



Supporting Information

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Effect of Metal-Assisted Assembling Mode of Redox States of Hexaazatriphenylene Hexacarbonitrile**

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Physical measurements

The electrochemical behaviors were investigated using a thin-layer cyclic voltammetry. Tetrabutylammonium tetrafluoroborate ($n\text{-Bu}_4\text{N}$) BF_4 was used as a supporting electrolyte with Ag/Ag^+ as the reference electrode on a ALS Electrochemical Analyzer model 650A. IR spectra were recorded on a Perkin Elmer System 2000 FT-IR with KBr pelet. Electroabsorption spectrum (UV and Visible) was measured with the Hewlett Packard 8452A diode array spectrophotometer.

DFT calculation

The stabilization energy of complexation on the model compounds, (A)–(E) depicted in Figure S6 was calculated using DFT with the Gaussian 03 program. The B3LYP functional was used, along with the 6–31G (6d) basis set for H, C, and N atoms, the 6–31G* (6d) for P atom, and the LANL2DZ (6d) basis set for Cu and Fe atoms. All geometries except B were fully optimized at the above levels using default optimization criteria of the program. The optimization of the molecule B was converged under fixation of the free rotation of methyl groups.

The derivatives of dppFc and dppFc* are compounds (D) and (E), respectively,

whose the PH_2 groups instead of PPh_2 groups. The model compound of the monocopper complex of $\text{HAT}(\text{CN})_6$ on *bpy* coordination to copper(I) ion is shown as (C). The complex of (C) + (D) and (C) + (E) are compounds (A) and (B), respectively. The total energy difference between (A) and (C) + (E) indicates the stabilization energy of complexation on (A), which is derived from two Cu–P coordination bonds. The stabilization energy on (B) is also estimated from the same way. The energy diagrams of the stabilization of complexation on (A) and (B) are described in Figure S7. The stabilization energies on (A) and (B) are 266 and 217 kJ/mol, respectively, which indicates that compound (B) is much more unstable than compound (A), *ca.* 49 kJ/mol. This instability is caused by the introduction of eight methyl groups to Fc moiety.

The consideration of reduction potentials of $[\{\text{Ru}(\text{bpy})_2\}_n(\text{HAT})]^{2n+}$

The degrees of the *net* charge of $[\{\text{Ru}(\text{bpy})_2\}_n(\text{HAT})]^{2n+}$, $\Delta E_{1/2}(\text{Ru}: n - 0)$, are +0.62, +0.97, +1.21 V for complexes of $n = 1-3$, respectively, which are calculated from the difference between the first reduction potential of the metal complexes ($n = 1-3$) and that of free HAT ($n = 0$). The effect of the first coordination to ruthenium(II) ion is corresponding to $\Delta E_{1/2}(\text{Ru}: 1 - 0) = +0.62$ V. Those of the second and third coordination are considered as $\Delta E_{1/2}(\text{Ru}: 2 - 1) = +0.35$ V and $\Delta E_{1/2}(\text{Ru}: 3 - 2) = +0.24$ V, respectively. This indicates the contribution of the first coordination accounts for half of the total shift of trinuclear compound. When the same ratio of the ‘normal’ effect is adopted into compound **1** ($\Delta E_{1/2} = +0.77$ V), the contribution of the first copper(I) coordination should be estimated as +0.39 V.

Table S1. Redox Potentials $E_{1/2}^{[a]}$ of HAT(CN)₆, **1**, and **2**.

Compound	$E_{1/2}(\text{dppX}/\text{dppX}^+)^{[b]}$	$E_{1/2}(\text{H}^0/\text{H}^+)^{[c]}$	$E_{1/2}(\text{H}^-/\text{H}^{2-})^{[c]}$	$E_{1/2}(\text{H}^{2-}/\text{H}^{3-})^{[c]}$
HAT(CN) ₆ ^[d]		-0.48	-0.93	-1.55
1 ^[e]	+0.63	+0.30 (+0.78) ^[f]	-0.09 (+0.84) ^[f]	-0.50 (+1.05) ^[f]
2 ^[e]	+0.21	-0.26 (+0.22) ^[f]	-0.76 (+0.17) ^[f]	-1.13 (+0.42) ^[f]

