having the D-prolines in the turns rather than in the strands, the model accounts for proline's strong propensity to break β-sheet structure.[3, 23, 24] The model is also consistent with the molecular areas determined from the Π-A isotherms. The molecular areas based on the hairpin dimensions and the measured ridge periods are $9.4\,\text{Å} \times \tfrac{1}{2} \times 59\,\text{Å} = 277\,\text{Å}^2$ for **1** and $9.4\,\text{Å} \times \tfrac{1}{2} \times 74\,\text{Å} = 348\,\text{Å}^2$ for **2**. These are within 18 % and 9 % of their experimentally determined values ($230\,\text{Å}^2$ and $320\,\text{Å}^2$). Finally, the model accounts for how peptide length can be used to control the ridge period. Because the strands are perpendicular to the ridges, **2** should produce ridge periods 13.8 Å longer than those of **1** since it is four residues longer ($4 \times 3.45\,\text{Å}$). This is within 8 % of the observed difference.

In summary, AFM images obtained using single-wall carbon nanotube tips show that LB monolayers of **1** and **2** are organized into two-dimensional domains of laterally assembled cross-β sheets. These sheets appear as ridges in the AFM images. Individual domains extend for hundreds of nanometers in LB monolayers of **1** and tens of nanometers in LB monolayers of **2**. Finally, the size of the ridges can be directly controlled through the peptide length.

Experimental Section

The preparation of **1** has been described elsewhere.[13] Peptide **2** was prepared by the same method and characterized by electrospray ionization mass spectrometry ($M^- = 2360.7$, expected: 2360.3). Peptides were spread from solutions in 1:1 DIW:ethanol. Isotherms were measured 30 min after spreading on DIW at room temperature on a Nima 611 LB Trough with a compression rate of 5 cm^2 min^{-1}. See Supporting Information for details of peptide concentration determination in the spreading solutions and subphase. LB films were deposited using a KSV 5000 LB trough by rapidly compressing monolayers to 10 mN m^{-1}, holding for 10 min, then lifting freshly cleaved mica substrates through the surface at 2 mm min^{-1}. AFM measurements were made in air using a Digital Instruments Multimode Nanoscope IIIa in Tapping Mode. SWNT tips were prepared as described previously.[25]

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An Unprecedented Mixed-Charged State in a Supramolecular Assembly of Ligand-Based Mixed-Valence Redox Isomers $(\mathrm{ET}^{\bullet+})_3[\mathrm{Cr^{III}}(\mathrm{Cl_4SQ})_2(\mathrm{Cl_4Cat})]^-[\mathrm{Cr^{III}}(\mathrm{Cl_4SQ})(\mathrm{Cl_4Cat})_2]^{2-}$**

Ho-Chol Chang and Susumu Kitagawa*

A metal complex containing noninnocent ligands serves as a useful module for synthesizing functional supramolecular assemblies whose physical and/or chemical properties are based on charges and spins. This is exemplified by the family of homoleptic *o*-quinone complexes, which provides unique charged and spin states irrespective of their simple constituent, $C_6O_2X_4$ (X = H or a halogen atom).[1] The freedom of their electronic states, for instance, is related to the redox forms of the ligand; *o*-benzoquinone, (BQ), *o*-semiquinonate (SQ), and catecholate (Cat). We have focused our interest on the ligand-based mixed-valence (LBMV) state of the ligands,

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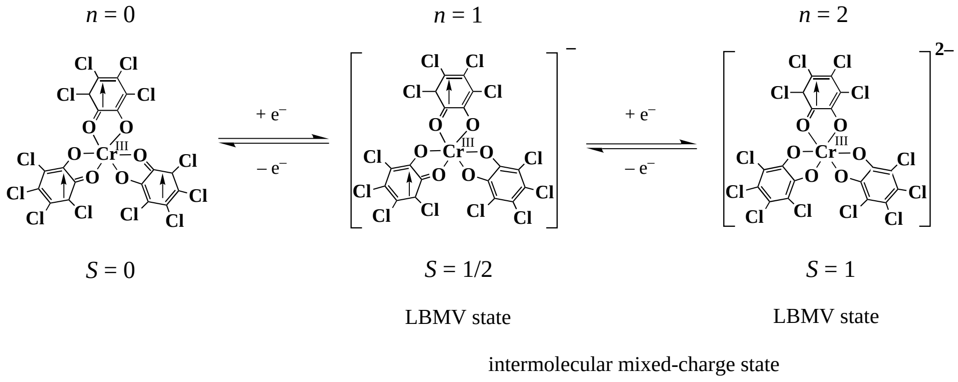
Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.



