Encapsulation Controlled Single Molecule Magnetism in Tetrathiafulvalene-Capped Cyanide-Bridged Cubes

*Kiyotaka Mitsumoto,[1] Hiroyuki Nishikawa,[1,2] Graham N. Newton,[1] and Hiroki Oshio[1]**

Supporting Information

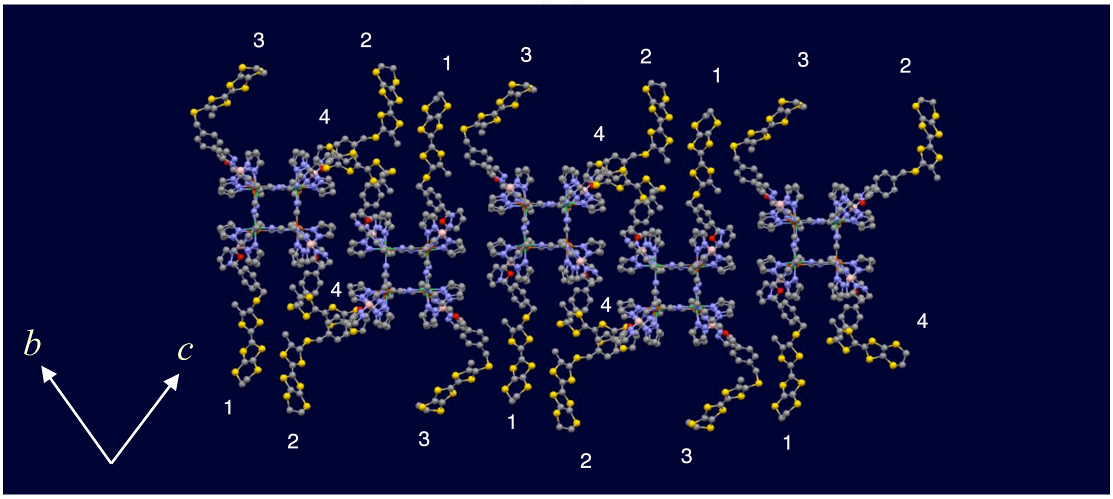

Figure S1. Interactions between TTF moieties.

TTF1 interacts with TTF 1(inversion symmetry), TTF2 and TTF3.
TTF2 & 3 interact only with TTF1.
TTF4 has no direct interaction with another TTF group.

The overlap between TTF1 is largest although there is no S-S contact between them, probably due to face-to-face π-π interaction.

Overlap integrals S ($\times 10^{-3}$ eV)

$$S_{1\text{-}2} = 1.284,\quad S_{1\text{-}3} = -1.400,\quad S_{1\text{-}1} = 11.42$$

