Coordination Modes

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

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Metal-directed self-assembly through several molecular recognition events on polydentate ligands with a suitable arrangement of binding sites has provided a route for the spontaneous but controlled generation of supramolecular architectures.[1] In particular, the properties of inorganic supramolecules with redox-active units are of intense interest with respect to their potential for application in sensors,[2] machines,[3] and electronic devices.[4] However, much less is known about the simultaneous control of both the assembly and the redox-state of these units. Organocyanides with low-lying π^* orbitals are particularly promising candidates for redox-active units because of their characteristic electronic structures, which are based on different, readily accessible oxidation states (neutral and anion radical states) and give rise to fascinating conductive and magnetic materials.[5] In addition, a metal-directed approach with these π-accepting molecules has the advantage not only of rational bottom-up construction, with its regulated coordination geometry, but also plays an important role in influencing the ligand-centered redox potential. A net charge transfer on complexation operates in metal/π ligand systems. This transfer gives rise to the "normal" effect,[6] which causes a large anodic shift because of the σ-polarization effect of coordination.[7] However, strong π back donation often occurs and overcompensates the σ-polarization effect, thus affording a cathodic shift.[8] Hence, we have focused on controlling the oxidation states of the ligand through metal-directed self-assembly.

Among the π-accepting organocyanides, hexaazatriphenylene hexacarbonitrile hat-$(CN)_6$ is an intriguing molecular unit[9,10] because of its characteristic electron-deficient heterocyclic core, which affords three reversible redox transitions as well as two possible modes of coordination: the bipyridine chelating (bpy sites) and the terminal nitrile N-binding sites (CN sites, Figure 1). Herein, we report two supramolecules of

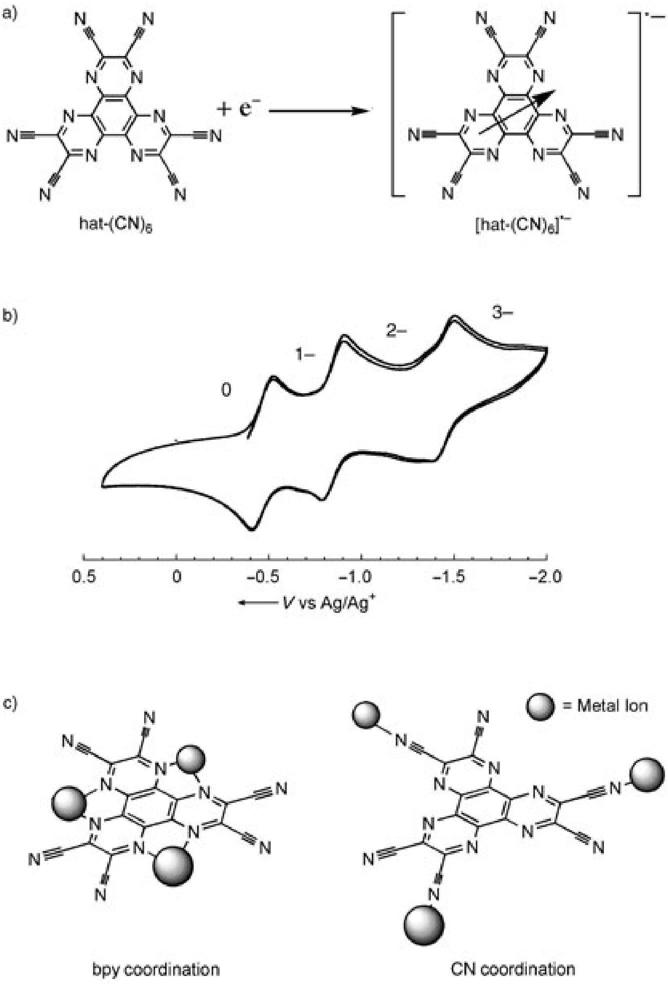

Figure 1. a) Two readily accessible different oxidation states of hat-$(CN)_6$: a neutral (left) and an anion radical form (right). b) Cyclic voltammogram of hat-$(CN)_6$ in THF showing three electrochemically reversible reduction waves. c) Two possible coordination modes of hat-$(CN)_6$: bpy (left) and CN (right) coordination modes.

