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A biferrocenium salt containing paramagnetic tetracyanoquinodimethane hexamers: Charge disproportionation via donor–acceptor interactions†

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[Dineopentyl-biferrocene]$_2$[Cl$_1$TCNQ]$_7$, which has an unprecedented high donor–acceptor ratio of 2:7, contains a linear paramagnetic hexamer of Cl$_1$TCNQ. Both the donor and acceptor molecules exhibit charge disproportionation in the crystal through mutual electrostatic interactions.

Crystal engineering of mixed valence compounds has been a topic of continuous interest for many years. Biferrocene is an electron donor (D) comprised of two ferrocene units exhibiting both mixed-valence monocation (D$^+$) and non-mixed-valence dication (D^{2+}) oxidation states. To date, many biferrocenium salts containing D$^+$ have been prepared, and their valence states have been extensively investigated.[1] Recently, we prepared a series of alkyl-biferrocenium salts with various acceptor (A) molecules, including tetracyanoquinodimethane (TCNQ) derivatives.[2,3] Salts with a D/A ratios of 1:1–1:3 were obtained; the valency of the donor changes from D$^+$ to D^{2+} with increasing stoichiometry. In particular, the intermediate salts contain both D^{2+} and D$^+$ molecules.[2a,b] The coexistence of dications and monocations is an interesting phenomenon that has also been found in viologen salts.[4] Charge disproportionation, or charge separation, is an important topic in the physics of charge-transfer salts.

This communication reports the structure and valence state of a biferrocenium salt, i.e., [dineopentyl-biferrocene]$_2$[Cl$_1$TCNQ]$_7$ **1** (**Fig. 1**), with a D/A ratio of 2:7,[5] which is the highest ratio to date among reported biferrocenium salts. We reported previously that [dineopentyl-biferrocene][F$_1$TCNQ]$_3$ exhibits a charge-transfer phase transition between the monovalent state ([D]$^+$[A$_3$]$^-$) and divalent state ([D]$^{2+}$[A$_3$]$^{2-}$) at around 120 K. The transition can be controlled by molecular modification while maintaining the crystal structure.[3] However, the use of Cl$_1$TCNQ, which has comparable electron affinity but slightly larger molecular volume than F$_1$TCNQ, afforded the salt of **1** with a different D/A ratio and structure. As described below, both the donor and acceptor units exhibit charge disproportionation in this salt, the valence state of which is represented as [D]$^{2+}$[D]$^+$[A$_6$]$^{3-}$[A]^0. Interestingly, this salt contains a paramagnetic hexamer of the acceptor.
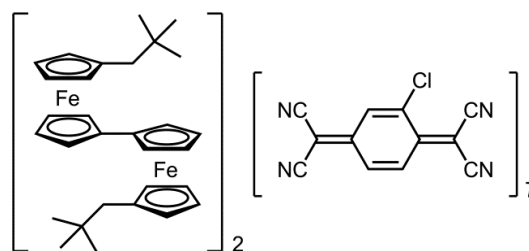

Fig. 1. Structural formula of [dineopentyl-biferrocene]$_2$[Cl$_1$TCNQ]$_7$ **1**.