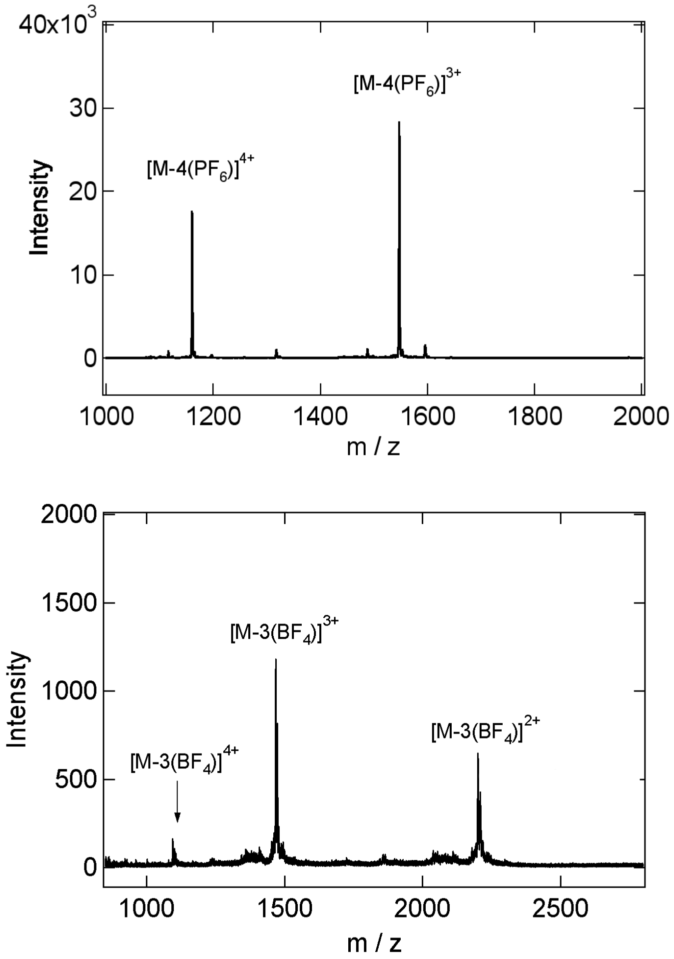

Figure S2. ESI mass spectra of **2** (top) and **3** (bottom). For **2** $[M{-}4(PF_6)]^{3+}$ seen at 1547.6 *m/z* (calcd: 1547.5) and $[M{-}4(PF_6)]^{4+}$ at 1160.6 (1160.7) *m/z* (M = $[Fe_4Ni_4(CN)_{12}(pztp)_4(L2)_4](PF_6)_4$.