[a] Potentials in V versus Ag/Ag⁺ measured by the thin-layer cyclic voltammetry (CV).^[ref.S1] [b] dppX (X = Fc for **1**, Fc* for **2**) [c] H = HAT(CN)₆ [d] The CV of HAT(CN)₆ was measured in THF. [e] The CVs of **1** and **2** were measured in dichloromethane. [f] Parenthesis indicates the difference in the potential of complex **1** or **2** from that of free HAT(CN)₆, ($\Delta E_{1/2} = E_{1/2}(\mathbf{1} \text{ or } \mathbf{2}) - E_{1/2}(\text{freeL})$).

[ref.S1] K. Unoura, A. Iwase, H. Ogino, J. Electroanal. Chem. **1990**, 295, 385.

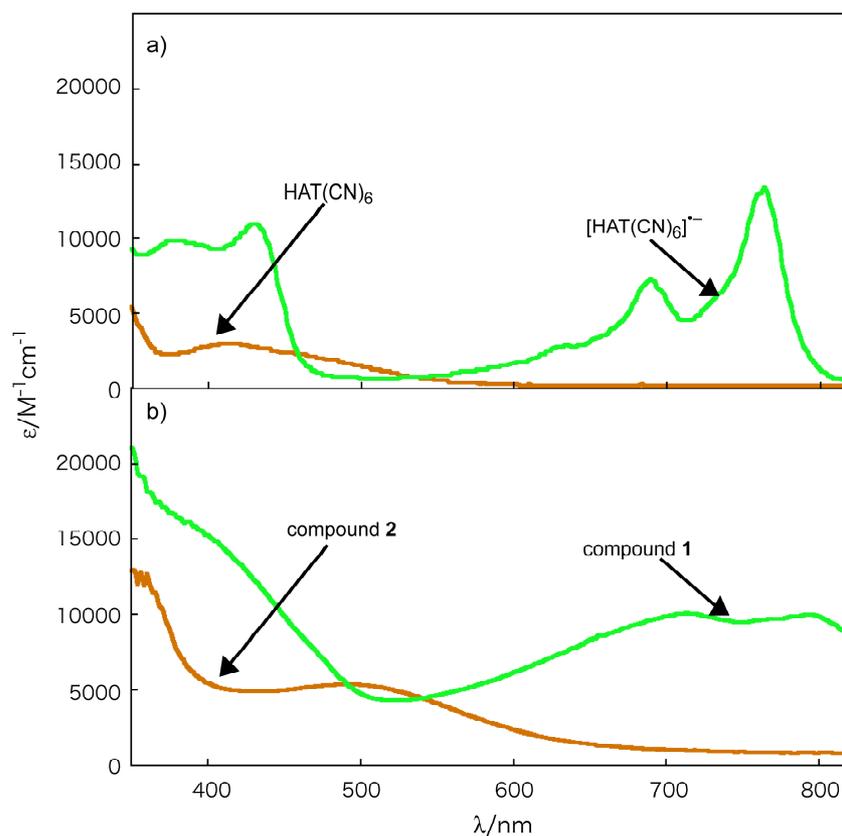


Figure S1. a) The electronic absorption spectra of $HAT(CN)_6$ (brown) and electrochemically generated $[HAT(CN)_6]^{\bullet-}$ (green) in acetone solution. $HAT(CN)_6$ was reduced in acetone with tetra(n-butylammonium)tetrafluoroborate as the supporting electrolyte. b) The electronic absorption spectra of **1** (green) and **2** (brown) in dichloromethane solution.