X-Ray crystallography revealed that this salt has a segregated-stack structure, where the donor and acceptor each form a columnar stack along the [1 0 –2] direction (**Fig. 2a**, **Fig. S1**, ESI†).[6] Two crystallographically independent donor molecules, D^{2+} and D$^+$, exist in the crystal, as determined from the differing bond lengths.[2,7] Both are located on inversion centers, and the valence in the latter molecule is averaged owing to rapid electron transfer between Fe^{3+} and Fe^{2+}. This charge disproportionation is ascribed to the difference in local electrostatic interactions between the donors and acceptors, similar to previously reported salts containing D^{2+} and D$^+$.[2a] The molecular arrangement viewed along the stacking direction is shown in **Fig. 2b**. Each Fe atom in the D^{2+} state is surrounded by three electronegative cyano groups from the acceptors (CN···Fe distances: 4.098, 4.128, and 4.260 Å), which stabilizes the dication state. Such CN···Fe proximity often dominates the valence state in biferrocenium salts.[2] In contrast, the Fe atoms in the D$^+$ state have only one nearby cyano group at a longer CN···Fe distance of 4.326 Å.
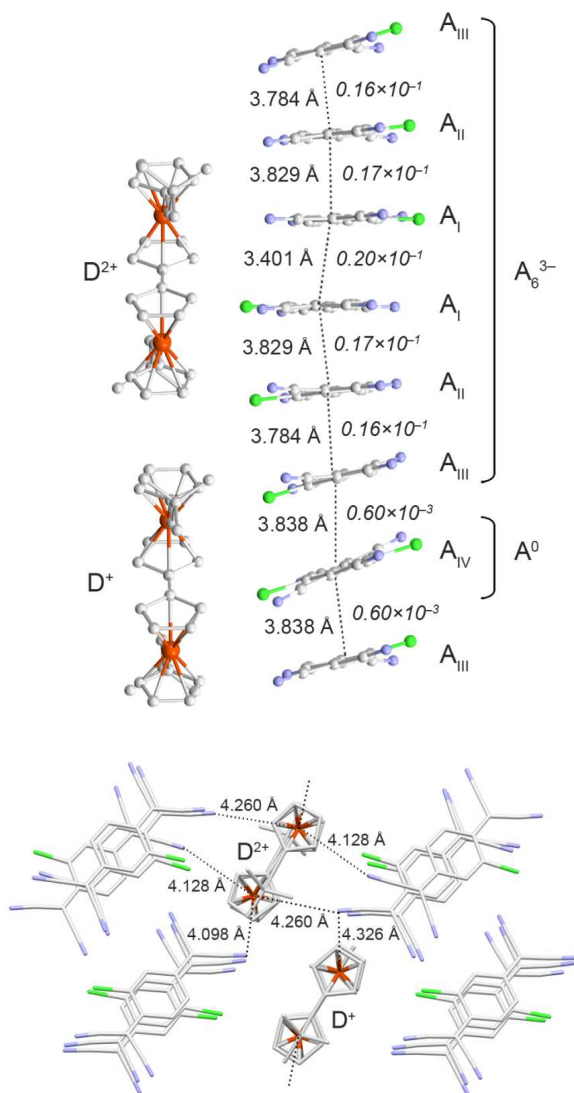
Fig. 2. Molecular arrangement of **1** viewed a) perpendicular to the stacking direction, where intermolecular centroid–centroid distances are indicated by dashed lines and the values of the overlap integrals are shown in italics, and b) along the stacking direction, where short CN···Fe intermolecular distances are indicated by dotted lines.

The acceptor molecules also exhibit charge disproportionation. In the acceptor column, four crystallographically independent molecules (A_I–A_{IV}) are present, of which A_I–A_{III} have negative charges of −0.5 and A_{IV} is neutral.[9] A_I–A_{III} form a linear centrosymmetric hexamer, i.e., $[A_{III}$–A_{II}–A_I–A_I–A_{II}–$A_{III}]^{3-}$, that accommodates three electrons (**Fig. 2a**). The neutral molecule, A_{IV}, is located between the hexamers and is more tilted with respect to the stacking axis than A_I–A_{III}. The intermolecular overlap integrals calculated using the EHMO method[10] were comparable in the hexamer (16–20×10^{-3}, shown in **Fig. 2a**), although the interplane distances in the unit exhibited some variation (centroid–centroid: 3.40–3.83 Å, centroid–plane: 3.26–3.30 Å). The overlap integrals between the neutral and adjacent molecules were much smaller (0.6×10^{-3}); therefore, the hexamer can be regarded as an electronically isolated uniform unit. The charge disproportionation in the crystal is again accounted for by intermolecular electrostatic interactions: A_I–A_{III} have short

CN···Fe distances with cations via one or two cyano groups, while A_{IV} has no such interaction. Furthermore, the negatively charged hexamer is adjacent to D^{2+}, while A_{IV} is adjacent to D^+ (**Fig. 2**).

