-3-cyclobutene-1,2-dione[12]



A mixture of squaric acid (2 g, 17.5 mmol, 1 eq), thionyldichloride (2.5 ml, 35.1 mmol, 2 eq), DMF (10 drops), NaCl (20 mg, 0.35 mmol, 0.02 eq) and KCl (26 mg, 0.35 mmol, 0.02 eq) in dry 1,2-dichloroethane (18ml) was reflux (88°C) for 5 h directly in a sublimation apparatus. The solvent was removed with industrial vacuum to get a brown oil, which was purified by sublimation under vacuum (20 mbar) to yield 1.3 g (50%).

^{13}C NMR (101 MHz, $CDCl_3$, δ ppm): 188.2, 189.6.
MS (EI+): 149.7 (149.9 for M^+).

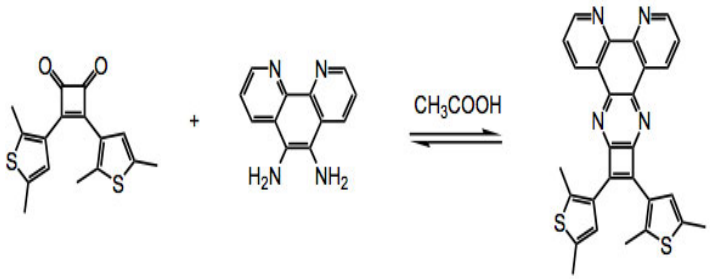
1.11 **Synthesis of 1,2-Bis(2,5-dimethylthien-3-yl)cyclobutenedione**[10]

A solution of 2,5-dimethylthiophene (1.1 ml, 8.6 mmol, 1eq) in heptane (7 ml) and a solution of squaric acid dichloride (0.65 g, 4.3 mmol, 0.5 eq), in dichloroethane (7 ml) were added drop wise under stirring to a suspension of $AlCl_3$ (2.3 g, 17.2 mmol, 2 eq) in heptane (7 ml) at a temperature between –15 to –20°C under argon. After 3h dichloroethane (21 ml) was added, the temperature was increased to 7-10°C, and the reaction mixture were stirred at this temperature for 16 h. The reaction mixture was poured onto ice and the aqueous phase was extracted with CH_2Cl_2 (3 x 40 ml). The

combined organic phase was washed with a 3% $NaHCO_3$ solution (30 ml), water (3 x 30 ml), and dried with $MgSO_4$. The solvent was removed and the residue purified on a chromatographic column (Al_2O_3; hexane/AcOEt 6:1, Rf: 0.58) yield 1.2 g (46 %).

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.42 (6H, s, CH_3), 2.48 (6H, s, CH_3), 6.87 (2H, s, H_{het}).
^{13}C NMR (101 MHz, $CDCl_3$, δ ppm): 15.2, 16.0, 124.8, 126.9, 138.4, 154.4, 183.1, 195.9.
MS (EI+): 302.1 (302.0 for M^+).
Elem. Anal.: calcd for $C_{16}H_{14}O_2S_2$: C 63.55, H 4.67; found : C 63.67, H 4.80.

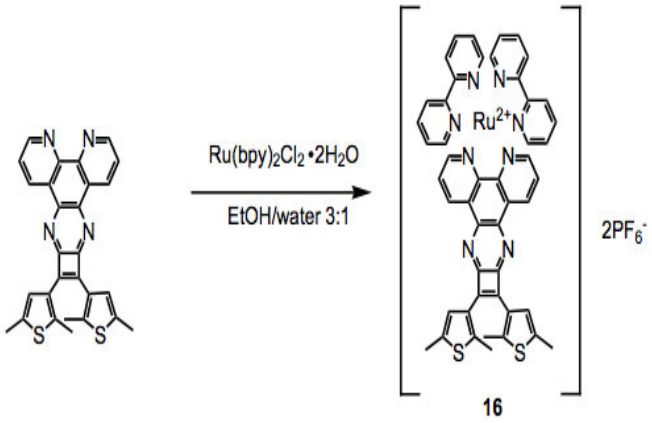
1.12 Synthesis of 10,11-bis-(2,5-dimethylthiophen-3-yl)-4,5;9;12-tetraazacyclobuta-[6]triphenylene[11]



In a Dean-Stark assembling, the corresponding1,2-diketone (362 mg, 1.2 mmol, 1.0 eq.) and phenanthroline-5,6-diamin[13] (252 mg, 1.2 mmol, 1.0 eq) was dissolved in deaerated toluene (20 ml) and acetic acid (4 ml) under argon. The reaction mixture was stirred for 24 hours at reflux (130°C). Solvents were removed. The crude product was purified by chromatographic column (CH_2Cl_2/TEA 30:1) to yield 185mg (32 %) of desired product.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.44 (6H, s, CH_3), 2.84 (6H, s, CH_3), 6.88 (2H, s, $H_{thiophene}$), 7.66 (2H, dd, $^{3}J_1$=4.3 Hz, $^{3}J_2$=8.4 Hz, $H_{phenanthroline}$), 9.14 (2H, dd, $^{3}J_1$=4.3 Hz, ^{4}J =1.6 Hz, $H_{phenanthroline}$), 9.24 (2H, dd, $^{4}J_3$=1.8 Hz, $^{3}J_2$=8.2 Hz, $H_{phenanthroline}$).
^{13}C NMR (101 MHz, C_6D_6, δ ppm): 174.2, 153.1, 146.5, 144.0, 137.7, 135.9, 135.1, 131.9, 125.6, 123.1, 15.8, 14.9.
MS (EI+): 477.13 M^++1 (476.11for M^+).

1.13 Synthesis of the ruthenium complex (16)



A 25ml, one necked, round-bottem flask were charged with ligand (20 mg, 4.42•10^{-2} mmol, 1 eq), $Ru(bpy)_2Cl_2$ • $2H_2O$ (25 mg, 4.86•10^{-2} mmol, 1.1 eq) ethanol (15 ml) and water (5 ml). The solution was refluxed over night under argon. The organic phase was extracted with water (3x) and the water phase was extracted with CH_2Cl_2 (3x). The dicholormethane in the water phase was removed under vacuum and NH_4PF_6 (0.5 g) was added and the precipitate was collected by filtration and purified on silica gel plate (acetonitrile/methanol/water/aqueous solution of potassium nitrate 40 :10:10:1) yielding the final product (32 mg, 61 %).

^{1}H NMR (400 MHz, CD_3CN, δ in ppm): 2.39 (6H, s, CH_3), 2.41 (6H, s, CH_3), 6.63 (2H, s, $H_{thiophene}$), 7.26 (2H, dd, J_1=6.4 Hz, J_2=6.4 Hz), 7.47 (2H, dd, J_3=6.4 Hz, J_4=6.4 Hz,), 7.69 (2H, d, J_5=5.0 Hz), 7.85 (2H, d, J_6=5.5 Hz), 7.87 (2H, d, J_7=5.5 Hz), 8.01 (2H, dd,

J_8=7.7 Hz, J_9=7.7 Hz), 8.12 (J_{10}=7.9 Hz, J_{11}=7.9 Hz), 8.17 (2H, d, J_{12}=5.0 Hz), 8.52 (2H, d, J_{13}=8.2 Hz), 8.56 (2H, d, J_{14}=8.2 Hz), 9.51 (2H, d, J_{15}=8.2 Hz).
MS (ESI+): 1035.12 (1035.12 for M^+-$PF6^-$).

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