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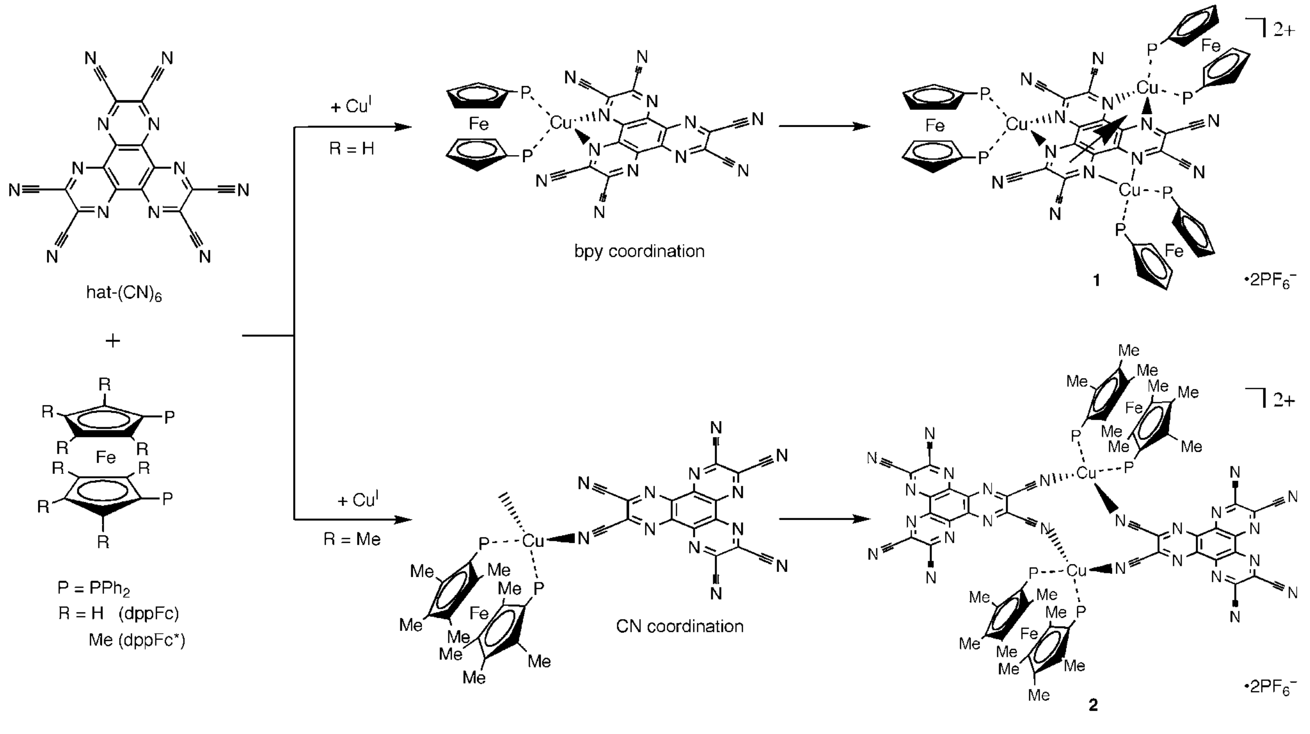
hat-(CN)$_6$, [{Cu(dppFc)}$_3${hat-(CN)$_6$}](PF$_6$)$_2$ (**1**) and [{Cu(dppFc*)}$_2${hat-(CN)$_6$}$_2$](PF$_6$)$_2$ (**2**) (dppFc = 1,1′-bis(diphenylphosphino)ferrocene, dppFc* = 1,1′-bis(diphenylphosphino)octamethylferrocene), which possess different oxidation states; **1** contains the anion radical [hat-(CN)$_6$]$^{\bullet -}$ while **2** contains the neutral state hat-(CN)$_6$. Interestingly, the coordination mode of hat-(CN)$_6$ exerts a drastic effect on its reduction potentials through the "normal" effect of σ polarization.

The key to this synthesis was to design diphosphine coligands with ferrocene units on the secondary coordination sphere, namely dppX (X = Fc for **1** or Fc* for **2**; Fc = ferrocene, Fc* = octamethylferrocene). We used hat-(CN)$_6$ and [Cu(CH$_3$CN)$_4$](PF$_6$) as the common assembling components, and dppX for modification of the mode of coordination. The overall process is shown in Scheme 1. Regardless of the ratio of the starting components (hat-(CN)$_6$, [Cu(CH$_3$CN)$_4$](PF$_6$), and dppFc) the reaction proceeded at room temperature in dichloromethane/acetone to give a dark green solution. Single crystals of **1** were obtained by diffusion of hexane into a solution of the compound in dichloromethane. However, the use of dppFc* instead of dppFc under the same reaction conditions afforded a red solution. Crystals of **2** were obtained by diffusion of THF/hexane.