Scheme 1.

and have previously prepared charge transfer (CT) compounds of the series of redox isomers $[Cr^{III}(X_4SQ)_{3-n}(X_4Cat)_n]^{n-}$ (X = Cl and Br, $n = 0-2$) (Scheme 1) by the reaction of tris(tetrahalogeno-*o*-semiquinonate)chromium(III), $Cr^{III}(X_4SQ)_3$, with several donor molecules.[2] The *intra*molecular antiferromagnetic nature of the $Cr^{III}-SQ$ moieties provides $S = 0$, 1/2, and 1 magnetic ground states for the $n = 0$, 1, and 2 isomers, respectively, accompanied by their oxidation states (Scheme 1).[2, 3]

The intra- and intermolecular freedom with regard to the charge and spin may allow the creation of a novel type of molecular assembly containing new supramolecular synthons,[4] such as SQ ⋯ SQ magnetic type, SQ ⋯ Cat CT type, and cation ⋯ Cat and cation ⋯ SQ interactions, in terms of the oxidation state of the ligands. Herein, we present an unprecedented phase of a molecular assembly from a mixed-charge isomer, which displays unique properties.

The reaction of $Cr^{III}(Cl_4SQ)_3$ with bis(ethylenedithio)tetrathiafulvalene (ET) yields an insoluble black crystalline product, which has the stoichiometry of $(ET)_3[Cr(Cl_4C_6O_2)_3]_2$ (**1**).[5] The crystal structure of **1** (Figure 1 a) is composed of a two-dimensional (2D) layer constructed from the mix-stacked ET and chromium complexes. The layer contains three independent $\pi \cdots \pi$ interactions between the ligands of the chromium complexes and ET units, namely, [I ⋯ A], [I ⋯ C], and [II ⋯ B] (see Figure 1 a). The interplaner spacings and dihedral angles are 3.513(4), 3.598(4), and 3.435(3), and 6.7, 4.7, and 12° for [I ⋯ A], [I ⋯ C], and [II ⋯ B], respectively. Each ET unit is encapsulated by the four ligands of the two chromium complex anions, leading to a ratio of ET:[Cr] of 3:2; ET unit A is arranged in a face-to-face fashion with ligands I and I′ (Figure 1 b), while ligands III and III′ lie nearly perpendicular to the ET unit A (Figure 1 c). Similarly, ET unit B (C) is surrounded by ligands II (I) (parallel), II′ (I′) (parallel), III (II) (perpendicular), and III′ (II′) (perpendicular).

In addition to the $\pi \cdots \pi$ interactions, an atomic contact[7] between the S(8) and S(8*) atoms of the adjacent ET unit B results in a one-dimensional (1D) chain structure along the *a* axis (Figure 1 d). The contact renders the layers to be packed closely with an S ⋯ S distance of 3.321(3) Å, which is shorter than the sum of the van der Waals radii (3.7 Å).

The oxidation state of the ET molecule was estimated to be +1.011, +1.324, and +1.183 for A, B, and C, respectively, by using the well-known correlation: Q (estimated charge) = $6.347 - 7.463\delta$, where the parameter δ is defined by the four bond lengths of the ET molecule.[8] In addition, compound **1** displays an IR band at 1394 cm^{-1} and two Raman bands at 1416 and 1450 cm^{-1} at 296 K, which indicates a charge of +1 for the ET molecules.[9] Based on this spectroscopic evidence and on the composition of the compound, a

