Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Dinuclear Ru(II) complexes of bis-(dipyrid-2'-yl)triazine ligands as efficient electron reservoirs.

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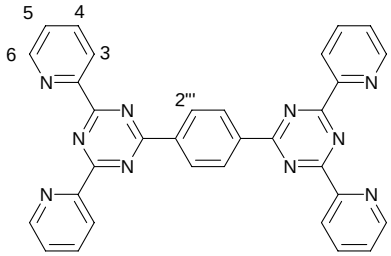
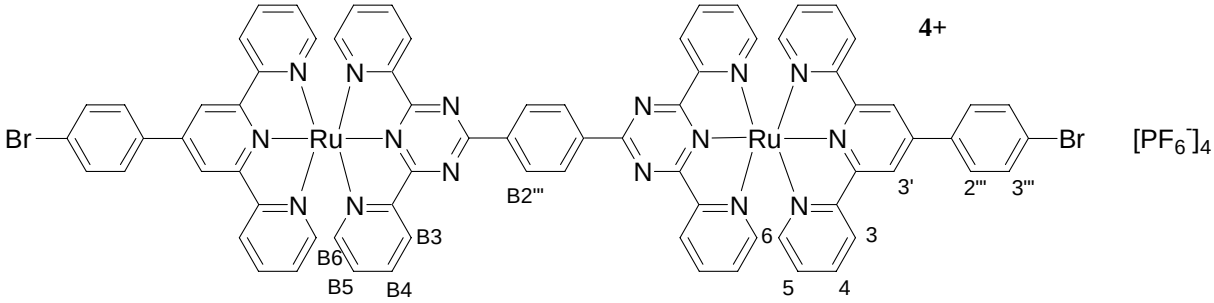
Starting materials such as ligands 4'-(*p*-bromophenyl)-2,2':6',2"-terpyridine (**4**),[1] 2,4-bis(2-pyridyl)-6-*p*-bromophenyl-1,3,5-triazine (**5**),[2] and complexes (**4**)$RuCl_3$[3] and (**5**)$RuCl_3$[3] were prepared following their respective published procedures.

Ligand 1.



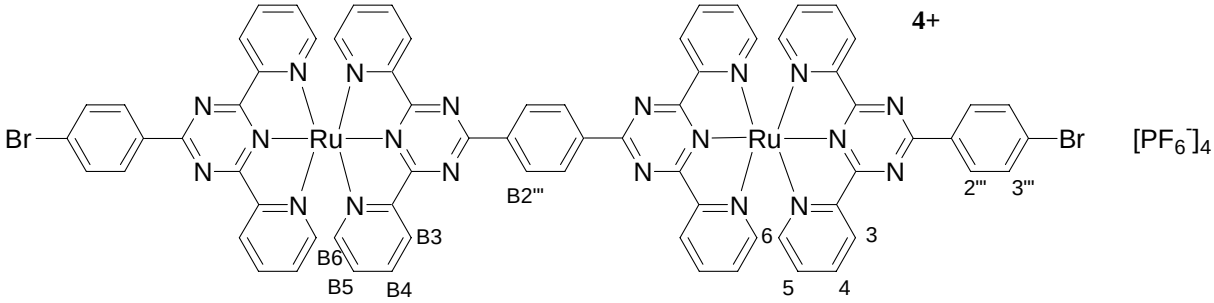
1,4-Dicyanobenzene (1.0 g, 7.8 mmol) in dry THF (30 mL) was added to a mixture of nBuLi (4.9 mL, 7.8 mmol) and $HNMe_2$ (3.9 mL, 7.8 mmol) in dry Et_2O (160 mL). During addition, the mixture turned form colourless to pale green then yellow, orange and brown. The mixture is left stir overnight before 2-cyanopyridine was added (3.0 mL, 31.2 mmol). After stirring overnight under N_2, the mixture was left open to air, and then a dark solid was isolated by filtration, was washed with Et_2O (5×30 mL), and then was recristallized in EtOH affording **1** as a pale yellow solid (500 mg, 16%). ^1H NMR (d_6-DMSO, 400 MHz, 298 K): δ 9.01 (s, 4H, $H_{2'''}$), 8.96 (d, J = 5 Hz, 4H, H_3), 8.83 (d, J = 8 Hz, 4H, H_6), 8.18 (td, J = 8 Hz, 1 Hz, 4H, H_4), 7.76 (td, J = 6 Hz, 1 Hz, 4H, H_5). ESI-MS: $[M+H]^+$ calcd for $C_{32}H_{21}N_{10}$ 545.1945; found 545.1937. Anal. Calcd for $C_{32}H_{28}N_{10}O_4$: C, 62.33; H, 4.58; N, 22.71. Found: C, 62.65; H, 4.38; N, 21.79.

