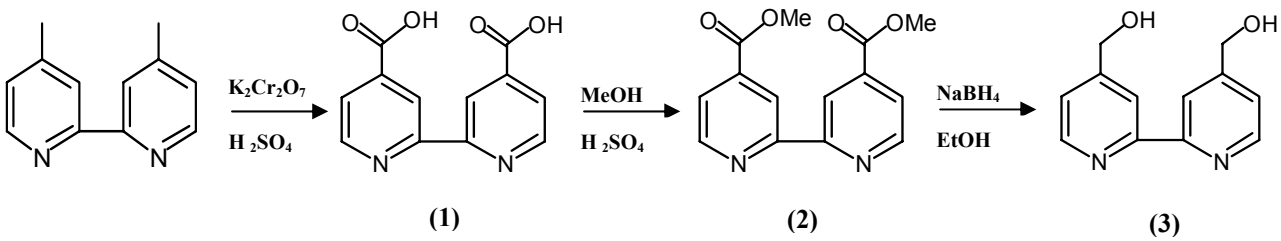
Electronic Supplementary Information for Chemical Communications

I- Synthesis of ligands and complexes:

4,4'-Dicarboxy-2,2'-bipyridine (1):
To solution of 4,4'-dimethyl-2,2'bipyridine (5.8g, 28mM) in sulphuric acid (100ml, 96%) was added potassium dichromate (24g, 86mM). The reaction mixture was stirred at 70°c for 30 min and then cooled to room temperature. The resulting mixture was poured into cold water (800ml). The resulting yellow precipitate was filtered off and stirred in KOH aqueous solution for 2h and filtered to remove unreacted starting material. The solution was acidified to pH 3 with 2M HCl aqueous solution. The resulting precipitate was filtered and washed with methanol and diethyl ether. After drying, **1** was obtained as white powder (6.5g, 93%).
H^1-NMR (250MHz/ NaOD): δ(ppm)= 7.82(d,2H), 8.33(d,2H), 8.72(d,2H)

4,4'-Dimethoxycarboyl-2,2'-bipyridine (2):
The diacid (**1**) (6.5g, 26mM), methanol (100 ml) and concentrated sulphuric acid (13 ml) were heated under reflux for 62h. The reaction mixture was cooled, poured into water (350ml) and basified to pH 8 with 25% sodium hydroxide. The mixture was then extracted with methylene chloride (3 x 250ml) and the combined organic layers were dried (sodium sulphate) and evaporated to colorless crystalline material. This residue was recrystallized from toluene to obtain **2** (4.5g, 62%).
H^1-NMR (250MHz/ $CDCl_3$): δ (ppm)= 4.79(s,6H), 7.87(d,2H), 8.81(d,2H), 8.93 (s,2H)

4,4'-Bis(hydroxymethyl)-2,2'-bipyridine (3):
The diester (**2**) (4.5g, 16 mM) was suspended in absolute ethanol (40 ml) and sodium borohydride (13.9g) was added in one portion. The mixture was refluxed for 3 hours, cooled to room temperature and the borohydride excess was eliminated by addition of saturated aqueous solution of ammonium chloride (300 ml). The ethanol was evaporated and precipitated solids were dissolved by addition of the minimum amount of water. The resulting solution was extracted three times with 300 ml portions of ethyl acetate. The extract was dried (sodium sulphate) and evaporated. **3** was obtained as a white crystalline powder (2.25g, 65%).
H^1-NMR (250MHz/ $CDCl_3$): δ(ppm)= 4.79(s,4H), 7.48(d,2H), 8.31(d,2H), 8.93 (s,2H).



(1) **(2)** **(3)**

Figure 1. Scheme for synthesis of 4,4'-Bis(hydroxymethyl)-2,2'-bipyridine

4,4'-bis(biotin)-2,2'bipyridine (4):
Biotin (488mg, 2mM), dicyclohexylcarbodiimide (412mg, 2mM), and NHS (230mg, 2mM) in DMF (20ml) were stirred at 80° under argon for 3 hours and cooled to room temperature. To this solution, were added 4,4'-bis(hydroxymethyl)2,2'bipyridine (151mg, 0.7mM) and 4-(dimethylamino)pyridine (61mg, 0.5mM). The reaction mixture was stirred at 60° for 60 hours then cooled to room temperature and filtered. The organic solvent was removed under vaccum and the residue was recrystallized from AcOEt to obtain ligand **4** (668 mg,48%).
H^1-NMR (DMSO, 250MHz): δ(ppm) 1.20 (m,4H), 1.24 (m,4H), 1.46 (m,4H), 2.00 (t,4H), 2.74 (d,2H), 2.80 (d,2H), 3.06 (m,2H), 4.09 (m,2H), 4.26 (m,4H), 5.24 (s,4H), 6.37 (s,2H), 6.45 (s,2H), 7.44 (d,2H), 8.36 (s2H), 8.69 (d,2H). FAB/MS(NBA): m/z = 669[MH^+].

