Prolonged luminescence lifetimes in Ru(II) complexes via the multichromophore approach: Can the excited-state storage element be on a ligand not involved in the MLCT emitting state?

Jianhua Wang, Garry S. Hanan,*

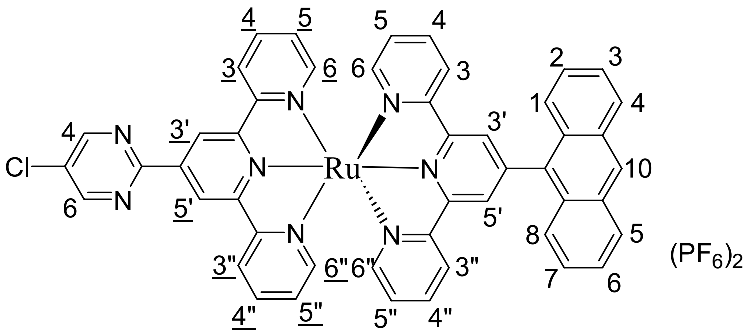
Département de chimie, Université de Montréal, Montreal, Québec, Canada H3T 1J4. Fax: +1 514 343 7586; Tel: +1 514 343 7056, E-mail:garry.hanan@umontreal.ca;

Frédérique Loiseau and Sebastiano Campagna.*

Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, 98166 Messina, Italy. Fax: (39) 090-393756, E-mail: photochem@chem.unime.it

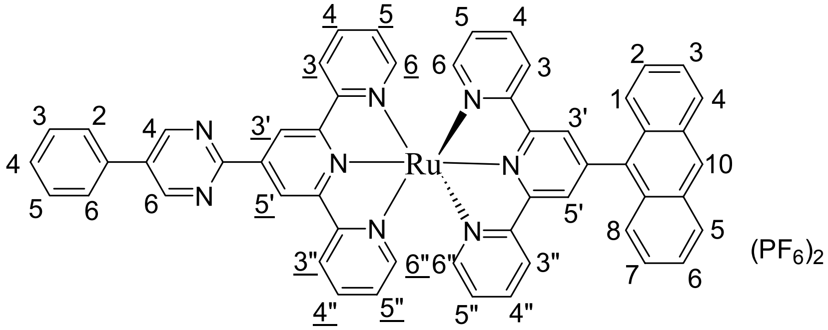
Heteroleptic ruthenium complexes 1-3:

Complex **1**: [ClPmTpyRuTpyAn]$(PF_6)_2$



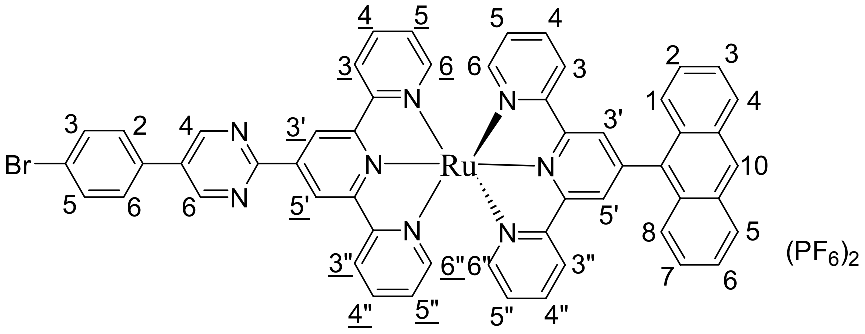
Ligand 4’-(9-anthryl)-2,2’:6’,2”-terpyridine[1] (0.021g, 0.051 mmol), 4’-(5-chloro-2-pyrimidyl)terpyridine ruthenium trichloride (0.028 g, 0.051 mmol) and silver nitrate (0.026 g, 0.15 mmol) were refluxed in anhydrous DMF (20 mL) for 2h. The mixture was filtered through celite and the filtrate was evaporated to dryness. The residue was then chromatographed on a silica gel column with 7:1 acetonitrile and saturated aqueous KNO_3. Anion exchange with NH_4PF_6 gave pure product (0.047 g, 0.041 mmol, 82%). Care was taken in order to avoid full laboratory light over the reaction vessel. Purification was accomplished in dim light. ^{1}H NMR (400 MHz; CD_3CN): δ 9.70 (s, 2H, $H_{\underline{3'}, \underline{5'}}$), 9.19 (s, 2H, $H_{Pm4, 6}$), 8.95 (s, 2H, $H_{3', 5'}$), 8.90 (s, 1H, H_{An10}), 8.76 (d, 2H, $H_{\underline{3}, \underline{3''}}$, J = 8.1 Hz), 8.45 (d, 2H, $H_{3, 3''}$, J = 8.0 Hz), 8.32 (d, 2H, $H_{An4 ,5}$, J = 8.3 Hz), 8.20 (d, 2H, $H_{An1, 8}$, J = 8.5 Hz), 8.05 (t, 2H, $H_{\underline{4}, \underline{4''}}$, J = 7.9 Hz), 7.89 (t, 2H, $H_{4, 4''}$, J = 8.0 Hz), 7.69 (m, 6H, $H_{6, 6'', An2, 3, 6, 7}$), 7.49 (d, 2H, $H_{\underline{6}, \underline{6''}}$, J = 5.5 Hz), 7.38 (t, 2H, $H_{5, 5''}$, J = 6.5 Hz), 7.19 (t, 2H, $H_{\underline{5}, \underline{5''}}$, J = 6.5 Hz). ^{13}C NMR (75 MHz; CD_3CN): δ 159.5, 158.5, 158.3, 157.3, 156.5, 155.7, 153.3, 153.1, 147.8, 143.9, 138.7, 138.6, 132.5, 132.4, 131.8, 130.3, 129.3, 129.2, 128.2, 127.9, 127.4, 126.9, 126.5, 126.3, 125.3, 125.2, 122.0. ESI-MS: 428.1 ([(ClPmTpy)Ru(TpyAn)]$^{2+}$).

Complex **2**: [PhPmTpyRuTpyAn]$(PF_6)_2$



4'-(9-Anthryl)-2,2':6',2"-terpyridine ruthenium trichloride (0.039g, 0.063 mmol), 4'-(5-phenyl-2-pyrimidyl)terpyridine (0.031 g, 0.080 mmol) and silver nitrate (0.032 g, 0.19 mmol) were refluxed in anhydrous DMF (20 ml) for 2h. The mixture was filtered through celite and the filtrate was evaporated to dryness. The residue was then chromatographed on a silica gel column with 7:1 acetonitrile and saturated aqueous KNO_3. Anion exchange with NH_4PF_6 gave pure product (0.054 g, 0.045 mmol, 72%). Care was taken in order to avoid full laboratory light over the reaction vessel. Purification was accomplished in dim light. ^1H NMR (400 MHz; CD_3CN) δ 9.80 (s, 2H, $H_{\underline{3'},\,\underline{5'}}$), 9.46 (s, 2H, $H_{Pm4,\,6}$), 8.96 (s, 2H, $H_{3',\,5'}$), 8.92 (s, 1H, H_{An10}), 8.80 (d, 2H, $H_{\underline{3},\,\underline{3''}}$, J = 7.8 Hz), 8.45 (d, 2H, $H_{3,\,3''}$, J = 8.0 Hz), 8.33 (d, 2H, $H_{An4\,,5}$, J = 8.2 Hz), 8.20 (d, 2H, $H_{An1,\,8}$, J = 8.5 Hz), 8.06 (t, 2H, $H_{\underline{4},\,\underline{4''}}$, J = 7.8 Hz), 7.98 (d, 2H, $H_{Ph2,\,6}$, J = 7.4 Hz), 7.90 (t, 2H, $H_{4,\,4''}$, J = 7.7 Hz), 7.68 (m, 6+3H, $H_{6,\,6'';\,An2,\,3,\,6,\,7;\,Ph3,\,4,\,5}$), 7.52 (d, 2H, $H_{\underline{6},\,\underline{6''}}$, J = 5.4 Hz), 7.38 (t, 2H, $H_{5,\,5''}$, J = 6.2 Hz), 7.20 (t, 2H, $H_{\underline{5},\,\underline{5''}}$, J = 6.4 Hz). ^{13}C NMR (75 MHz; CD_3CN) δ 160.1, 158.6, 158.4, 156.5, 156.4, 155.8, 153.3, 153.1, 147.7, 144.8, 138.7, 138.6, 134.3, 134.2, 131.8, 130.3, 130.0, 129.3, 128.2, 128.0, 127.7, 127.4, 126.9, 126.5, 126.4, 132.5, 129.3, 128.1, 125.3, 125.2, 121.9. ESI-MS: 449.0 ($[(PhPmTpy)Ru(TpyAn)]^{2+}$)