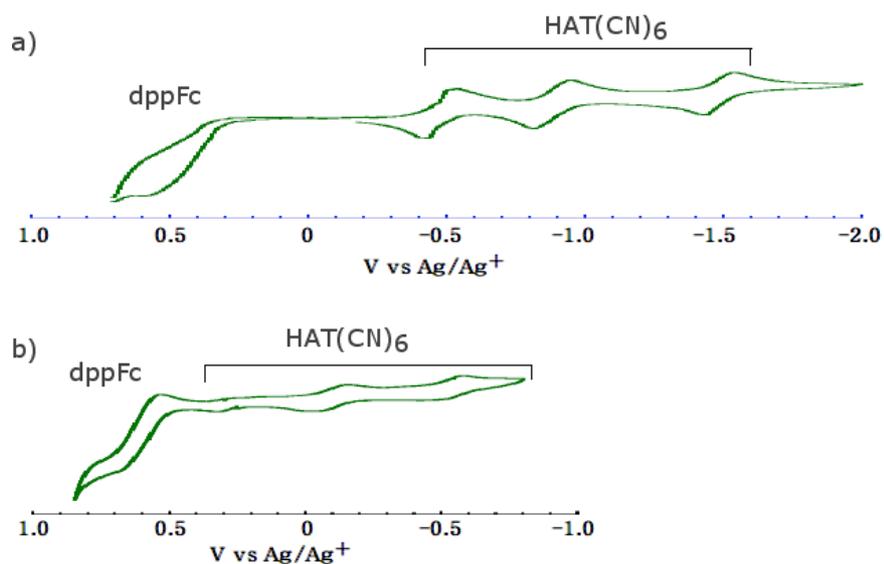


Figure S2. The cyclic voltammograms of a) free $\text{HAT}(\text{CN})_6$ and free dppFc in THF and b) compound **1** in dichloromethane.

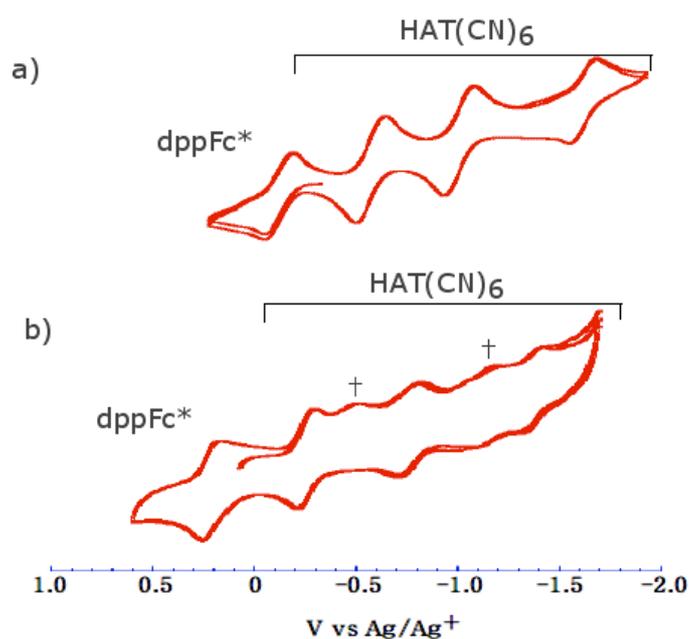


Figure S3. The cyclic voltammograms of a) free $\text{HAT}(\text{CN})_6$ and free dppFc* in THF and b) compound **2** in dichloromethane. The compound **2** is partially dissociated in dichloromethane, which shows the redox waves corresponding to those of free $\text{HAT}(\text{CN})_6$ indicated as the cross, †.

