Photofunctional Materials

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An Unexpected Photoelectronic Effect from $[Co(en)_3]_2(Zr_2F_{12})(SiF_6)\cdot 4H_2O$, a Compound Containing an H-Bonded Assembly of Discrete $[Co(en)_3]^{3+}$, $(Zr_2F_{12})^{4-}$, and $(SiF_6)^{2-}$ Ions**

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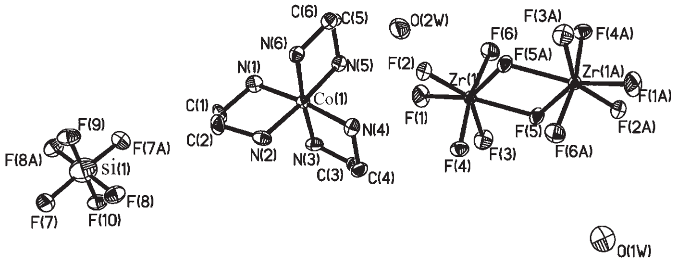

Figure 1. Thermal ellipsoid plot (50%) of $[Co(en)_3]_2(Zr_2F_{12})(SiF_6)\cdot 4H_2O$ (**1**).

Photofunctional materials are important because of their unique optical and electrical properties and are widely used in solar-energy conversion, semiconductor surface sensitization and modification, and nanoelectronics.[1–5] In recent decades, much effort has been directed toward the synthesis of pnictide- and chalcogenide-based inorganic semiconductor materials such as GaN,[6] SiC,[7] ZnO_2,[8] and SnO_2[9] because of their comparatively wide HOMO–LUMO gaps. There has been little investigation, however, of the photoelectronic properties of molecular solids.

Recently, by using an optically pure or a racemic mixture of a chiral cobalt complex such as $[Co(en)_3Cl_3]$ or $[Co(dien)_2Cl_3]$ as the template, we prepared a series of open-framework metal phosphates and oxides with chiral structure characters.[10,11] In order to explore new metal fluorides formed with a chiral cobalt complex as the template, we prepared a new cobalt complex-containing zirconium–silicon compound, namely $[Co(en)_3]_2(Zr_2F_{12})(SiF_6)\cdot 4H_2O$ (**1**), which contains an H-bonded network of discrete $[Co(en)_3]^{3+}$, $[Zr_2F_{12}]^{4-}$, and $[SiF_6]^{2-}$ ions. Unexpectedly, this new compound exhibits intriguing photoelectronic effects in the near-UV region.

A single-crystal X-ray diffraction analysis[12] indicated that **1** crystallizes in a monoclinic unit cell with space group *C*2/*c* (no. 15). Each asymmetric unit (Figure 1) contains one unique Co atom, one unique Zr atom, and one unique Si atom that is located on the two-fold axis. Two $[ZrF_7]^{3-}$ units share edges through difluoro bridges to form a $[Zr_2F_{12}]^{4-}$ pentagonal-bipyramid cluster with Zr–F bond lengths in the range of 1.988(4)–2.213(3) Å. The $[Co(en)_3]^{3+}$ cation and $[SiF_6]^{2-}$ anion display a disordered and a near regular octahedral geometry, respectively, with the Co–N and Si–F distances in the range of 1.965(6)–1.984(5) and 1.660(6)–1.742(6) Å, respectively. Each asymmetric unit also contains two H_2O molecules. As seen in Figure 2a, an extensive H-bonding network exists connecting the discrete $[Zr_2F_{12}]^{4-}$, $[Co(en)_3]^{3+}$, and $[SiF_6]^{2-}$ ions, in which the N atoms serve as H-bond donors and the F atoms as H-bond acceptors. As seen in Figure 2b, each $[Zr_2F_{12}]^{4-}$ unit interacts with six nearby complex cations through H-bonds. The N···F distances are in the range of 2.766(7)–3.106(7) Å, with angles in the range of 111.60–170.83°, both of which are typical values for H-bonding interactions between F and N atoms observed in a variety of metal fluorides.[13] The six complex cations are three pairs of enantiomers of the chiral $[Co(en)_3]^{3+}$ ion with *C*2 point symmetry; they are related by an inversion center.