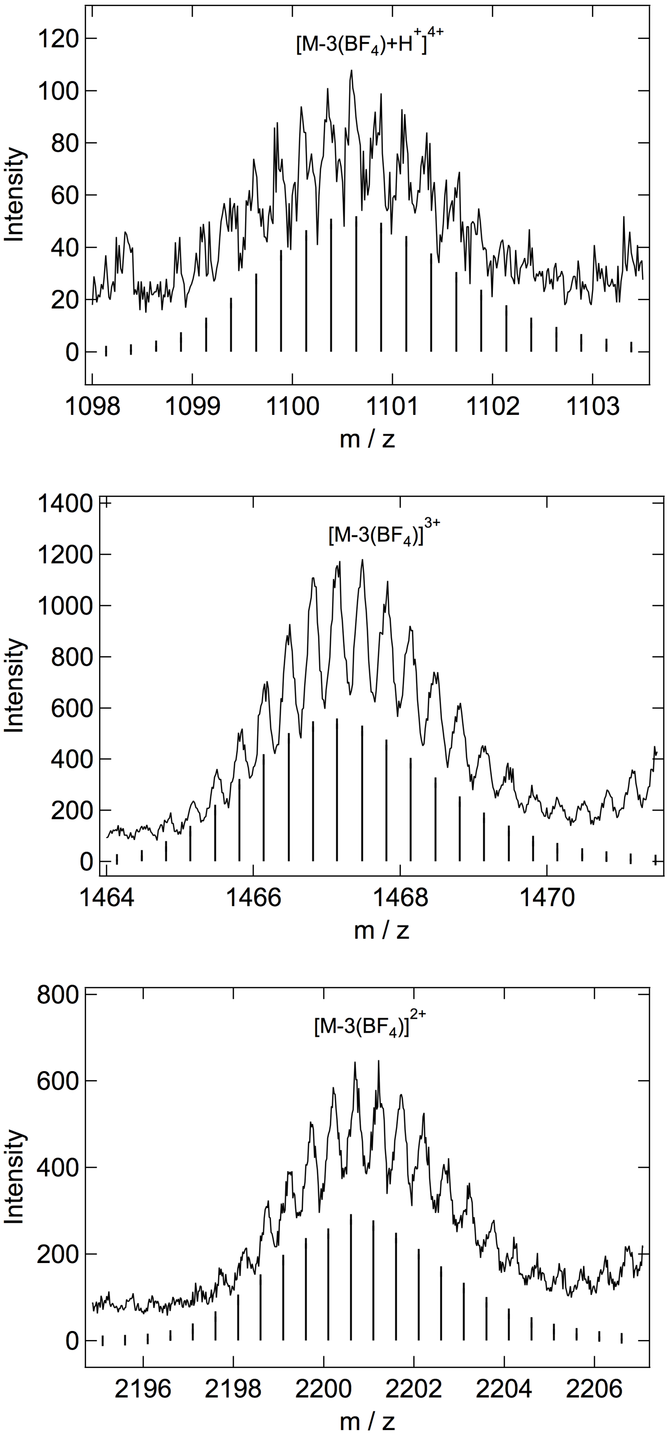

Figure S3. ESI-MS spectra of **3**. Isotope pattern of the $[M{-}3(BF_4){+}H^+]^{4+}$ (top), $([M{-}3(BF_4)]^{3+}$ (centre) and $([M{-}3(BF_4)]^{2+}$ (bottom) peaks at [found (calcd.)] 1100.6 (1100.5), 1467.1 (1467.1) and 2200.6 (2200.5) *m/z* respectively. M = $Na[Fe_4Ni_4(CN)_{12}(tp)_4L2_4](BF_4)_3$

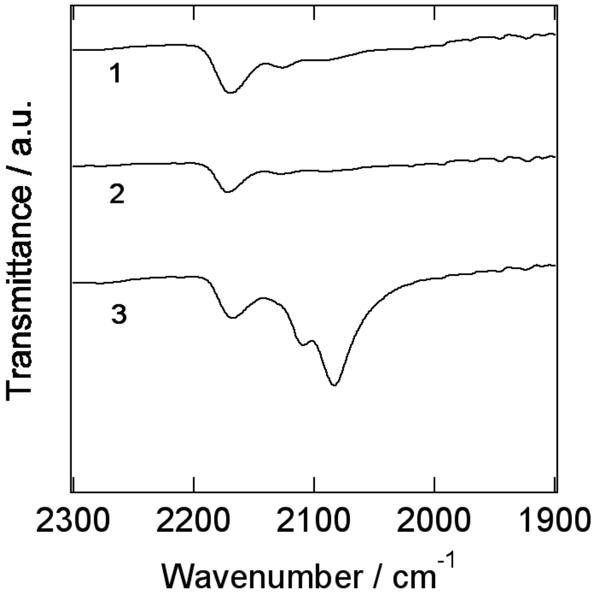

Figure S4. IR spectra of **1**, **2**, and **3**.

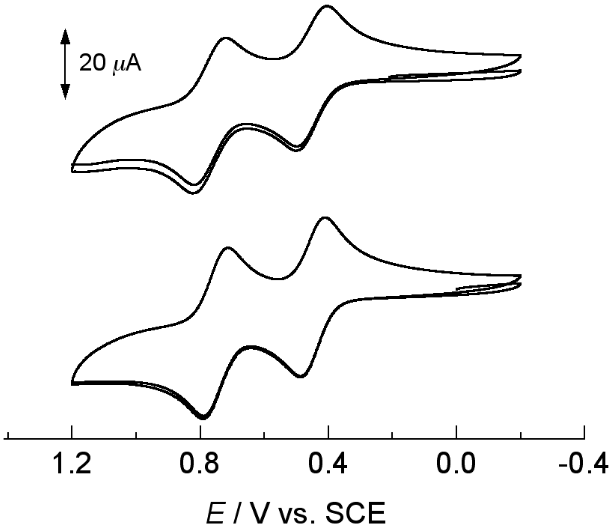

Figure S5. Cyclic voltammograms of L1 (top) and L2 (bottom) at a carbon electrode in 1.0 mM solution of MeCN using *n*-Bu_4NPF_6 as an electrolyte at a scan rate of 0.10 Vs^{-1}.

