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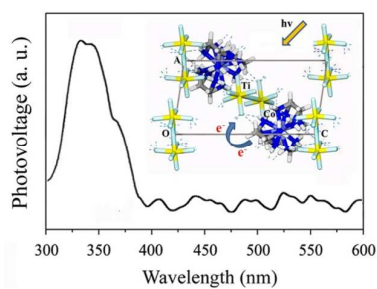
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A charge transfer from cobaltamine complex to zirconium fluoride ions occurring in molecular solids [Co(en)₃](Ti₂F₁₁) is responsible for novel photoelectronic effect.

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ARTICLE TYPE

Charge Transfer from Cobaltamine Complex to Metal Fluoride Ions in Molecular Solids with Novel Photoelectronic Effects (Metal: Zirconium, Titanium)

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5 Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

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[Co(en)₃](Ti₂F₁₁) containing H-bonded assembly of discrete cobaltamine complex cation and titanium fluoride anion was successfully synthesized under solvothermal conditions. A novel photoelectronic effect was observed in the near-UV region. By extending our understanding of this compound, taking into
10 account our previously reported three cobalt complex-containing zirconium fluorides, the mechanism of photoelectronic effects from these molecular solids were determined by investigating the relative work function for their component species with the help of Scanning Kelvin probe. The results suggest that the charge transfer from the excited cobaltamine complex cations to the metal fluoride anions as a result of the cooperative behaviors might occur upon illumination, which is responsible for these novel
15 photoelectronic effects.

1. Introduction

Photofunctional materials, particularly pnictide- and chalcogenide-based inorganic semiconductor materials, such as SiC, GaN, ZnO and TiO₂, have been extensively studied in solar energy
20 conversion, surface sensitization and modification of semiconductors and nanoelectronics.^{1–10} However, only a few investigations have been reported on the photoelectronic properties of molecular solids, although molecular solids have the advantages of facile synthesis, flexible composition, unique and
25 tunable optical and electronic properties.^{11–15} Even less work on the optoelectronic property of fluorides were reported, presumably because of their extra wide LUMO-HOMO gap, which makes it difficult to induce electron/hole separation and generate photoelectronic effect.

30 Yu et al. first demonstrated a cobalt complex-containing zirconium–silicon fluoride with an unexpected photoelectronic effect in the UV region, which led to an increased interest in fluorides molecular solids.¹⁶ Subsequently, zirconium fluoride molecular solids with mesostructure were reported to
35 significantly enhanced the photoelectronic conversion compared to that of its bulk counterpart, which may be attributed to a remarkable increase of the density of accessible optically active sites in the mesostructured molecular solid material.¹⁷ However, there has been little investigation on the mechanism of these
40 novel effects from molecular solids containing cobaltamine complex and zirconium fluoride ions.

Herein, molecular solid [Co(en)₃](Ti₂F₁₁) (**1**) containing H-bonded assemblies of discrete cobaltamine complex cations and titanium fluoride anions is successfully synthesized under

45 solvothermal conditions. Interestingly, it exhibits novel photoelectronic effects in the near-UV region. By extending our understanding of this compound, taking into account our previously reported molecular solids that are built up from discrete cobaltamine complex and zirconium fluoride ions,^{16,17}
50 the mechanism of photoelectronic properties of these metal fluorides is determined by investigating the relative work function for their component species with the help of Scanning Kelvin probe. The studies suggest that the charge transfer from the excited cobaltamine complex cations to the metal fluoride
55 anions might occur upon illumination, which is responsible for these novel photoelectronic effects. The successful synthesis of these compounds and the discovery of their unusual physical properties as results of the cooperative behaviors between their component species will provide a route in the search for materials
60 with useful photoelectric properties.

2. Experimental section

2.1. Synthesis

In the typical solvothermal synthesis of **1**, TiCl₄ (0.190 g, 1.00 mmol) was dissolved into ethylene glycol (10 mL). Subsequently,
65 Co(en)₃I₃ (0.157 g, 0.25 mmol) and H₃PO₄ (0.340 mL, 85 wt %, 2.00 mmol) were added under vigorous magnetic stirring, followed by adding HF (0.5 mL, 40 wt % aq, 10.00 mmol). HF should be handled with extreme care because it is corrosive and readily destroys tissue. After stirring for 30 minutes, the synthesis
70 solution was transferred into a teflon-lined stainless steel autoclave (20 mL) and heated at 140 °C for 6 days. The resulting product, orange color and rod-like crystal, was collected by

