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TCNQ Dianion-Based Coordination Polymer Whose Open Framework Shows Charge-Transfer Type Guest Inclusion

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Porous coordination polymers have attracted the attention of chemists who have scientific interest in developing nanometer-sized pores that provide novel guest assemblies and in guest-stressed and guest-activated phenomena.[1] For these purposes, functionalization of the pore surfaces is a very attractive idea for applications in storage,[2] separation,[3] and catalysis.[3a,4] Porous frameworks in this category can be designed and synthesized by using appropriate ligands with interaction sites, such as hydrogen-bonding sites[3d,5] and open metal sites.[2d,4a,6]

On the other hand, charge transfer (CT) interactions play a significant role in various functional materials, although only a few examples of this type of interaction in porous compounds have been seen to date.[7] With this background, we have designed electrically flexible pore surfaces to achieve CT between a host framework and a guest molecule by incorporating a redox active module into the framework to act as an interaction site, which can provide selective accommodation or sensing properties based on the combination of CT and van der Waals interactions. 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ) is a well-known multi-redox active ligand that can act as a good acceptor and a weak or a strong donor when its valence is 0, −1, or −2, respectively. We predicted that a CT interaction between a host framework and a guest molecule would occur if TCNQ were directly incorporated into the pore walls of a polymer. Here, we show a new redox active three-dimensional (3D) coordination framework containing TCNQ with Zn ions and 4,4′-bipyridine (bpy) and demonstrate unusual guest accommodations accompanying the CT interaction.

Yellow crystals of $\{[\mathrm{Zn(TCNQ)bpy}]\cdot 6\mathrm{MeOH}\}_n$ (**1**⊃MeOH) were synthesized by reacting $\mathrm{Zn(NO_3)_2\cdot 6H_2O}$ with LiTCNQ and bpy in MeOH. Figure 1 shows the crystal structure of **1**⊃MeOH. The Zn ions are octahedrally coordinated to the four cyanide nitrogen atoms of TCNQ in the equatorial plane and the two nitrogen atoms of the bpy at the axial sites. The Zn ions are linked by TCNQ molecules to give a two-dimensional (2D) corrugated layer in the *ab* plane. The bpy ligands act as pillars, with the Zn ions in the adjacent layers linked to form a 3D pillared layer structure. This crystal possesses 2D channels with cross-sections of approximately 3.4 × 5.9 Å^2 and a void space of about 50.7%, if the van der Waals radii of the constituting atoms are considered.[8]

Considering the charge balance of the framework, charge number of the TCNQ is estimated to be −2 (Zn: +2, TCNQ: −2, bpy: 0), because no counteranion is observed in the cavity by both X-ray structure and IR spectrum. In addition, the molecular bond length, which reflects charge number, indicates almost −2 form, especially bond **a** and **c** (Table 1).[9−11] Moreover, the infrared spectrum for the ν_{CN} stretching frequencies of the TCNQ also indicates −2 form.[10−14] (see Supporting Information). The production process of resulting TCNQ^{2-} is not clear, but that may be a disproportionation reaction of TCNQ$^-$.[15]

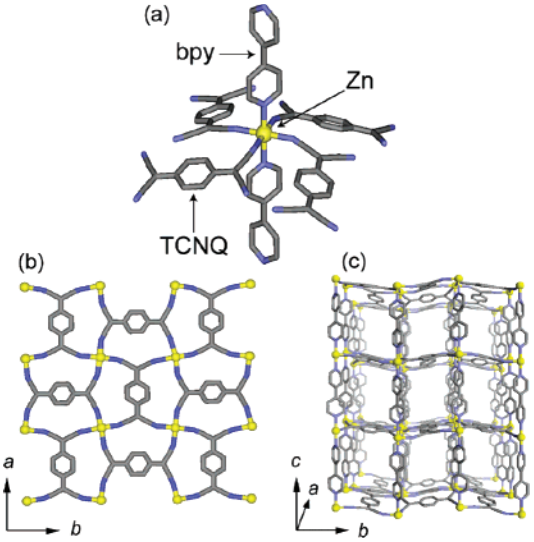
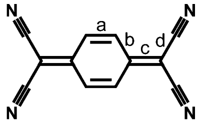


Figure 1. (a) Coordination environment of Zn(II) ion and (b) top view and (c) side view of **1**⊃MeOH. One of the doubly disordered bpy, the hydrogen atoms, and guest molecules are omitted for clarity.

Table 1. Bond Lengths (Å) of TCNQ Molecules in **1** and Related Compounds



	a	b	c	d
TCNQ$^-$ [a]	1.358−1.378	1.385−1.435	1.402−1.431	1.407−1.440
TCNQ^{2-} [b]	1.371−1.380	1.38−1.395	1.481−1.491	1.37−1.392
1⊃$\mathrm{CH_3OH}$	1.380(6)	1.402(6)	1.472(5)	1.405(5)

[a] Reference 10. [b] Reference 11.