Complex **3**: [BrPhPmTpyRuTpyAn]$(PF_6)_2$



4’-(9-Anthryl)-2,2’:6’,2”-terpyridine ruthenium trichloride (0.031g, 0.050 mmol), 4’-(5-phenyl-2-pyrimidyl)terpyridine (0.023 g, 0.050 mmol) and silver nitrate (0.026 g, 0.15 mmol) were refluxed in anhydrous DMF (15 ml) for 2h. The mixture was filtered through celite and the filtrate was evaporated to dryness. The residue was then chromatographed on a silica gel column with 7:1 acetonitrile and saturated aqueous KNO_3. Anion exchange with NH_4PF_6 gave pure product (0.044 g, 0.035 mmol, 70%). Care was taken in order to avoid full laboratory light over the reaction vessel. Purification was accomplished in dim light. ^{1}H NMR (400 MHz; CD_3CN) δ 9.79 (s, 2H, $H_{\underline{3'},\,\underline{5'}}$), 9.42 (s, 2H, $H_{Pm4,\,6}$), 8.96 (s, 2H, $H_{3',\,5'}$), 8.90 (s, 1H, H_{An10}), 8.79 (d, 2H, $H_{\underline{3},\,\underline{3''}}$, J = 8.0 Hz), 8.47 (d, 2H, $H_{3,\,3''}$, J = 8.1 Hz), 8.32 (d, 2H, $H_{An4,5}$, J = 7.1 Hz), 8.22 (d, 2H, $H_{An1,\,8}$, J = 8.1 Hz), 8.07 (t, 2H, $H_{\underline{4},\,\underline{4''}}$, J = 7.8 Hz), 7.88 (m, 6H, $H_{4,\,4'';\,Ph2,\,3,\,5,\,6}$), 7.70 (m, 6H, $H_{6,\,6'';\,An2,\,3,\,6,\,7}$), 7.55 (d, 2H, $H_{\underline{6},\,\underline{6''}}$, J = 5.7 Hz), 7.40 (t, 2H, $H_{5,\,5''}$, J = 6.6 Hz), 7.22 (t, 2H, $H_{\underline{5},\,\underline{5''}}$, J = 6.6 Hz). ^{13}C NMR (75 MHz; CD_3CN) δ 160.4, 158.5, 158.4, 156.4, 156.4, 155.8, 153.3, 153.1, 147.8, 144.7, 138.7, 138.6, 133.4, 133.2, 133.0, 132.5, 131.8, 130.3, 129.6, 129.4, 129.3, 128.2, 128.0, 127.4, 127.0, 126.5, 126.4, 125.3, 125.2, 123.9, 121.9. ESI-MS: 488.0 ($[(BrPhPmTpy)Ru(TpyAn)]^{2+}$).

References

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[1] E. C.Constable and D. R. Smith *Supramol. Chem.* 1994, **4**, 5-7.