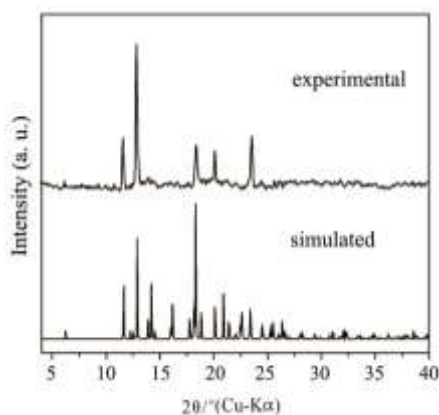


Figure 1 Experimental and simulated X-ray powder diffraction patterns for **1**

filtration, washed with deionized water, and dried under ambient conditions. The yield of the product was about 68 % based on the amount of cobaltamine complex. 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 (Figure 1). Inductively coupled plasma (ICP) analysis indicated a Ti : Co molar ratio of 2:1, in agreement with the empirical formula of $[\text{Co}(\text{en})_3](\text{Ti}_2\text{F}_{11})$ given by single-crystal structure analysis. The thermal stability was tested by calcining as-synthesized **1** at 150, 180 and 200 °C, respectively. A X-ray diffraction study indicated that **1** was thermally stable below 180 °C.

2.2. Characterization

X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. The UV-Vis absorption spectrum was recorded on a PerkinElmer Lambda 20 UV-Vis spectrometer using BaSO_4 pellet. SPS were measured with a solid junction photovoltaic cell (ITO/sample/ITO) using light source-monochromator-lock-in detection technique. The principle and setup diagram of SPS measurement have already been described in detail elsewhere.¹⁸ The potential of the irradiated electrode with respect to the back electrode denoted the signs of the applied electrical field. The measurement was performed under atmospheric pressure and ambient temperature (about $20 \pm 2 \text{ }^\circ\text{C}$). Work function maps were recorded on a SKP5050 with the Au reference probe.

2.3. Structural determination

The suitable single crystal with dimensions of $0.3 \times 0.2 \times 0.8 \text{ mm}^3$ was selected for single-crystal X-ray diffraction analyses for **1**. The intensity data were collected on a Siemens SMART CCD diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) at a temperature of $20 \pm 2 \text{ }^\circ\text{C}$. Data processing was accomplished with the SAINT processing.¹⁹ The structure was solved by direct methods and refined by full matrix least-squares techniques with the SHELXTL²⁰ crystallographic software package. The Ti, Co atoms were easily located, and F, C and N atoms were subsequently located in the difference Fourier maps. H atoms attached to the metal complex cations of this compound were placed geometrically and refined using a riding model. It

45 Table 1 Crystal data and structure refinement for **1**

Identification code	$[\text{Co}(\text{en})_3](\text{Ti}_2\text{F}_{11})$
Empirical formula	$\text{C}_{18}\text{H}_{24}\text{CoF}_{11}\text{N}_6\text{Ti}_2$
Formula weight	544.04
Temperature	293(2) K
50 Wavelength	0.71073 \AA
Crystal system, space group	triclinic, $P-1$
Unit cell dimensions	$a = 7.9858(16) \text{ \AA}$, $\alpha = 93.98(3)^\circ$, $b = 8.3733(17) \text{ \AA}$, $\beta = 96.26(3)^\circ$, $c = 14.325(3) \text{ \AA}$, $\gamma = 113.76(3)^\circ$.
55 Volume	$864.7(3) \text{ \AA}^3$
Z, Calculated density	2, 2.090 Mg/m^3
Absorption coefficient	1.966 mm^{-1}
F(000)	544
Crystal size	$0.3 \times 0.2 \times 0.8 \text{ mm}$
60 Theta range for collection	3.20 to 27.48°
Limiting indices	$10 \leq h \leq 10$, $-10 \leq k \leq 10$, $16 \leq l \leq 18$
Reflections collect / unique	8037 / 3917 [R(int) = 0.0564]
Completeness to $\theta = 23.25$	98.6%
Refinement method	Full-matrix leastsquare on F^2
65 Data / restraint / parameter	6357 / 0 / 330
Goodness-of-fit on F^2	1.053
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.1407$, $wR2 = 0.4451$
R indices (all data)	$R1 = 0.1614$, $wR2 = 0.47454$
Largest diff. peak and hole	0.818 and $-0.626 \text{ e. \AA}^{-3}$

70 was noted that the N atoms of the $\text{Co}(\text{en})_3^{3+}$ cation was positionally disordered. The low-temperature X-ray study had been tried at 80K, but there was no improvement for the disorder of N atoms in the structure. All non-hydrogen atoms were refined anisotropically. Detail for crystal determination of **1** was listed in Table 1. The selected bond distances and bond angles are of **1** presented in Table 1s. CCDC 997841 contains the supplementary crystallographic data for this paper.