The electronic absorption spectrum of **1** in dichloromethane (see the Supporting Information) shows two intense characteristic bands at 715 and 805 nm which correspond to the π–π* transition band of the electrochemically generated anion radical [hat-(CN)$_6$]$^{\bullet -}$ (690 and 764 nm). In the case of **2**, no bands attributable to the anion radical form were observed, while one at 492 nm was detected, which was assigned to an MLCT transition from a copper(I) center to hat-(CN)$_6$. The vibration spectra of the complexes also supported the electronic characterization of hat-(CN)$_6$ deduced from the electronic absorption spectra. A single nitrile stretching band found at 2210 cm^{-1} for **1** was shifted to a lower energy region than that of free hat-(CN)$_6$ (at 2241 cm^{-1}). In contrast, compound **2** showed two bands at 2241 and 2194(sh) cm^{-1}, which were ascribed to the metal-free CN sites and the coordinated CN sites of the neutral hat-(CN)$_6$, respectively.[11]

The X-ray crystallographic structure of **1** (Figure 2) reveals a novel Cu$_3$Fc$_3$ hexanuclear supramolecule with a trianglar shape.[12] Complex **1** is composed of three [Cu(dppFc)]$^+$ units, with each of the copper(I) ions chelated by two P sites of dppFc (average Cu···P distance: 2.258(4) Å). The remaining two basal sites of the tetrahedral Cu coordination environment are occupied by two N atoms from bpy sites of [hat-(CN)$_6$]$^{\bullet -}$ which link three [Cu(dppFc)]$^+$ units (average Cu···N distance: 2.079(9) Å). Two PF$_6^-$ counterions are accommodated in the cavities on each side of the planar [hat-(CN)$_6$]$^{\bullet -}$ that are created by the 12 phenyl groups of the three dppFc units.

The crystal structure of **2** shows a tetranuclear Cu$_2$Fc*$_2$ complex[13] containing two hat-(CN)$_6$ molecules and two [Cu(dppFc*)] units (average Cu···P distance: 2.286(3) Å) as depicted in Figure 3. The remaining vacant sites on the tetrahedral copper(I) ions of each [Cu(dppFc*)] unit are occupied by two nearest-neighbor CN groups of each hat-(CN)$_6$ in two characteristic coordination arrangements: a linear arrangement (Cu···N distance: 1.999(7) Å, Cu-N-C angle: 175.2(7)°) and a bending arrangement (Cu···N distance: 2.115(7) Å, Cu-N-C angle: 147.3(7)°) which afford a dimer complex of hat-(CN)$_6$. It should be noted that the intramolecular π–π stacking interaction (3.31(1) Å) between the phenyl rings of dppFc* and hat-(CN)$_6$ compensates for the



Scheme 1. Self-assembly of the hexanuclear complex **1** and the tetranuclear complex **2**.

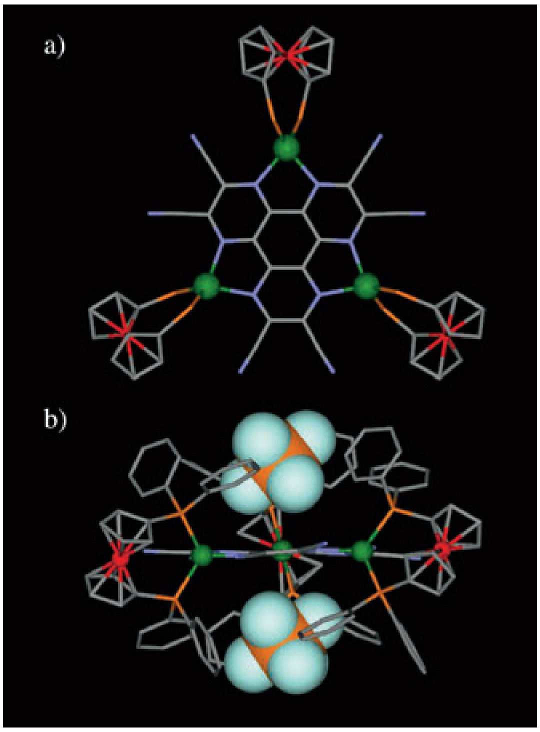


Figure 2. Molecular structure of the hexanuclear complex **1**. a) The top view of **1**. The phenyl groups of dppFc and the PF$_6^-$ counterions are omitted for clarity. b) The side view of **1** with PF$_6^-$ trapped within the cavities.