[(4)Ru(1)Ru(4)](PF$_6$)$_4$, 2.



Complex **2** [(**4**)RuCl$_3$] (51 mg, 0.08 mmol), AgNO$_3$ (43 mg, 0.25 mmol) and ligand **1** (38 mg, 0.07 mmol) were suspended in DMF (50mL) and refluxed for 30 min. After cooling, the solid thus formed was removed and the filtrate was evaporated. The solid residue was dissolved in acetonitrile and KPF$_6$ was added to precipitate the crude product. The solid was purified by chromatography (SiO$_2$, acetonitrile–saturated aqueous KNO$_3$; 9 : 1): the third purple band was collected and precipitated by addition to an aqueous solution of KPF$_6$. The precipitate was redissolved in acetonitrile and the solution poured into water thus precipitating the product again. The procedure was repeated by dissolving the product in acetonitrile and precipitating it again by the addition of Et$_2$O to give the complex **2** (30 mg, 20 %). ^{1}H NMR (CD$_3$CN, 400 MHz, 298 K): δ 9.50 (s, 4H, $H_{B2'''}$), 9.24 (d, J = 8 Hz, 4H, H_{B3}), 9.11 (s, 4H, $H_{3'}$), 8.73 (d, J = 8 Hz, 4H, H_3), 8.24 (dd, J = 8, 1 Hz, 4H, H_{B4}), 8.19 (d, J = 8 Hz, 4H, $H_{2'''}$), 8.01(m, 8H, $H_{4+3''''}$), 7.75 (d, J = 5 Hz, 4H, H_{B6}), 7.56 (d, J = 6 Hz, 4H, H_6), 7.52 (dd, J = 8, 1 Hz, 4H, H_{B5}), 7.22 (dd, J = 8, 1 Hz, 4H, H_5). ESI-MS: [M]$^{4+}$ calcd for $C_{74}H_{48}N_{16}Br_2Ru_2$ 380.5169; found 380.5174; [M+PF6]$^{3+}$ calcd for $C_{74}H_{48}N_{16}Br_2Ru_2PF_6$ 555.6775; found 555.6781; [M+2PF$_6$]$^{2+}$ calcd for $C_{74}H_{48}N_{16}Br_2Ru_2P_2F_{12}$ 905.9987; found 905.9996.

[(5)Ru(1)Ru(5)](PF$_6$)$_4$, 3.



Complex **3** [(**5**)RuCl$_3$] (0.192 g, 0.32 mmol), AgNO$_3$ (0.171 g, 0.96 mmol) and ligand **1** (0.087 g, 0.16 mmol) were suspended in DMF (70 mL). The mixture was refluxed for 2 h turning to deep purple. After cooling, the solid formed was removed and the filtrate was evaporated. The same procedure as described for **4** gave purple complex **5** (70 mg, 50%). ^{1}H NMR (CD$_3$CN, 400 MHz, 298 K): δ 9.53 (s, 4H, $H_{B2'''}$), 9.26 (d, J = 8 Hz, 4H, H_{B3}), 9.17 (d, J = 7 Hz, 4H, H_3), 9.04 (d, J = 9 Hz, 4H, $H_{2'''}$), 8.24 (td, J = 8 Hz, 1 Hz, 4H, H_{B4}), 8.20 (td, J = 8 Hz, 1 Hz, 4H, H_4), 8.07 (d, J = 9 Hz, 4H, $H_{3'''}$), 7.81 (d, J = 5 Hz, 8H, H_{B6+6}), 7.46 (m, 8H, H_{B5+5}). ESI-MS: [M]$^{4+}$ calcd for $C_{70}H_{44}N_{20}Br_2Ru_2$ 381.5122; found 381.5123.

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[3] Santoni, M.-P.; Medlycott, E. A.; Hanan, G. S.; Hasenknopf, B.; Proust, A.; Nastasi, F; Campagna, S.; Chiorboli, C.; Argazzi, R.; Scandola, F *Dalton Trans.* **2009**, 3964-3970.