3. Results and discussion

80 3.1. Crystal Structure

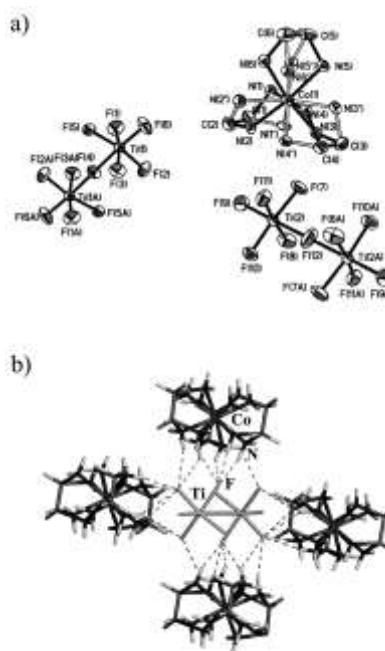


Figure 2 a) Thermal ellipsoid plot (50%) showing the labeling schemes, b) One $[\text{Ti}_2\text{F}_{11}]^{3-}$ unit interacting with four complex cations through H-bonds in **1**

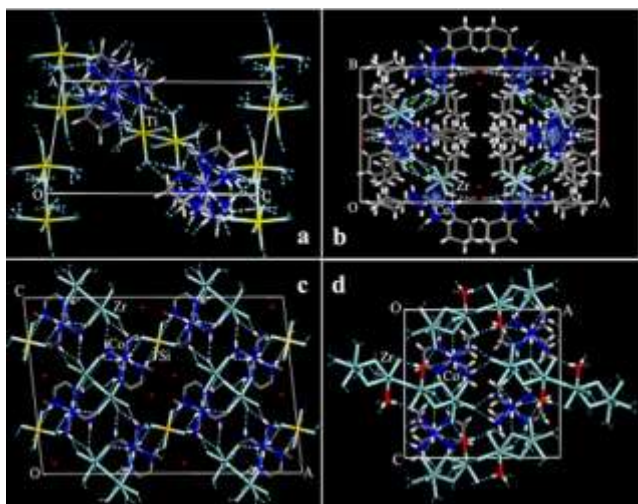


Figure 3 H-bonding network of discrete species in **1** (a), **2** (b), **3** (c) and **4** (d)

A single-crystal X-ray diffraction analysis indicates that **1** crystallizes in a triclinic unit cell with space group *P*-1 (no.2). Each asymmetric unit (Figure 2a) contains one unique Co atom, two unique Ti atoms. Two octahedral $[\text{TiF}_6]^{2-}$ units share vertex through fluoro bridge to form a $[\text{Ti}_2\text{F}_{11}]^{3-}$ cluster with Ti-F bond lengths in the range of 1.772(5) – 1.949(14) Å. The $[\text{Co}(\text{en})_3]^{3+}$ cation displays a near regular octahedral geometry with the Co-N distances in the range of 1.888(9) – 2.039(9) Å. The $\text{Co}(\text{en})_3^{3+}$ is either the delta or the lambda enantiomer of a chiral identity, As a consequence, the two isomers randomly occupy the lattice positions. The disorder of the C and N atoms in the complex is similar to those in $[\text{Co}(\text{en})_3][\text{In}_3(\text{H}_2\text{PO}_4)_6(\text{HPO}_4)_3] \cdot \text{H}_2\text{O}^{21}$ and $\text{Co}(\text{en})_3[\text{AlP}_2\text{O}_8] \cdot x\text{H}_2\text{O}^{22}$. As observed in Figure 2b, each $[\text{Ti}_2\text{F}_{11}]^{3-}$ unit interacts with four nearby $[\text{Co}(\text{en})_3]^{3+}$ cations through H-bonds, in which the N atoms serve as H-bond donors and the F atoms as H-bond acceptors. The $\text{N} \cdots \text{F}$ distances are in the range of 2.773 (11) – 3.189(12) Å, with angles in the range of 110.5 – 178.4°, both of which are typical values for H-bonding interactions between F and N atoms observed in a variety of metal fluorides.²³⁻²⁵