As a result, a dense array of strong donor sites (TCNQ^{2-}) is formed on the pore surface of the open framework of **1**, providing a highly electron-rich surface for the guest molecules. Only one coordination polymer composed of TCNQ^{2-} has been reported to date,[11] and **1** is the first example of a regular array of TCNQ^{2-} embedded in the pore wall of a 3D open framework.

Given the exceptional highly electron-rich surface of **1**, we sought to test its ability to accommodate various aromatic guest molecules. When the crystal of **1**⊃MeOH was immersed into benzene, the guest MeOH can be exchanged with benzene to form **1**⊃benzene within 10 seconds, which is red rather than the yellow of the parent compound (see Supporting Information). This is a guest-induced crystal-to-crystal transformation. Marked changes were observed in the crystal structure of **1**⊃benzene, while the coordination environment around the Zn ion was similar to the MeOH analogue.

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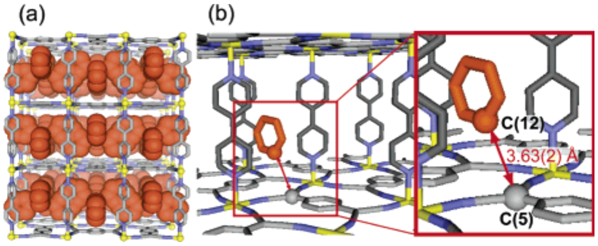

Figure 2. (a) Side view of **1**⊃benzene. The occupancy of benzene molecule is 0.5. (b) View of the nearest C−C distance between the benzene molecule and TCNQ.

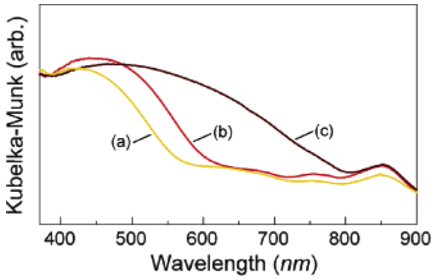

Figure 3. Diffuse reflectance UV−vis spectra of (a) **1**⊃anisole, (b) **1**⊃benzene, and (c) **1**⊃nitrobenzene.

The layer based on TCNQ and Zn ion in **1**⊃benzene was planar, although that in **1**⊃MeOH was considerably corrugated. Furthermore, the cell volume increased slightly by 2%, and the pore size expanded to approximately 3.5 × 7.9 Å^2.[8]

The two benzene molecules per Zn ion filled the channel, and were located between the pillar ligands at right angles to the layer, with a unique interaction between the host and the guest molecule. The C(12) carbon atoms of the benzene molecule were located only 3.63(2) Å away from the most negative charged carbon atom, the C(5) atom of TCNQ (see Figure 2b).[16] This exceptionally short C(5)···H(8)−C(12) bond distance is shorter than the sum of the van der Waals radii between the C(5) and C(12), which results from a C−H···C-type hydrogen bonding, representing the existence of an electrostatic and/or CT interaction between the TCNQ and the benzene. This crystal transformation is attributed to an accommodation of the benzene molecules into **1** with a dilatation of the channels, and this maintains the pore size by pillaring the layer on a host−guest interaction.

For other guests (toluene, ethylbenzene, anisole, benzonitrile, and nitrobenzene), changes in color different to **1**⊃MeOH, similar to that for benzene, were seen, except for anisole and nitrobenzene, where the occlusion of anisole and nitrobenzene formed light-yellow and dark-brown crystals, respectively. The color of the crystals is specific to the guest, and the guest exchange is reversible upon removal/accommodation of the guests. This compound does not possess the permanent porosity characterized by sorption measurement but the accessible channel to exchange the guests. (See Supporting Information)

Figure 3 shows the UV−vis spectra of **1** with anisole (**1**⊃anisole), benzene (**1**⊃benzene), and nitrobenzene (**1**⊃nitrobenzene). The visible spectra showed absorption bands in the 400−700 nm region in the following order: **1**⊃anisole (418 nm), **1**⊃benzene (445 nm), and **1**⊃nitrobenzene (480 nm), which were associated with the electron-accepting characteristics of the guest molecule. In particular, the band associated with **1**⊃nitrobenzene was quite broad, extending out to 800 nm. This is ascribed to the CT interaction between TCNQ and the aromatic molecule.[17]

In summary, we have synthesized a new coordination polymer with a redox-active module, owing to the CT interaction between the host framework and guest molecule. The CT interaction sites incorporated into the framework will be useful to the design and synthesis of new framework-guest hybrid compounds with unique physical properties and/or chemical reactions.

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Supporting Information Available: Experimental detail, table of crystal data, TGA, IR measurements, and photographs of the crystals; X-ray crystallographic file (CIF) in different states. This material is available free of charge via the Internet at http://pubs.acs.org.

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