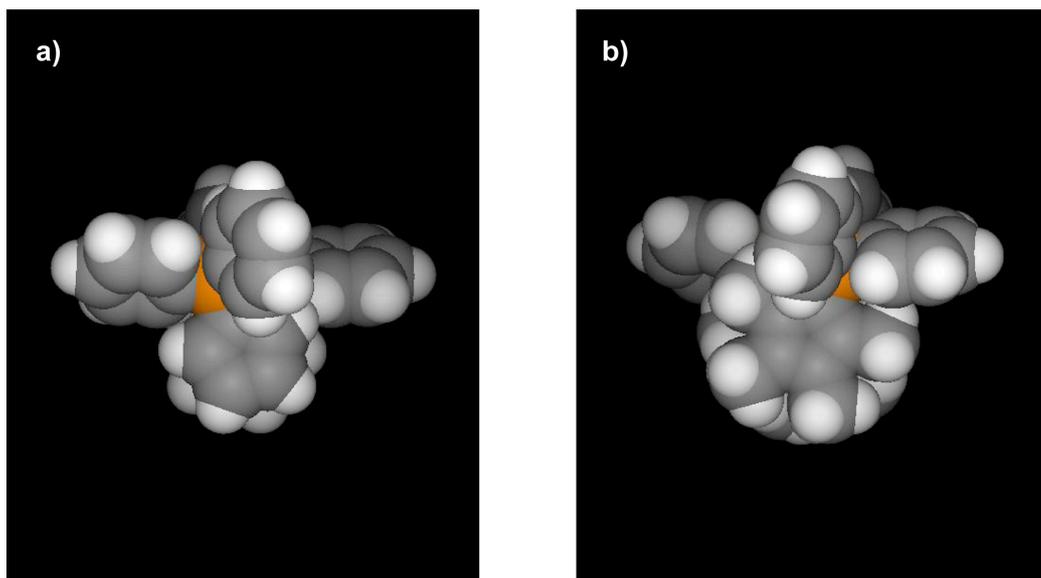


Figure S4. Space-filling representations of Structures of diposphine ligands, a) dppFc and b) dppFc* in the same scale.

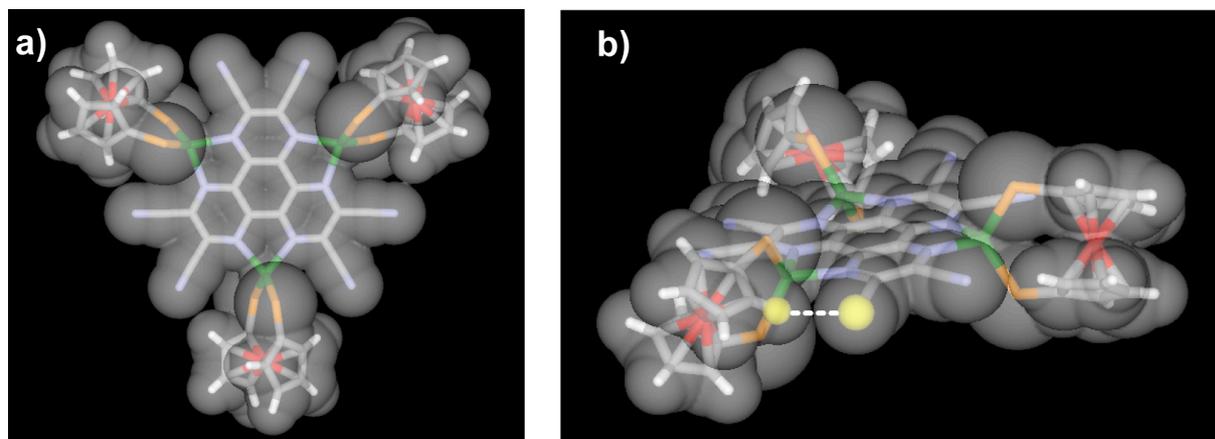


Figure S5. Stick representation of compound **1** with von der Waals surface model. The phenyl groups of dppFc and counter anions were omitted for the sake of clarity. a) Top view of **1**. b) Side view of **1**. The yellow atoms represents the nearest atoms between dppFc and HAT(CN)₆ with the distance (2.78 Å) between N atom of CN group and H atom of Fc moiety.