The valence state of **1** was further investigated by magnetic susceptibility measurements (**Fig. 3**). The χT value was 2.16 emu K mol^{-1} at room temperature and nearly temperature independent down to ~20 K, below which the value sharply decreased. As the hexamer accommodates three electrons in delocalized molecular orbitals, one unpaired spin should remain. The magnetic moments of the organic radical and ferrocenium cation are 0.375 and ~0.6 emu K mol^{-1}, respectively.[2] The observed susceptibility is in excellent agreement with one spin on the hexamer and three spins on the Fe atoms, of which two are from D^{2+} and one is from D^+ ($0.375 + 0.6 \times 3 = 2.175$ emu K mol^{-1}). The temperature independent behavior indicates that the magnetic interaction between the hexamers is small. In the ESR spectrum, a very broad isotropic signal was observed at room temperature ($g = 2.01$, $\Delta H_{p-p} = 300$ G; **Fig. S2a**, ESI†), which is ascribed to the spin delocalized on the hexamer. Signals from the cation spins were unobserved at room temperature because of the fast relaxation, whereas a typical anisotropic signal[11] of the cation spin ($g_{\parallel} = 3.40$, $g_{\perp} = 2.00$) appeared at 77 K (**Fig. S2b**, ESI†). The temperature dependence of the ESR spectra of the single crystals, which displayed separate signals of the cation spin and anion spin, is consistent with this feature (**Fig. S3**, ESI†).
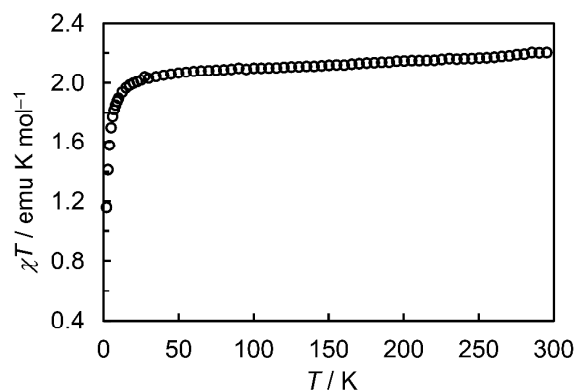

Fig. 3. Temperature dependence of the magnetic susceptibility (χT) of **1**.

The hexamer unit, in which the unpaired electron is confined, is regarded as a quantum well that is ~2 nm length. Electronic excitations in the hexamer were observed as a very broad absorption peak in the infrared region around 3500 cm^{-1} (**Fig. S4**, ESI†), similar to the very broad peak at around 3300 cm^{-1} exhibited by $(F_1TCNQ)_3{}^-$.[12] The electrical conductivity along the stacking axis of the crystal is 2×10^{-2} S cm^{-1} at room temperature. This salt is a semiconductor with an activation energy of 90 meV.

In summary, a biferrocenium salt with a high D/A ratio containing an electronically isolated paramagnetic hexamer of Cl_1TCNQ was synthesized. This salt is another example of a biferrocenium salt in which D^{2+} and D^+ coexist in a single crystal; charge disproportionation occurs via donor–acceptor electrostatic interactions. TCNQ derivatives often form one-dimensional stacks; high D/A ratios in their salts are rare.[13,14a] Several salts containing pentamers[14] or heptamers[15] of TCNQ have been reported, but most of them have interunit interactions and non-magnetic ground states. The hexamer unit in this salt is a quantum well that is nanometer sized. Therefore, arrays of

quantum wells are aligned on the crystal surfaces of this salt. This feature is interesting from the perspective of electronic applications.

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†Electronic supplementary information (ESI) available: Crystal structure, ESR spectra, NIR/MIR spectrum, and crystallographic data. CCDC 992524 (**1**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/

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5 A hot dichloromethane solution (3 mL) of chloro-tetracyanoquinodimethane (2.8 mg, 1.2×10^{-2} mol) was added dropwise to a hot dichloromethane solution (1 mL) of 1′,1‴-dineopentyl-1,1″-biferrocene (6.0 mg, 1.2×10^{-2} mmol), and the solution was stirred for several minutes. Vapor diffusion of pentane into the solution at room temperature produced black elongated plate crystals. Yield: 3.7 mg (23%). Anal. Calcd for $C_{144}H_{97}N_{28}Cl_7Fe_4$: C, 64.27; H, 3.63; N, 14.57. Experimental: C, 64.38; H, 3.77; N, 14.01. IR (KBr, cm^{-1}): 3433, 2181 (CN), 1561, 1528, 1328, 1244, 1169, 1034, 774, 647.

6 Crystal data for **1** at 90 K: triclinic, $P-1$, $a = 10.484(5)$ Å, $b = 16.267(7)$ Å, $c = 19.578(9)$ Å, $\alpha = 86.044(6)°$, $\beta = 79.030(6)°$, $\gamma = 71.980(7)°$, $V = 3117(2)$ Å^3, $Z = 1$, $R_1 = 0.0848$, and $wR_2 = 0.2101$. See ESI† for details.

7 The Fe–C_5H_4R (centroid) distance and Fe–C_{C5H4R} average distance in D^{2+} are 1.713 Å and 2.098 Å, respectively, which corresponds to the values for ferrocenium cation. The corresponding distances in D^+ are 1.686 Å and 2.079Å, respectively, which are both intermediate values of neutral ferrocene and ferrocenium cation.²ᵃ

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