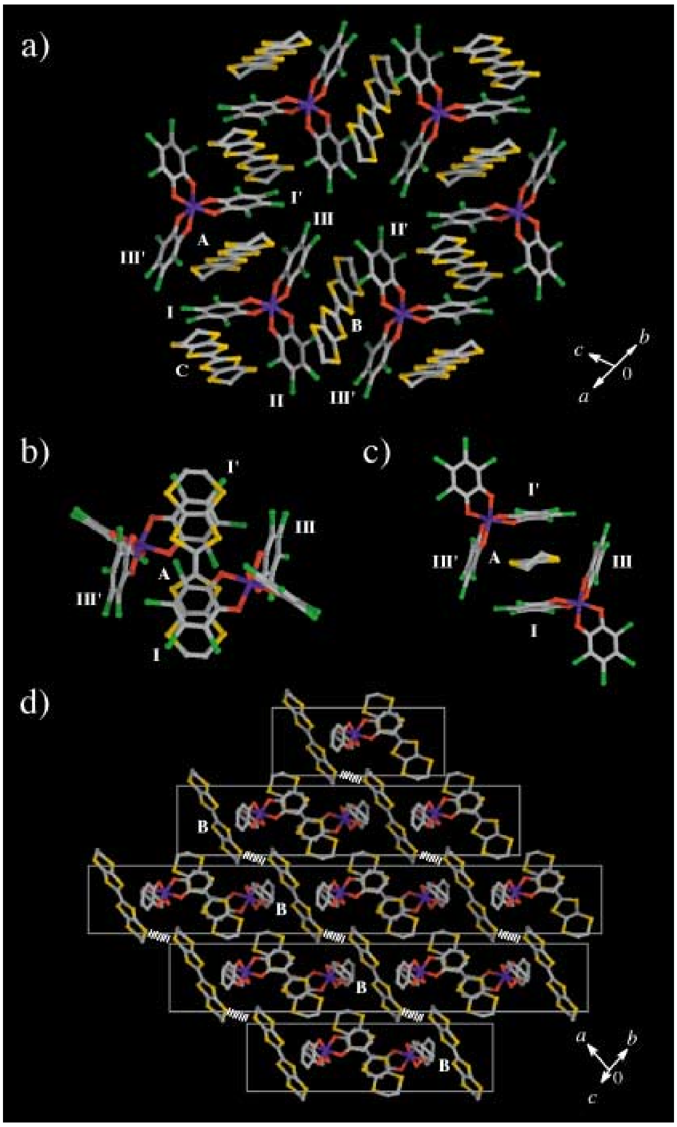


Figure 1. a) Stick representations of 2D layer, b) top, and c) side views of the interactions between ET unit A and ligands I, I′, III, and III′ (ET units B and C have similar packing structures with the surrounding ligands). d) 3D crystal packing structures of **1**. The dashed lines indicate the intermolecular S(8) ⋯ S(8*) contacts (the chlorine atoms are omitted for clarity). Crystallographically independent ligands and ET units are designated I–III and A–C, respectively. Color code; C: gray, O: red, Cl: green, Cr: blue, S: yellow. Average bond lengths [Å] and angles [°]: Cr-O 1.941(2), C-O 1.312(4), C-C (chromium complex) 1.399(5), central C-C (ET unit A) 1.376(7), central C-C (ET unit B) 1.401(6), central C-C (ET unit C) 1.389(7); O-Cr-O 82.9(1)°.

-3 charge should be distributable over two chromium complexes. As regards the structural parameters for the chromium complexes, only one crystallographically independent anion is found in which the average C–O bond lengths and O-Cr-O angles (Figure 1) are longer than those of $Cr^{III}(Cl_4SQ)_3$,[10] indicating the reduction occurs on the ligand moieties.

Figure 2a shows a NIR-IR absorption spectrum of **1** (KBr) compared with those of the $n = 1$ and $n = 2$ isomers. Compound **1** displays absorption maxima at 4170 and 5130 cm^{-1}. The $n = 1$ and $n = 2$ isomers are well-characterized by the intramolecular intervalence CT (IVCT) transition from Cat to SQ at 3920 and 5560 cm^{-1}, respectively.[2] From the comparison of these absorption bands with those of **1**, the bands at 4170 and 5130 cm^{-1} are assigned to the IVCT transition bands of the $n = 1$ and $n = 2$ isomers in **1**, respectively. Thus, this spectrum is consistent with the coexistence of both *intramolecular* mixed-valence $[Cr^{III}(Cl_4SQ)_2(Cl_4Cat)]^-$ ($n = 1$) and $[Cr^{III}(Cl_4SQ)(Cl_4Cat)_2]^{2-}$ ($n = 2$) isomers in the crystal of **1**, which exhibits the *intermolecular* mixed-charge state (Scheme 1). Consequently, compound **1** is best formulated as $(ET^{\cdot+})_3[Cr^{III}(Cl_4SQ)_2(Cl_4Cat)]^-[Cr^{III}(Cl_4SQ)(Cl_4Cat)_2]^{2-}$.

