

Supporting Information for

A supramolecular switch between ground high- and low-spin states using 2,2':6',2''-terpyridine-6,6''-diyl bis(*tert*-butyl nitroxide)

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Experimental Section

Preparation of tpybNO. A hexane solution (8.5 mL; 1.55 mol/L) of *t*-BuLi (13.2 mmol) was added dropwise to a tetrahydrofuran (THF) solution (50 mL) of 6,6''-dibromo-2,2':6',2''-terpyridine (1.17 g; 3.0 mmol) by a syringe at -78°C . The mixture was stirred at -78°C for 1.5 h. A THF solution (10 mL) of 2-methyl-2-nitrosopropane (0.59 g; 6.6 mmol) was added from a dropping funnel at -78°C . The mixture was further stirred for 2 h, and gradually warmed up to room temperature. Aqueous work-up and concentration gave a brown mixture solidified. The products were separated on a silica-gel chromatography eluted with 1/2 THF-hexane, to give tpybNOH as a yellow solid (0.372 g; 0.91 mmol; 30%). M.p. $181\text{--}184^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 500 MHz) δ 1.32 (s, 18H), 7.22 (2H, d, $J = 7.7$ Hz), 7.47 (2H, brs), 7.99 (2H, dd, $J = 7.7, 7.4$ Hz), 7.95 (1H, t, $J = 7.4$ Hz), 8.32 (2H, d, $J = 7.4$ Hz), 8.34 (2H, d, $J = 7.4$ Hz). ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 27.29, 60.48, 112.61, 113.65, 119.83, 138.07, 138.24, 152.02, 155.19, 163.42. MS (electro-spray ionization (ESI) in MeOH) m/z 430.2 ($\text{M}+\text{Na}^+$). IR (neat, attenuated total reflection (ATR)) 3208, 2972, 1567, 1427, 1196 cm^{-1} . Anal. Calcd.: C, 67.79; H, 7.17; N, 17.19% for $\text{C}_{23}\text{H}_{29}\text{N}_5\text{O}_2$. Found: C, 67.50; H, 7.21; N, 17.30%. To a CH_2Cl_2 solution (50 mL) involving tpybNOH (2.20 g; 5.40 mmol) was added Ag_2O (27 mmol) with being stirred at room temperature. After the mixture was stirred for further 1.5 h, the red product was isolated by silica-gel column chromatography eluted with CH_2Cl_2 -AcOEt. Recrystallization from CH_2Cl_2 -hexane gave a red solid of tpybNO (1.82 g; 4.48 mmol; 83%). M.p. $158\text{--}159^{\circ}\text{C}$. MS (ESI in MeOH) m/z 428.2 ($\text{M}+\text{Na}^+$), 372.1 ($\text{M}+\text{Na}^+-\text{C}_4\text{H}_8$). IR (neat, ATR) 2933, 1557, 1420, 1361, 1284, 786 cm^{-1} . Anal. Calcd.: C, 68.13; H, 6.71; N, 17.27% for $\text{C}_{23}\text{H}_{27}\text{N}_5\text{O}_2$. Found: C, 67.85; H, 6.73; N, 17.29%.

Preparation of the metal-ion complexes. After tpybNO (45 mg; 0.11 mmol) and $\text{Zn}(\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$ ($x = 6\text{--}7$; 26 mg; 0.11 mmol) were dissolved in MeOH (2 mL), the mixture was allowed to stand at room temperature for a week. Red platelet crystals of Zn-tpybNO were precipitated and collected on a filter in 50% yield (39 mg; 0.055 mmol). IR (neat, ATR) 3535, 3466, 1583, 1566, 1467, 1179, 1092, 1021, 793 cm^{-1} . Anal. Calcd.: C, 42.38; H, 4.98; N, 9.88% for $\text{C}_{25}\text{H}_{35}\text{B}_2\text{F}_8\text{N}_5\text{O}_4\text{Zn}$. Found: C, 42.12; H, 4.89; N, 9.76%. According to a procedure similar to that of the Zn complex, complexation of tpybNO with $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ afforded $[\text{Cu}(\text{tpybNO})(\text{H}_2\text{O})_2](\text{BF}_4)_2$ as dark red platelet crystals. IR (neat, ATR) 3565, 3495, 1609, 1475, 1183, 1057, 1033, 798 cm^{-1} . Anal. Calcd.: C, 40.70; H, 4.60; N, 10.32% for $\text{C}_{23}\text{H}_{31}\text{B}_2\text{F}_8\text{N}_5\text{O}_4\text{Cu}$. Found: C, 40.98; H, 4.69; N, 10.61%. A similar synthesis using $\text{La}(\text{hfac})_3 \cdot \text{H}_2\text{O}$ gave $[\text{La}(\text{hfac})_2(\text{CF}_3\text{CO}_2)(\text{tpybNO})]$ as dark red block crystals (Hhfac stands for 1,1,1,5,5,5-hexafluoropentane-2,4-dione). IR (neat, ATR) 1652, 1526, 1510, 1252, 1194, 1137, 792, 658, 581 cm^{-1} .