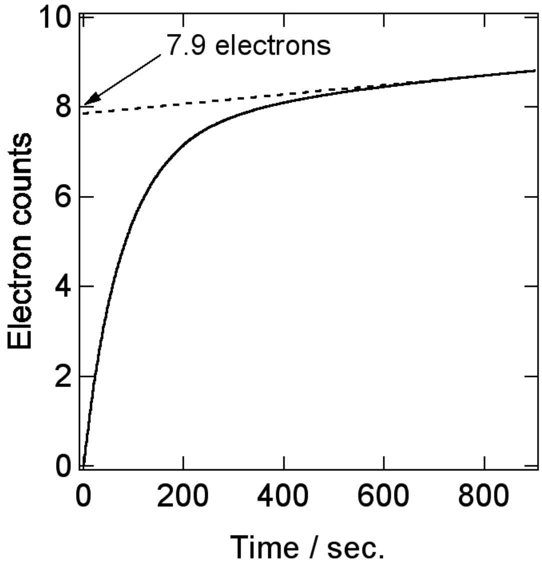

Figure S6. Bulk electrolysis with coulometry of **2** at 1.2 V versus SCE.

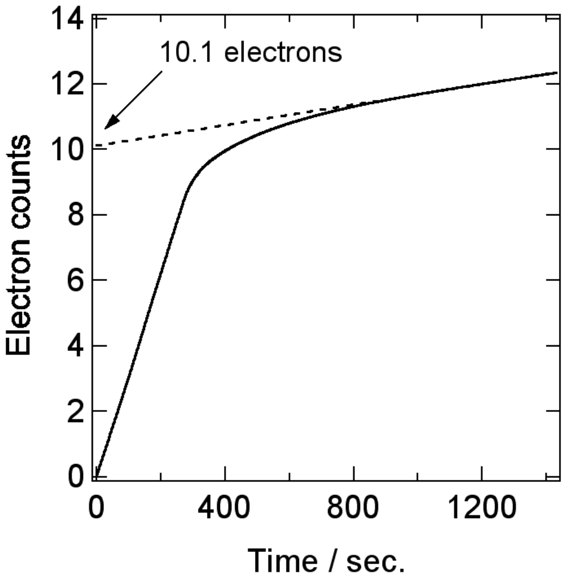

Figure S7. Bulk electrolysis with coulometry of **3** at 1.2 V versus SCE.