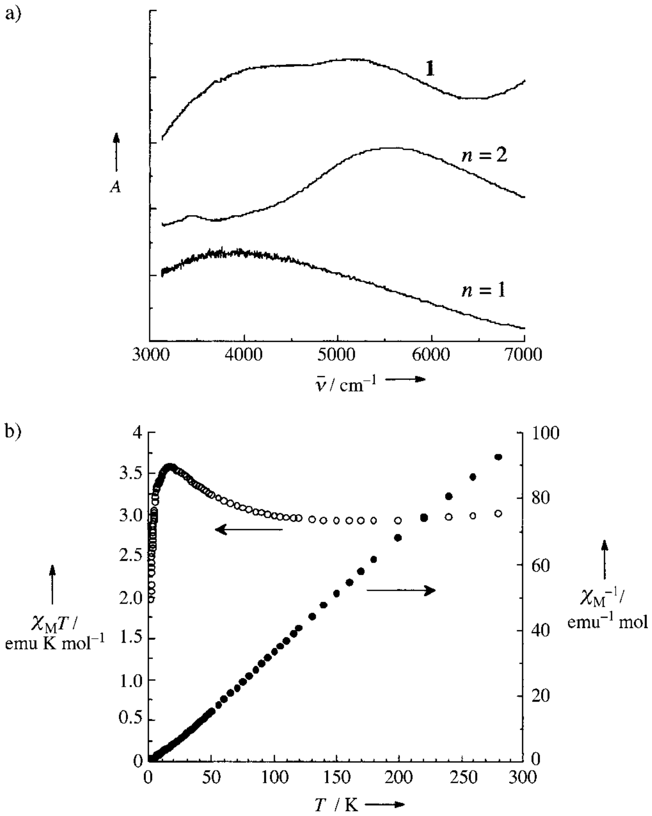


Figure 2. a) NIR-IR absorption spectra of **1** (top) and $(Co^{III}Cp_2)_n[Cr^{III}(Cl_4SQ)_{3-n}(Cl_4Cat)_n]$ ($n = 1$ (bottom) and $n = 2$ (middle)).[2] b) Temperature dependence of $\chi_M T$ (○) and χ_M^{-1} (●) of **1** under the field of 1 T.

A single crystal of compound **1** shows electric conductivity of $\sigma = 0.0076\ S\,cm^{-1}$ at 293 K, and its temperature dependence (77–296 K) reveals that **1** is a semiconductor with an activation energy of 0.14 eV.[11] The magnetic properties of compound **1** are shown in Figure 2b in the form of a $\chi_M T$ versus T curve and a χ_M^{-1} versus T curve (χ_M value is given per $(ET)_3[Cr(Cl_4C_6O_2)_3]_2$ unit). At 300 K, the $\chi_M T$ value is 3.05 emu K mol^{-1}, which first decreases very slowly, then gradually increases as the temperature is lowered down to 17 K and reaches a maximum at that temperature with a $\chi_M T$ value of 3.58 emu K mol^{-1}. When the temperature is lowered below 17 K, the value of $\chi_M T$ decreases to 1.98 emu K mol^{-1} (at 1.9 K). Based on the structural and spectroscopic data, five different magnetic components come from 1) the $n = 1$ and 2) the $n = 2$ isomers with $S = 1/2$ and 1 ground states, respectively,[2] and finally 3) three $ET^{\cdot+}$ ions with $S = 1/2$ spin. The observed value at 300 K is slightly larger than the theoretical value of 2.50 emu K mol^{-1} (derived from 0.375 ($n = 1$ isomer with $S = 1/2$) + 1.0 ($n = 2$ isomer with $S = 1$) + 3×0.375 ($3 \times ET^{\cdot+}$ with $S = 1/2$) assuming $g = 2.00$). The decrease of the value of $\chi_M T$ in the region of 150–300 K is due to an increase in the population for the ground state of the $n = 1$ and $n = 2$ isomers,[2] while the increase of the value of $\chi_M T$ below 150 K clearly indicates the presence of a dominant ferromagnetic interaction. For the latter, the possible intermolecular interactions occur in 1) $[ET]^{\cdot+}\cdots[Cr^{III}(Cl_4SQ)(Cl_4Cat)_2]^{2-}$, 2) $[ET]^{\cdot+}\cdots[Cr^{III}(Cl_4SQ)_2(Cl_4Cat)]^-$, and 3) $[ET\ unit\ B]^{\cdot+}\cdots[ET\ unit\ B]^{\cdot+}$. Although it is not clear which one is responsible for the observed ferromagnetic coupling, the best candidate seems to be 1) and/or 2) because of their stacked structures. While the intramolecular electronic structures and magnetic properties of the transition metal complexes with *o*-quinone ligands have been extensively studied,[1, 12] compound **1** first provides a principle for designing molecular assemblies in a ternary system by using redox-active transition metal complexes. The results obtained in this study indicate that the flexibility and diversity of charged and spin states of the *o*-quinone complexes open up a new dimension to the chemistry of molecular assemblies.