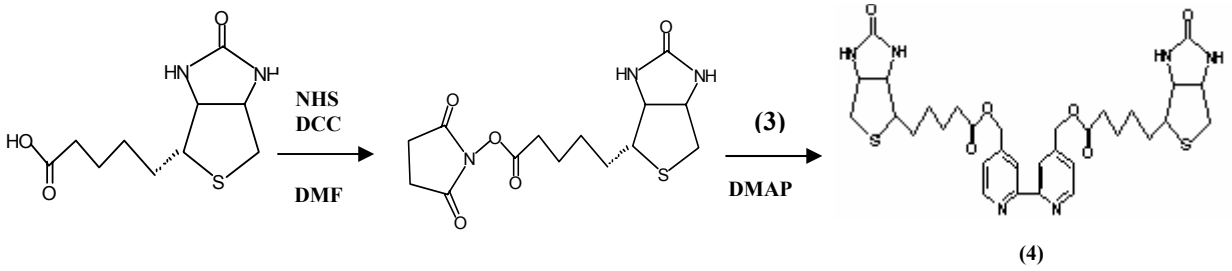


Figure 2. Scheme for synthesis of 4,4'-bis(biotin)-2,2'-bipyridine

3-pyrrole-1-bromo-propyl (5):
A mixture of 2,5-dimethoxytetrahydrofuran (6.6g; 0.05M), 3-amino-1-bromo-propyl (10.3g; 0.05M), acetic acid (40mL) and water (60 mL) is heated under reflux for 4 hours and then stirred at room temperature. The reaction mixture was extracted with ether and the excess acetic acid was decomposed by addition of sodium hydrogen carbonate to the organic phase. The latter was dried with sodium sulfate, filtered and evaporated to give a brown oil (5.8g; 62%).
H^1-NMR (250MHz / $CDCl_3$): δ (ppm)= 2.31(d,2H), 3.37 (s2H), 4.14(d,2H), 6.26 (s,2H), 6.76 (s,2H).

4,4' bis (4-pyrrole-1-butyl)-2,2'-bipyridine (6):
BuLi (9.6 mL) was added to a solution of diisopropyl amine (3.3 mL) in 15 mL of tetrahydrofuran, and the resulting mixture was stirred for 15 min. 2.1 g of 4,4'-dimethyl-2,2'bipyridine in 80 mL tetrahydrofuran was then added from dropping funnel and the color changed to orange-brown. After 2 hours, 4.5g of **5** in 40 mL tetrahydrofuran was added to the solution, whose color slowly turned green. After an additional 1 hour of stirring, the reaction mixture was quenched with water and extracted with methylene chloride. Evaporation of solvent and subsequent purification (chromatography on silica with CH_2Cl_2/CH_3OH [9/1]) gave of a white solid (1.8g, 40%).
H^1-NMR (250MHz / $CDCl_3$): δ (ppm)= 1.67 (m,4H), 1.83(m,4H), 2.68 (t,4H), 3.90 (t,4H), 6.12 (s,4H), 6.62(s,4H), 7.10(d,2H), 8.21 (s2H), 8.56(d,2H).