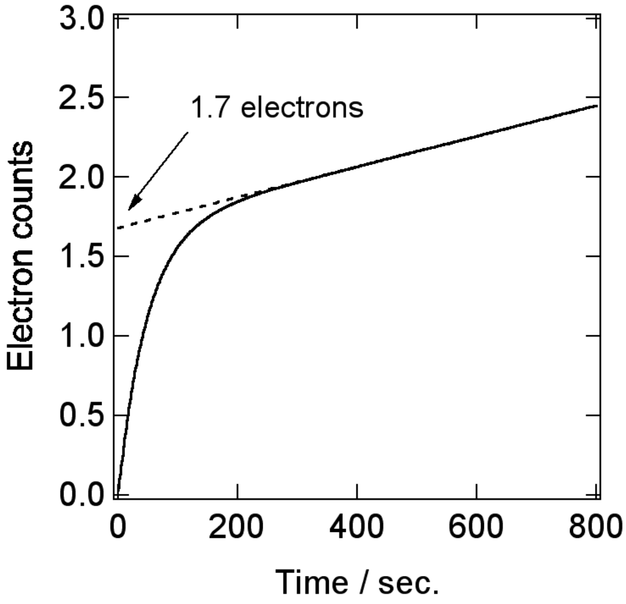

Figure S8. Bulk electrolysis with coulometry of **3** at -0.4 V versus SCE**.**

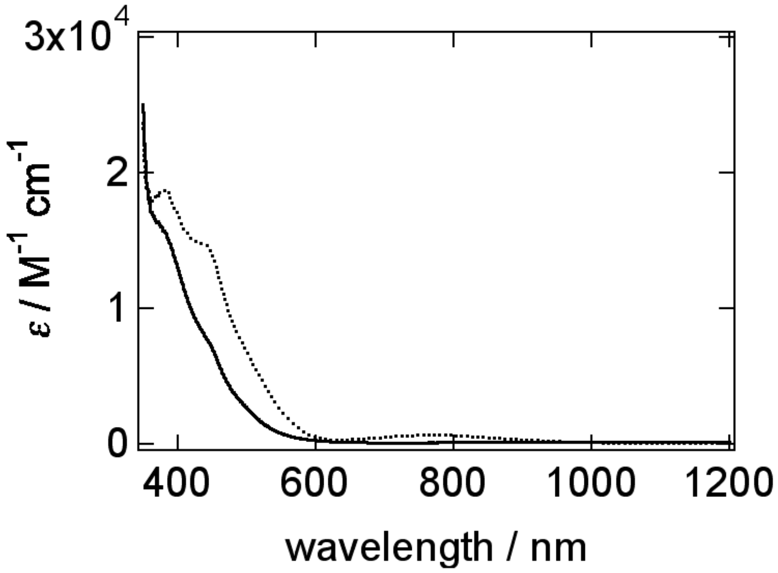

Figure S9. Uv-vis-nir spectra of **2** (dotted line) and **3** (solid line).

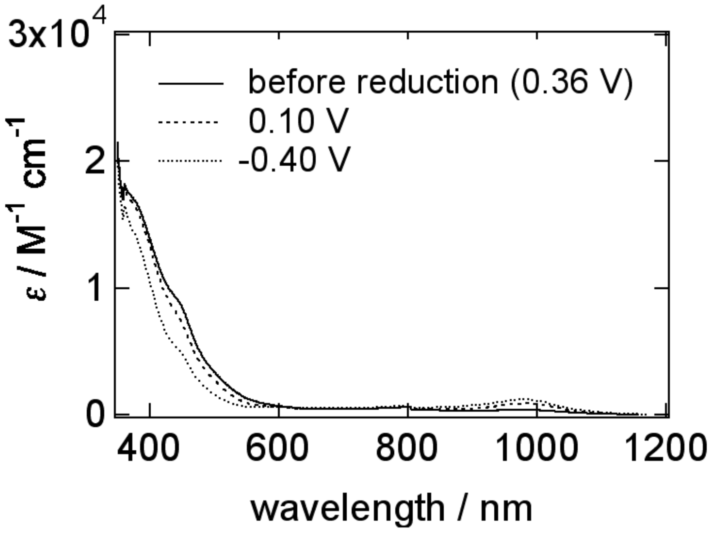

Figure S10. Electronic absorption spectra of **3** upon electrochemical reduction from 0.36 to -0.40 V (potential vs. SCE, 1.0 mM, 0.1 M *n*-Bu_4NPF_6 in acetonitrile, with Pt mesh working electrode, and Pt wire counter electrode).

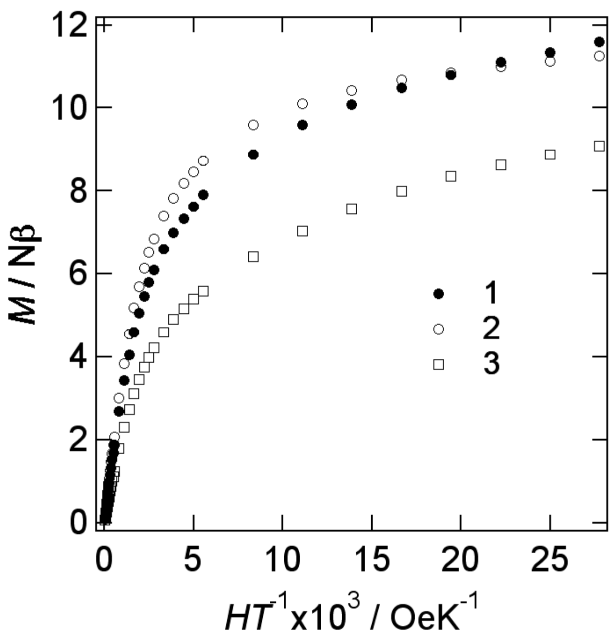

Figure S11. Magnetic field induced magnetization for **1**, **2**, and **3** at 1.8 K.