Synthesis of ligands

3-(2-pyridin-2-yl-benzimidazol-1-yl)acetic acid **L_2**

The ester pbimCH_2COOEt (1.0 g, 3.6 mmol) was dissolved in 25 ml 75 % aqueous ethanol solution. To the solution NaOH (1,5 g, 37.5 mmol) was added and the mixture was warmed at low steam for 40 min. After the reaction, the mixture was cooled down and 50 ml cold water was added and the pH value of the solution was adjusted to 2. The precipitate was filtered and washed with water, acetone and diethyl ether (0.88 g, 97 %). White powder, m.p. 248 ~ 249 ^{o}C. ^{1}H NMR (DMSO-d_6) δ 8.68 (s, 1 H), 8.40 (d, 1 H), 8.00 (t, 1 H), 7.70 (dd, 2 H), 7.50 (t, 1 H), 7.30 (q, 2 H), 5.62 (s, 2 H). Anal. Calcd for $C_{16}H_{15}N_3O_2$: C, 66.40; H, 4.34; N, 16.60. Found: C, 66.10; H, 4.00; N, 16.53.

3-(2-pyridin-2-yl-benzimidazol-1-yl)propanoic acid **L_3**

2-(2-Pyridyl)benzimidazole (2.0 g, 10.2 mmol) and ethyl acrylate (1.3 ml, 12 mmol) were dissolved in 10 ml anhydrous DMF under N_2. To this solution 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]-pyrimidine was added and were heated at 60 ^{o}C for 24 h while stirring. After reaction, cold water (50 ml) was added. The precipitate was filtered, washed with water. The crude product was dissolved in 25 ml 75% aqueous ethanol and NaOH (2.0 g, 50 mmol) was added. The mixture was heated at low steam for 40 min and cold water (50 ml) was added after reaction upon cooling. The solution was adjusted to pH = 2 with hydrochloric acid and the precipitate was filtered, washed with water, acetone and diethyl ether, air dried (1.78 g, 87% yield). White powder, m.p. 236 ~ 237 ^{o}C. . ^{1}H NMR (DMSO-d_6) δ 8.85 (d, 1 H), 8.43 (d, 1 H), 8.12 (t, 1 H), 7.82 (dd, 2 H), 7.64 (t, 1 H), 7.40 (q, 2 H), 5.10 (t, 2 H), 3.00 (t, 2 H). Anal. Calcd for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.87; N, 15.73. Found: C, 67.10; H, 4.69; N, 15.29.

4-(2-pyridin-2-yl-benzimidazol-1-yl)butanoic acid **L_4**

2-(2-Pyridyl)benzimidazole (2.0 g, 10.2 mmol) was dissolved in 10 ml DMF under N_2. To this solution K_2CO_3 (2.0 g, 14.5 mmol) and trace of BuN_4I were added. The mixture was stirred for 5 min and ethyl bromobutyrate (1.8 ml, 12 mmol) was added dropwise and then stirred for 24 h at room temperature. After reaction, cold water (50 ml) was added and the precipitate was filtered ,washed with water. The crude product was dissolved in 25 ml 75% aqueous ethanol and NaOH (2.0 g, 50 mmol) was added. The mixture was heated at low steam for 40 min and cold water (50 ml) was added after reaction upon cooling. The solution was adjusted to pH = 2 with hydrochloride acid and the precipitate was filtered, washed with water, acetone and diethyl ether, air dried (1.8 g, 62% yield). White powder, m.p. 196 ~ 198 ^oC. . ^1H NMR (DMSO-d_6) δ 8.90 (d, 1 H), 8.40 (d, 1 H), 8.15 (t, 1 H), 7.96 (d, 1 H), 7.85 (d, 1 H), 7.70 (t, 1 H), 7.50 (q, 2 H), 4.88 (t, 2 H), 2.30 (t, 2 H), 2.05 (q, 2 H). Anal. Calcd for $C_{16}H_{15}N_3O_2$: C, 68.32; H, 5.34; N, 14.95. Found: C, 68.08; H, 4.97; N, 14.88.

Synthesis of complexes

(4) Cis-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$[5]

$RuCl_3$ $3H_2O$ (3.0 g, 11.5 mmol), bipyridine (3.61 g, 23.1 mmol) and LiCl (1g, 23.6 mmol) were refluxed in DMF under argon for 8 h. The reaction mixture was cooled to room temperature and 100 ml acetone was added. The resultant solution was cooled at 0 ^oC overnight. The precipitate was filtered and washed with water (3 × 10 ml) and diethyl ether (3 × 20 ml). The product was dried by suction, 68 % yield.

2c *$[Ru(bpy)_2(pbim(CH_2)_2COOH)](PF_6)_2$*

$[(bpy)_2Ru(pbimC_3)](PF_6)_2$ was prepared by following the same procedure as that for the preparation of $[(bpy)_2Ru(pbimH)](PF_6)_2$ except that $pbim(CH_2)_2COOH$ was used as the starting material, 96% yield. ^1H NMR (DMSO-d_6) δ 8.83 (dd, 3H), 8.72 (d, 1H), 8.68 (d, 1H), 8.18 (br, 5 H), 7.99 (d, 1 H), 7.90 (d, 1H), 7.82 (d, 1H), 7.73 (br, 3H), 7.50 (br, 6 H), 7.08 (t, 1 H), 5.69 (t, 1 H), 5.14 (t, 2 H), 3.00 (t, 2H).

Anal. Calcd for $C_{35}H_{29}F_{12}N_7O_2P_2$: C, 43.30; H, 2.99; N, 10.10. Found: C, 42.95; H, 2.65; N, 10.02.

2d *$[Ru(bpy)_2(pbim(CH_2)_3COOH)](PF_6)_2$*

This was prepared by following the same procedure as that for the preparation of $[(bpy)_2Ru(pbimH)](PF_6)_2$ except that $pbim(CH_2)_3COOH$) was used as the starting material, 90% yield. Red microcrystal, m.p. 200 ~ 202 ^oC. ^1H NMR (DMSO-d_6) δ 8.87 (br, 4H), 8.71 (d, 1H), 8.20 (br, 5 H), 7.98 (d, 1 H), 7.88 (d, 1 H), 7.80 (d, 2 H), 7.72 (d, 1 H), 7.67 (d, 1 H), 7.52 (br, 6 H), 7.05 (t, 1 H), 5.65 (t, 1 H), 4.90 (t, 2 H), 2.30 (t, 2 H), 2.05 (q, 2 H). Anal. Calcd for $C_{36}H_{32}F_{12}N_7O_3P_2$: C, 43.50; H, 3.22; N, 9.87. Found: C, 43.50; H, 2.85; N, 9.84.

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