The UV/Vis absorption spectrum of **1** shows three bands with maxima at approximately 237, 337, and 465 nm (Fig-

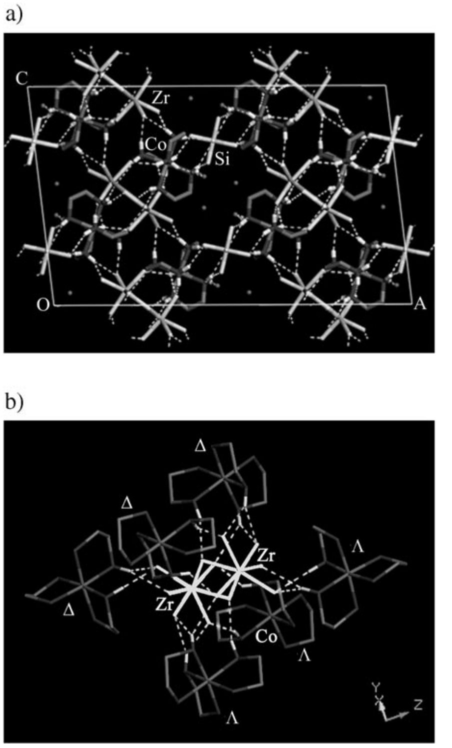

Figure 2. a) H-bonding network of discrete $[Co(en)_3]^{3+}$, $[Zr_2F_{12}]^{4-}$, and $[SiF_6]^{2-}$ ions viewed along the *b* axis. b) One $[Zr_2F_{12}]^{4-}$ unit interacts with six complex cations through H-bonds.

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ure 3a). The two absorptions at 337 and 465 nm are d–d transitions characteristic of the $[Co(en)_3]^{3+}$ complex cation,[14] whereas that at about 237 nm, which is absent in $K_4Zr_2F_{12}$ but is commonly found in many zirconium-containing compounds,[15] is tentatively assigned to a ligand-to-metal charge-transfer (LMCT) from the fluoride to the zirconium center. As $K_4Zr_2F_{12}$ itself does not absorb at wavelengths longer than 200 nm, the absorption at about 237 nm in **1** suggests that the HOMO–LUMO gap of $[Zr_2F_{12}]^{4-}$ in **1** may be smaller than that in $K_4Zr_2F_{12}$.

Studies by surface photovoltage spectroscopy (SPS) revealed that compound **1** possesses unusual photoelectronic properties (Figure 3b). When illuminated in absence of an external electric field, **1** shows a signal for the surface photovoltage (SPV) at 337 nm that is coincidental with one of the UV/Vis adsorption transitions of the $[Co(en)_3]^{3+}$ ions (Figure 3a). In contrast, no photovoltage response is generated when either $[Co(en)_3Cl_3]$ or $K_4Zr_2F_{12}$ are illuminated by photons with wavelengths longer than 300 nm. It is supposed that the electrons of the $[Zr_2F_{12}]^{4-}$ ion in $K_4Zr_2F_{12}$ are unable to transfer from the HOMO to the LUMO energy levels upon illumination by light of 337 nm. In $[Co(en)_3Cl_3]$, even though the $[Co(en)_3]^{3+}$ ion can be excited by light of this wavelength, electron–hole pairs cannot be effectively separated because no perfect energy band is formed, and, as a result, no photovoltage signal is generated. Furthermore, the fact that the intensity of the SPV response increases with increasing positive electric-field strength is indicative of its *n*-type conduction character[8] (inset of Figure 3b).

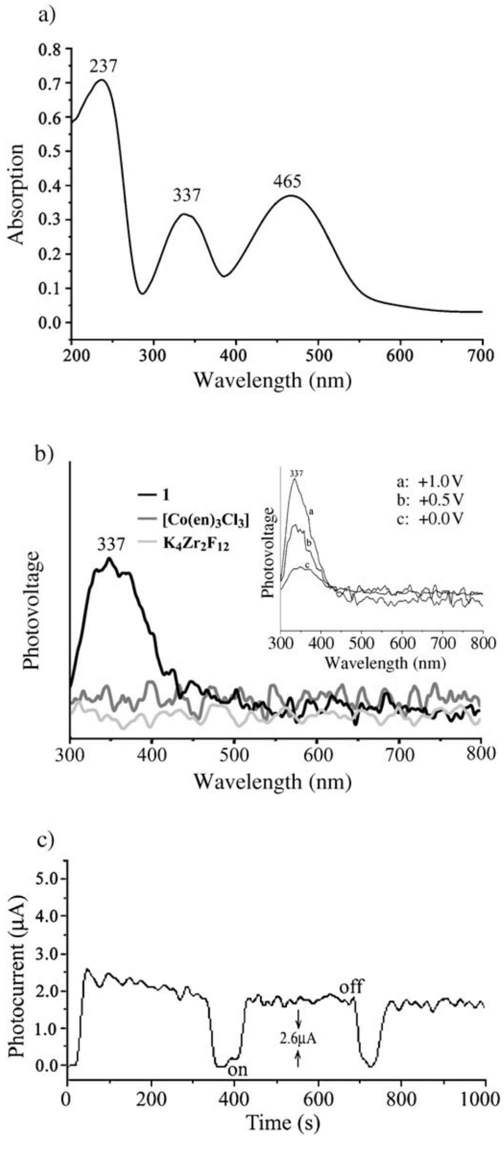

Figure 3. a) UV/Vis absorption spectrum of **1**. b) SPS of $[Co(en)_3Cl_3]$ (dark gray line), $K_4Zr_2F_{12}$ (light gray line), and **1** (black line). Inset: FISPS of compound **1** under positive field. c) Transient photocurrent response of compound **1** at 0.4 V versus SCE. (↑ and ↓ indicate when the light was turned on and off).