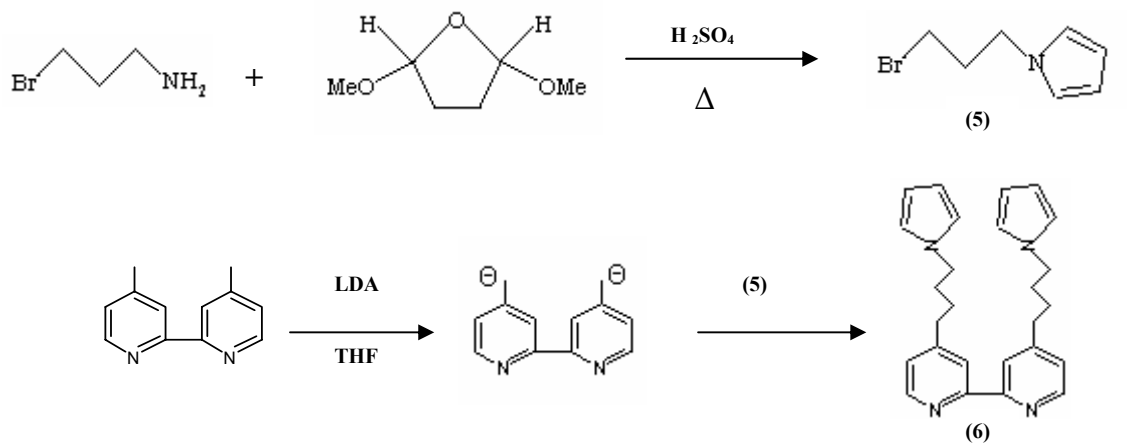


Figure 3. Scheme for synthesis of 4,4' bis (4-pyrrole-1-butyl)-2,2'-bipyridine

Ru(II) dichloro bis[4,4' bis (4-pyrrole-1-butyl)2,2'bipyridyl]:
$RuCl_3.3H_2O$ (149 mg, 0.75mM) was dissolved in DMF under Ar. The bipyridyl ligand **6** (454 mg, 1.14 mM) was added to this solution. The mixture was refluxed with vigorous stirring in the dark under an argon atmosphere. After refluxing for 3 hours the reaction mixture was allowed to cool to room temperature and filtered. DMF was removed under vacuum. The resulting solid was washed with acetone-diethyl ether (1/4) and dried (325 mg, 45%).
H^1-NMR (250MHz / CD_3CN): δ (ppm)= 1.74 (m,4H), 1.90(m,4H), 2.86(t,4H), 3.96 (t,4H), 6.12 (d,4H), 6.68(d,4H), 7.81(m,2H), 7.92 (m,2H), 8.11(d,2H), 8.25(m,2H), 8.36 (d,2H), 8.42(s,2H).

Ru(II) [4,4' bis (4-pyrrole-1-butyl)2,2'bipyridyl](4,4'-bis(biotin)-2,2'bipyridyl)2PF_6^-:
A mixture of the dibipyridyl ruthenium complex (73 mg, 0.075 mM) and 4,4'-bis(biotin)-2,2'bipyridine (50mg, 0.075 mM) in ethanol (10 ml) was stirred at 80°C for 4 hours. The mixture was allowed to cool to room temperature and filtered. Potassium hexafluorophosphate aqueous solution (290 mg in 25 mL) was added. The resulting precipitate was filtered and purified by chromatography on alumina with CH_3CN/ CH_3OH (7/3) (10^{-3}M KPF_6) as eluant. The product was crystallized from (acetone/ diethyl ether) to give the complex (80 mg, 65%).
H^1-NMR (250MHz / CD_3CN) data for the ruthenium complex: δ(ppm)= 1.18 (m,4H), 1.22(m,4H), 1.45 (m,4H), 1.75 (m,4H), 1.90(m,4H), 2.03 (t,4H), 2.76 (m,4H), 2.80(d,2H), 2.85 (d,2H), 3.05(m,2H), 3.89 (t,4H), 4.16 (m,2H), 4.34 (m,4H), 5.24 (s,4H), 5.37 (s,2H), 5.43 (s,2H), 6.05 (s,4H); 6.62(s,4H), 7.16(m,4H), 7.32 (d,2H), 7.46 (m,4H), 7.64 (d,2H), 8.23 (s,4H), 8.43(s,2H).
UV-vis(CH_3CN) λmax/nm = 460(14200). EI-MS : m/z = 1710 [M-PF_6], 1565 [M-2PF_6].

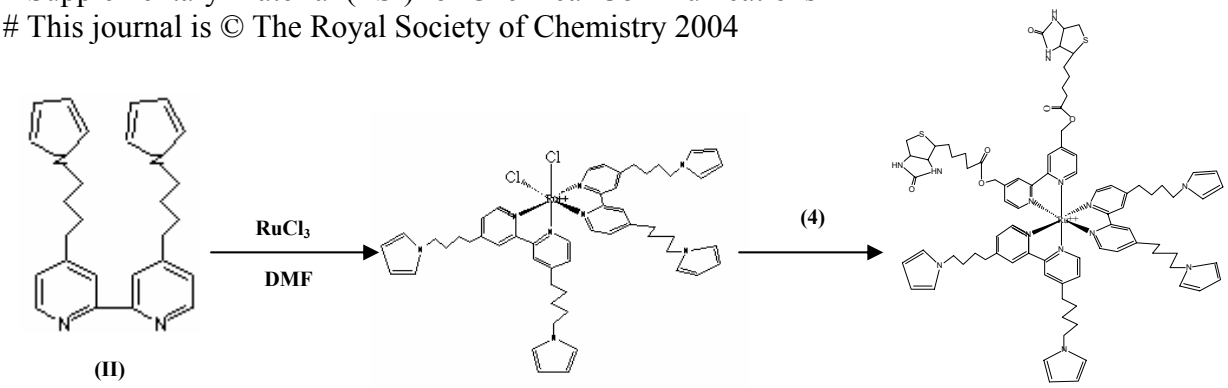


Figure 4. Scheme for synthesis of ruthenium complex