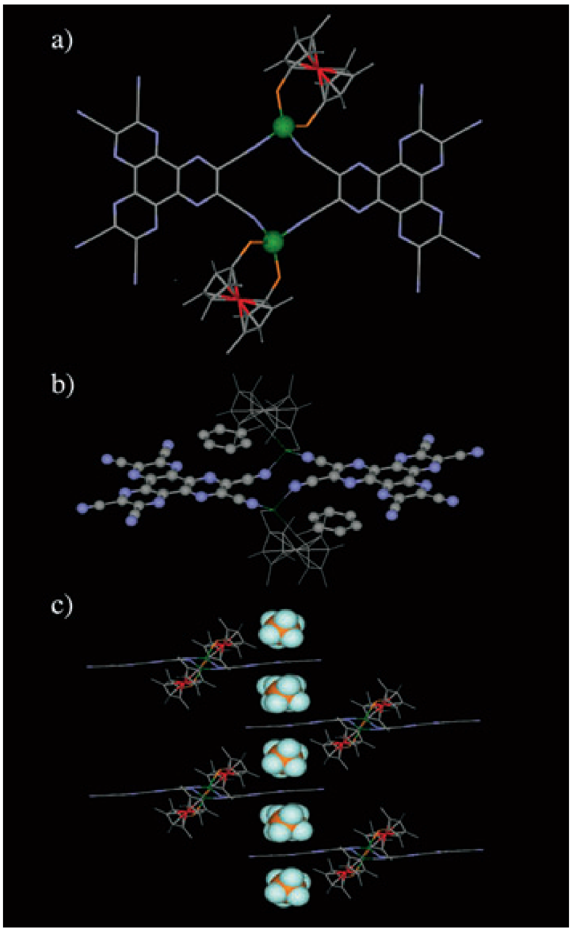


Figure 3. Molecular structure of the tetranuclear complex **2**. a) The top view of **2**. The phenyl groups of dppFc* and the PF$_6^-$ counterions are omitted for clarity. b) The side view of **2** showing the intramolecular π–π stacking interactions between the one of the phenyl rings of dppFc* and hat-(CN)$_6$. c) Infinite structure of **2**. The alternating assembles of hat-(CN)$_6$ and PF$_6^-$ afford the 1-D column structure.

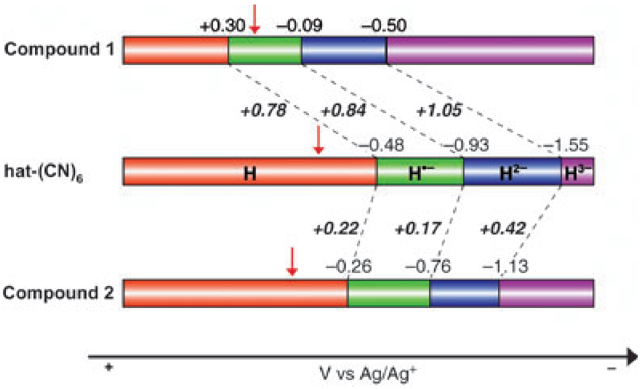


Figure 4. Schematic representation of redox potentials of hat-(CN)$_6$ (**H**) for **1**, **2**, and free **H**. The redox potentials of each compound are shown in normal fonts. The bold italic numbers indicate the difference in the potential of **1** or **2** from that of free **H**, ($\Delta E_{1/2} = E_{1/2}$(**1** or **2**)$-E_{1/2}$(free **H**)). The red arrow indicates the resting potential.

weaker bending coordination, thus resulting in stabilization of the supramolecular structure (Figure 3b). Although the four noncoordinated CN sites of hat-(CN)$_6$ give a large remaining area, which allows for intermolecular π stacking, this interaction is hampered by the PF$_6^-$ counterion located on the plane of the hat-(CN)$_6$ unit (Figure 3c). This situation arises because the electron-deficient heterocyclic core of hat may prefer the anion–π interaction[14] to intermolecular π-stacking interactions.