As seen in Figure 3a, an extensive H-bonding network exists connecting the discrete $[\text{Ti}_2\text{F}_{11}]^{3-}$ and $[\text{Co}(\text{en})_3]^{3+}$ ions. In order to extending our understanding, $[\text{Co}(\text{chxn})_3](\text{ZrF}_6)\text{Cl} \cdot 3.5\text{H}_2\text{O}$ (**2**; chxn=1,2-diaminocyclohexane), $[\text{Co}(\text{en})_3]_2(\text{Zr}_2\text{F}_{12})(\text{SiF}_6) \cdot 4\text{H}_2\text{O}$ (**3**) and $[\text{Co}(\text{en})_3](\text{Zr}_2\text{F}_{11}\text{H}_2\text{O})$ (**4**) are taking into account. **2**, **3** and **4** are built up from discrete $[\text{Co}(\text{chxn})_3]^{3+}$, $[\text{ZrF}_6]^{2-}$, discrete $[\text{Co}(\text{en})_3]^{3+}$, $(\text{Zr}_2\text{F}_{12})^{4-}$, $(\text{SiF}_6)^{2-}$ ions, and discrete $[\text{Zr}_4\text{F}_{22}\text{O}_2]^{10-}$, $[\text{Co}(\text{en})_3]^{3+}$ ions, respectively. There are extensive H-bonds between the cobaltamine complex and zirconium fluoride ions in **2**, **3** and **4** (Figure 3b, 3c, 3d). Crystal structures such as selected bond distances and bond angles have been reported in our earlier publications.^{16,17}

3.2. Property

As seen in Figure 4, each UV-Vis absorption spectra of **1**, **2**, **3** and **4** shows three absorption bands. The two bands at approximately 337 and 466 nm in Figure 4a, 4c and 4d are d-d transitions characteristic of $[\text{Co}(\text{en})_3]^{3+}$ cations in **1**, **3** and **4**, respectively. The two bands at 350 and 473 nm in Figure 4b are due to d-d

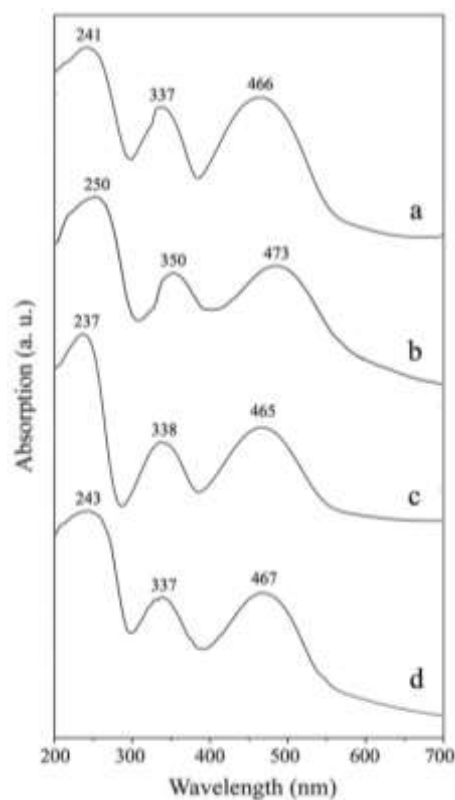


Figure 4 UV-Vis absorption spectra of **1** (a), **2** (b), **3** (c) and **4** (d)

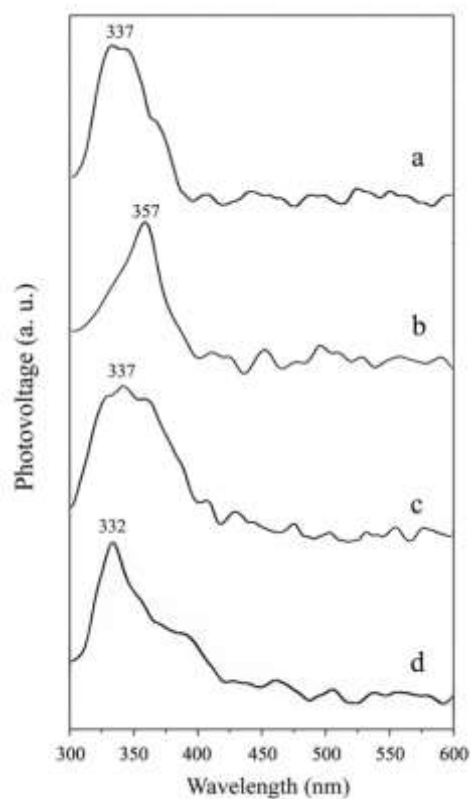


Figure 5 SPS of **1** (a), **2** (b), **3** (c) and **4** (d)