Figure 3c shows the transient photocurrent response of **1** recorded for several on–off cycles of illumination. The current reaches a steady-state value in approximately 300 s. The trace shows that an anodic photocurrent of about 2.6 μA is generated at a constant applied voltage of 0.4 V versus SCE, which is much higher than that of $(ZnO)_2(UO_2)_3(NA)_4(OAC)_2$ (0.2 μA) under the same measurement conditions.[16] In contrast to conventional oxide semiconductors,[17] the current density of compound **1** is very low. However, the lower current density, in combination with its lower electrical conductivity ($<10^{-5}$ S cm^{-1}), suggests that compound **1** might contain a controlled carrier density[18] similar to that of $(ZnO)_2(UO_2)_3(NA)_4(OAC)_2$.

We believe that a cooperative behavior between discrete $[Co(en)_3]^{3+}$ and $[Zr_2F_{12}]^{4-}$ ions through interionic interactions might be responsible for this unexpected photoelectric phenomenon in **1**. As expected, we have also observed an interesting photoelectric phenomenon in another cobalt complex-containing zirconium fluoride compound, namely $[Co(chxn)_3](ZrF_6)Cl\cdot3.5H_2O$ (**2**; chxn = 1,2-diaminocyclohexane).[19] Compound **2** is built up from discrete $[Co(chxn)_3]^{3+}$ and $[ZrF_6]^{2-}$ ions (see Supporting Information). As with **1**, there are extensive H-bonds between the $[Co(chxn)_3]^{3+}$ and $[ZrF_6]^{2-}$ ions in **2**. Upon illumination in absence of an external electric field, **2** shows a signal for the surface photovoltage at 357 nm, which is also coincidental with one of the UV/Vis adsorption transitions of the $[Co(chxn)_3]^{3+}$ ions (see Supporting Information).

In summary, compounds **1** and **2** both exhibit unusual photoelectric properties. The fact that the signal of the surface photovoltage is coincident with one of the UV/Vis absorption transitions of the cobalt complex implies that a charge transfer from the excited cobalt complex cation to the zirconium fluoride anion may occur upon illumination. The successful synthesis of compounds **1** and **2** and the discovery of their unusual physical properties as a result of the cooperative behavior between their component species will open-up new vistas in the search for materials with useful photoelectric properties. Further investigation of the mechanism of this intriguing photoelectric effect is ongoing.

Experimental Section

In a typical hydrothermal synthesis of **1**, zirconium tetrachloride (0.233 g, 1.00 mmol) was dissolved in distilled water (10 mL) and tris(ethylenediamine)cobalt(III) chloride (0.172 g, 0.50 mmol) and phosphoric acid (0.272 mL, 85 wt.%, 4 mmol) were added whilst stirring. Finally, hydrofluoric acid (HF, 0.5 mL, 40 wt.% aqueous solution, 10 mmol) and tetraethylorthosilicate (0.10 mL, 97 wt.% aqueous solution, 0.43 mmol) were added to the above reaction mixture. After stirring for 30 min, the final reaction mixture with a pH value of about 1.0 was transferred into a Teflon-lined, stainless-steel autoclave (20 mL) and heated at 130 °C for six days. The resulting orange, rod-like crystals were isolated by filtration, washed with deionized water, and dried in the air. The phase purity of **1** was checked by recording its X-ray powder diffraction pattern, which was consistent with that simulated on the basis of the single-crystal structure data. XRD studies indicated that compound **1** is thermally stable below 200 °C. Inductively coupled plasma (ICP) analysis indicated a Zr:Co:Si molar ratio of 1:1:0.5 for **1**.

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[12] Crystal data: $0.30\times0.20\times0.08$ mm^3, $C_{12}H_{56}N_{12}O_4F_{18}Co_2SiZr_2$, $M_r = 1103.08$, monoclinic, space group, $C2/c$ (no. 15), $a = 26.782(14)$, $b = 8.218(3)$, $c = 16.546(8)$ Å, $\beta = 96.630(19)°$, $V = 3617(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.025$ g cm^{-3}, $\mu = 1.629$ mm^{-1}, $T = 293(2)$ K. A total of 4611 reflections were collected, of which 3044 were independent ($R_{int} = 0.0683$). Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0474$, $wR_2 = 0.1128$, GOF = 1.020. CCDC-266808 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data - request/cif.
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[19] Compound **2** was obtained from a reaction mixture with a molar composition of $1\,ZrCl_4:3\,H_3PO_4:0.5\,Co(chxn)_3Cl_3:10\,HF:404\,H_2O$ at 110 °C for six days. The resulting orange-yellow, block-shaped crystals were isolated by filtration, washed with deionized water, and dried under ambient conditions.