Although the spectroscopic and structural results indicate that the oxidation state of hat-(CN)$_6$ is dependent on its coordination mode, the results of the electrochemical studies are even more striking. The redox potentials and assignments of each electrochemical process for compounds **1**, **2**, and free hat-(CN)$_6$ are summarized in Figure 4 (see also the Supporting Information). Compared with the redox potentials of free hat-(CN)$_6$, those of the metal complexes encounter a more positive shift because of the "normal" effect.[15,16] The strength of this effect, illustrated by the value of $\Delta E_{1/2}$, highlights the significant difference between **1** and **2**; the process of hat-(CN)$_6$/[hat-(CN)$_6$]$^{\bullet-}$ for **1** ($\Delta E_{1/2} = +0.78$ V) is much larger than that for **2** ($\Delta E_{1/2} = +0.22$ V). The larger positive shift for **1** allows hat-(CN)$_6$ to be reduced to [hat-(CN)$_6$]$^{\bullet-}$ by an outer-sphere electron-transfer reaction involving the oxidation of copper(I) to copper(II).[17] The difference in the "normal" effect between **1** and **2** is ascribed to the cooperation of the number of coordinated copper(I) ions (three ions and one ion per hat-(CN)$_6$ molecule in **1** and **2**, respectively) and the coordination mode (bpy sites in **1** and CN sites in **2**). Although studies of [{Ru(bpy)$_2$}$_n$(hat)]$^{2n+}$ (n = 1–3)[18] show that the larger positive shift of the reduction potentials of hat occurs with an increase in the number of coordinated metal ions, they also show that it is the coordination of the first metal ion, rather than the coordination of the second or third metal ion, that influences the reduction potentials of the hat ligand; the contribution of the first coordination is estimated to be half of the total shift for a trinuclear compound.[18,19] From this standpoint, the coordination of the ligand to the first copper(I) ion in **1** can be estimated as approximately $+0.39$ V,[19] which is much larger than the "normal" effect shown in complex **2** ($+0.22$ V). This result implies that the bpy coordination, rather than the terminal CN coordination, directly affects the electronic structure of the hat-$(CN)_6$ core.

Of the two possible coordination modes, coordination of the chelating bpy site is expected to be favored over coordination of the monodentate CN site. However, complex **2** is constructed by coordination of the CN groups, which implies that coordination to $[Cu(dppFc^*)]^+$ units at bpy sites is hampered. One of the most likely reasons for this is the steric repulsion between hat-$(CN)_6$ and the methyl groups of Fc*—the nearest distance between hat-$(CN)_6$ and dppFc in **1** is only 2.78 Å (estimated from the distance between the N atom of the CN groups and the H atom of the Fc moiety).[20] It is clear that the modification of Fc to Fc* causes the steric repulsion. In other words, hat-$(CN)_6$ recognizes the size of the Fc moieties on the bpy sites in the course of the self-assembling process, and chooses the preferable coordination mode for the metal centers.

In summary, this study demonstrates the effect of the coordination mode on the oxidation states of hat-$(CN)_6$ that can be achieved through a self-assembly process with copper(I) ions and ferrocene derivative coligands. The size of the ferrocene moieties plays a key role in determining the coordination mode, which causes a positive shift of reduction potentials of hat-$(CN)_6$ by net charge transfer. This approach paves the way not only to the accurate control of the oxidation state of redox-active ligands, but also to the close control of molecular and electronic structures of supramolecules.

Experimental Section

All operations were carried out in a nitrogen atmosphere by using standard Schlenk techniques. Hat-$(CN)_6$,[21] $[Cu(CH_3CN)_4](PF_6)$,[22] dppFc,[23] and dppFc*[24] were prepared according to literature procedures.