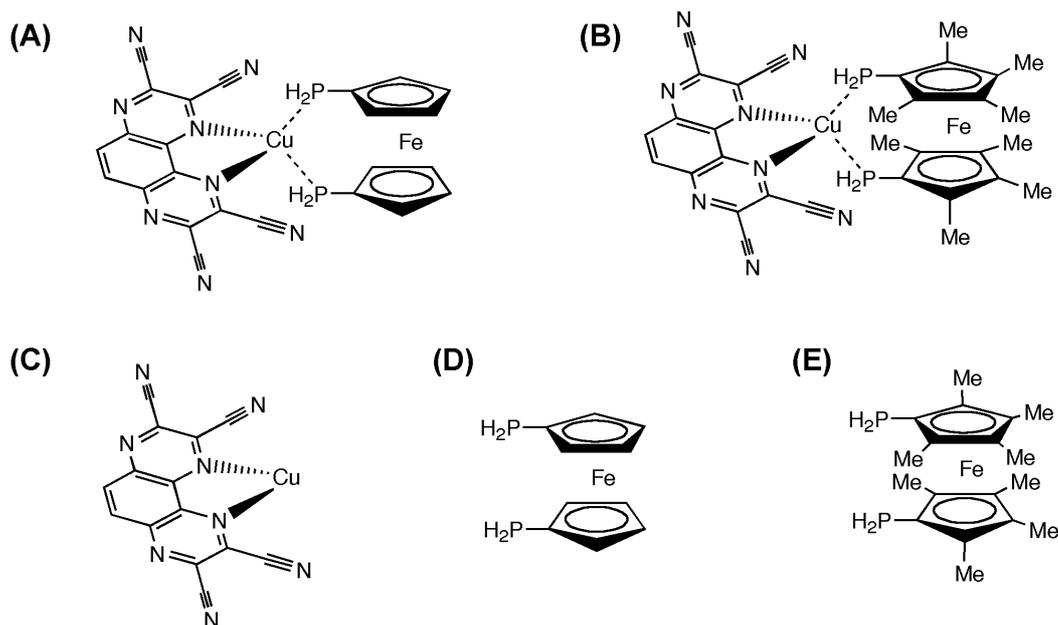


Figure S6. Model compounds for the DFT calculation.

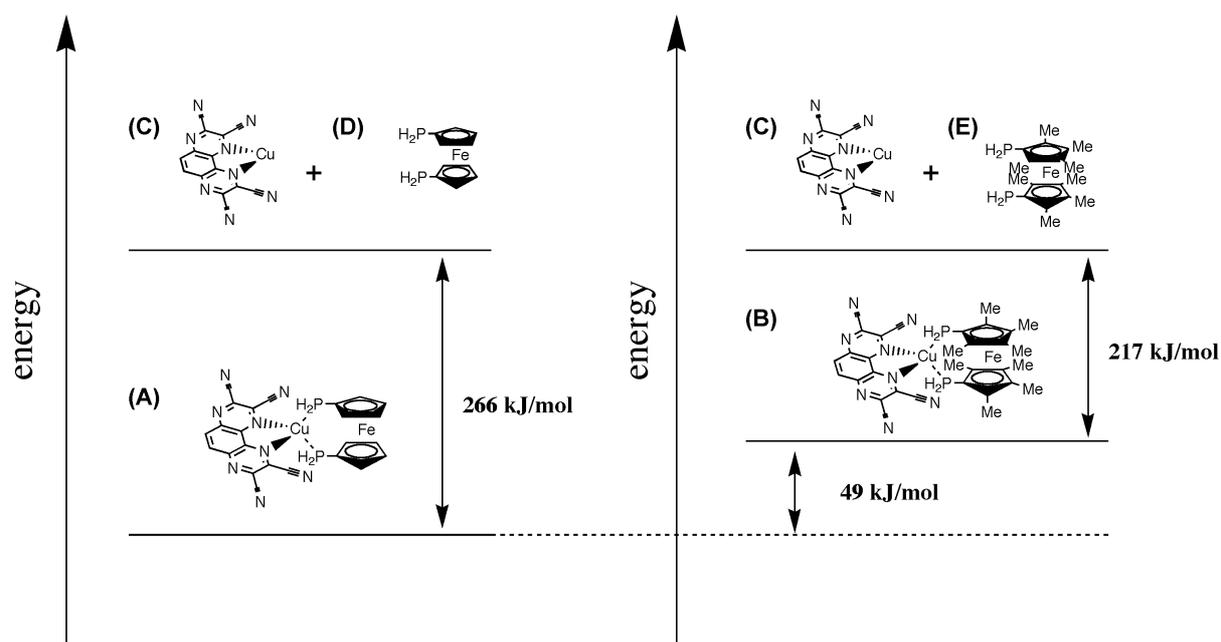


Figure S7. The energy diagrams of the stabilization of complexation of model compounds (A) and (B). The stabilization energy of complexation of (A), 266 kJ/mol (left), is larger than that of (B), 217 kJ/mol (right), which demonstrates that the substitution of eight methyl groups to Fc moiety (the change from Fc to Fc*) destabilize the complexation (49 kJ/mol).