Experimental Section

ET was purchased from Tokyo Kasei Kogyo Co., Ltd. $Cr^{III}(Cl_4SQ)_3 \cdot 4\,C_6H_6$ was prepared by the procedure described previously.[2a]

1: Single crystals of **1** were grown from a layered solution of a solution of $Cr^{III}(Cl_4SQ)_3 \cdot 4\,C_6H_6$ (0.227 mM) in CH_2Cl_2 and a solution of ET (0.481 mM) in CH_2Cl_2/CH_3CN (2:1). Black plate crystals were obtained after a week. Elemental analysis (%) calcd for $C_{66}H_{24}Cl_{24}Cr_2O_{12}S_{24}$: C 29.0, H 0.89; found: C 29.04, H 0.73; IR peaks (KBr): $\tilde{\nu} = 1397s$, 1315w, 1284m, 1111s, 1024m, 977s, 925vw, 894w, 882w, 810w, 792s, 737w, 691w, 670vw, 552w, 478w, 450m cm^{-1}.

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[11] The measurement of the resistivity was carried out by the four-probe dc method using gold wire contacted to a gold electrode deposited on the surface of the single crystal by thermal evaporation. The wires were fixed to four gold contacts arranged linearly using gold paint.

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A Pillared-Layer Coordination Polymer Network Displaying Hysteretic Sorption: $[Cu_2(pzdc)_2(dpyg)]_n$ (pzdc = Pyrazine-2,3-dicarboxylate; dpyg = 1,2-Di(4-pyridyl)glycol)**

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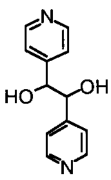
Recently developed porous coordination polymers have added a new dimension to materials-directed coordination chemistry; applications of these compounds range from gas storage and ion exchange to heterogeneous catalysis.[1–4] The key to this success is the establishment of permanent porosity even in the absence of guest molecules as well as inorganic zeolites, to afford the desired robust three-dimensional (3D) frameworks of metal ions and organic ligands. The next challenge is to develop a dynamic porous compound, a so-called third-generation compound,[5] which responds to a specific guest molecule and changes its microcavities into those well-suited for the shape and/or affinity of the guest molecule. Metal complex based compounds in this category are emerging[6–10] but still few. Herein, we have focused on developing the rational design and synthesis of this kind of framework. We have employed a pillared-layer motif because simple modification of the pillar module can control not only the channel size and shape but also the chemical functionality. The prototype structure was obtained by using Cu^{2+}, Na_2pzdc (pzdc = pyrazine-2,3-dicarboxylate), and a series of pillar ligands of pyridine derivatives.[11] We designed the new pillared-layer type coordination polymer with 1,2-dipyridylglycol (dpyg) as a flexible and functional pillar, and examined guest (CH_4, MeOH, and H_2O) inclusion properties.



dpyg

$[\{[Cu_2(pzdc)_2(dpyg)]\cdot 8H_2O\}_n]$ (**1**) was synthesized by the reaction of $Cu(ClO_4)_2\cdot 6H_2O$ with Na_2pzdc and dpyg in H_2O/EtOH media. The molecular structure of **1** was determined by X-ray crystallography, and Figure 1 shows the structure around the Cu^{II} centers. Each Cu^{II} atom is five-coordinate, residing in a distorted trigonal-bipyramidal environment, surrounded by three O atoms from three pzdc ligands, and two N atoms from a dpyg and a pzdc ligand. The $Cu_2(\mu\text{-}O)_2$ units are linked by the pzdc ligands to give a neutral two-dimensional layer in the *bc* plane (Figure 2a). The dpyg

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1433-7851/02/4101-0133 $ 17.50+.50/0