1: A solution of $[Cu(CH_3CN)_4](PF_6)$ (204 mg, 0.548 mmol) in acetone (5 mL) was added to a solution of dppFc (304 mg, 0.548 mmol) in CH_2Cl_2 (5 mL), and the resulting mixture was then added to a solution of hat-$(CN)_6$ (52.6 mg, 0.137 mmol) in acetone (10 mL). The reaction mixture immediately turned dark green. After the solvents had been removed in vacuo, the precipitate was washed with MeOH (5 mL) and THF (1 mL). The crystals were obtained by the diffusion method with CH_2Cl_2/hexane (30%). Although the composition obtained from the crystal structure is $\mathbf{1}\cdot 6\,CH_2Cl_2$, the elemental analysis is consistent with $\mathbf{1}\cdot 2\,CH_2Cl_2$. This difference arises because some solvent molecules are removed from the crystal on drying. Elemental analysis calcd for $C_{122}H_{88}Cl_4Cu_3F_{12}Fe_3N_{12}P_8$ ($\mathbf{1}\cdot 2\,CH_2Cl_2$): C 54.31, H 3.29, N 6.23; found: C 54.77, H 3.57, N 6.30.

2: This compound was prepared by a similar procedure as **1**, except that dppFc* was used as the starting material. The reaction mixture gave a red solution. After the solvents had been removed in vacuo, the precipitate was washed with EtOH (5 mL). The crystals were obtained by the diffusion method with THF/hexane (22%). Elemental analysis calcd for $C_{120}H_{88}Cu_2F_{12}Fe_2N_{24}P_6$ (**2**): C 57.22, H 3.52, N 13.35; found: C 56.72, H 3.70, N 12.34.

X-ray structure determination**:** Measurements were conducted on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). The structures were solved by Patterson methods (DIRDIF92/PATTY) and expanded using Fourier techniques. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. CCDC-258214 (**1**) and CCDC-258213 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[12] Crystal data for **1:** $C_{126}H_{96}Cl_{12}Cu_3F_{12}Fe_3N_{12}P_8$ (**1**·6 CH_2Cl_2), $M_r = 3037.61$, orthorhombic, space group *Pbcn* (no. 60), $a = 30.80(5)$, $b = 17.66(2)$, $c = 23.66(4)$ Å, $V = 12869(33)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.568$ g cm^{-3}, $\mu = 1.236$ mm^{-1}. Data collection ($6.0 < 2\theta < 50.0°$) was performed at 223 K. Non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were introduced as fixed contributors. The structure was refined on F^2 and converged for 6233 unique reflections with $I > 3\sigma(I)$ and 794 parameters to give $R1 = 0.1073$ and $wR2 = 0.2358$.

[13] Crystal data for **2**: $C_{80}H_{44}O_5CuF_6FeN_{12}O_5P_3$ (**2**·10 THF), $M_r = 1579.61$, triclinic, space group $P\bar{1}$ (no. 2), $a = 15.344(7)$, $b = 17.443(11)$, $c = 18.401(11)$ Å, $\alpha = 85.80(9)$, $\beta = 68.33(8)$, $\gamma = 65.41(7)°$, $V = 4142(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.266$ g cm^{-3}, $\mu = 0.558$ mm^{-1}. Data collection ($4.4 < 2\theta < 50°$) was performed at 163 K. The structure was refined on F^2 and converged for 7908 unique reflections with $I > 3\sigma(I)$ and 922 parameters to give $R1 = 0.0886$ and $wR2 = 0.2636$. Some of solvent molecules were refined isotropically, whereas other atoms were refined aniotropically. Hydrogen atoms were introduced as fixed contributors. One of the PF_6^- counterions was disordered, therefore it was refined as the disordered model.

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[16] Strongly π-accepting organocyanides such as TCNQ usually give negative shifts to the reduction potentials through π back donation,[10] with the exception of a tetranuclear rhenium complex.[9] Here, the "normal" effect dominates the reduction potentials of hat-$(CN)_6$.

[17] The possibility of dppFc acting as the reductant was also considered. However, since we have previously isolated the related compound with dppe,[11a] the copper(I) ion is the best candidate as the reducing agent.

[18] The reduction potentials of $[\{Ru(bpy)_2\}_n(hat)]^{2n+}$ are cited from the following reference (see also the Supporting Information): A. Masschelein, A. Kirsch-De Mesmaeker, C. Verhoeven, R. Nasielski-Hinkens, *Inorg. Chim. Acta* **1987**, *129*, L13.

[19] See the Supporting Information.

[20] DFT calculations on the model compounds also supports this steric effect by comparison of bpy coordination to [Cu(dppFc)] (**A**) and that to [Cu(dppFc*)] (**B**). As a result, the stabilization energy for the complexation to **B** is much smaller than that to **A**, about 49 kJ mol^{-1}, which indicates that the stable complexation is hampered by the methyl groups on Fc*. For details see the Supporting Information.

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