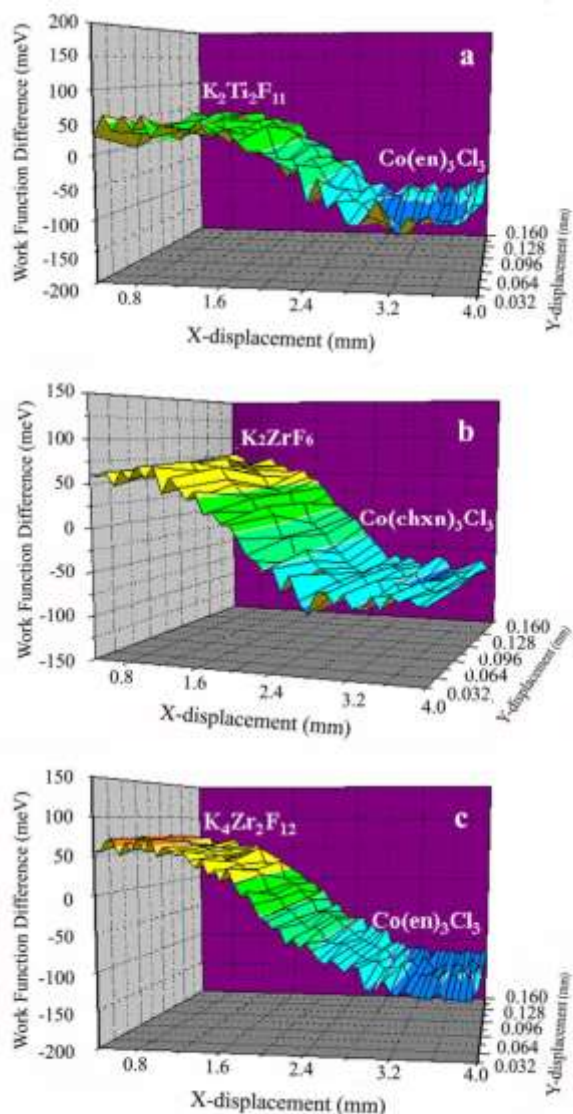


Figure 6 The relative work function (ΔWf) for the component species of compound **1** (a), **2** (b) and **3** (c).

transitions of $[\text{Co}(\text{chxn})_3]^{3+}$ cations in **2**.²⁷ The absorption bands of wavelength shorter than 300 nm are assignable as Ligand-to-Metal-Charge-Transfer (LMCT) transitions from the fluoride to the zirconium or titanium metal in these four compounds.^{28,29}

Strikingly, studies by surface photovoltage spectroscopy (SPS) reveal that **1**, **2**, **3** and **4** possess novel photoelectric properties (Figure 5). When illuminated in the absence of an external electric field, each compound shows a response for the surface photovoltage (SPV) that is coincidental with one of the UV/Vis adsorption transitions of the cobaltammine complex ions (Figure 4). The response band at approximately 337 nm in Figure 4a, 4c and 4d are accordant with one of the UV/Vis adsorption transitions of $[\text{Co}(\text{en})_3]^{3+}$ cations in **1**, **3** and **4**, respectively. The response band at 357 nm in Figure 4b is accordant with one of the UV/Vis adsorption transitions of $[\text{Co}(\text{chxn})_3]^{3+}$ cations in **2**. In contrast, no photovoltage response is generated when either cobaltammine complexes or metal fluorides are illuminated by photons with wavelengths longer than 300 nm (Figure 1S).

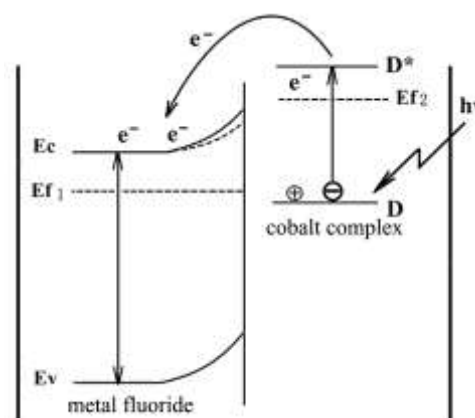


Figure 7 Scheme of energy band of the four compounds and proposed charge transfer process from cobaltammine complex cation to metal fluoride anion (D: ground state level; D*: excited state level; Ef: Fermi level; Ev: valence band maximum; Ec: conduction band minimum).

Furthermore, These novel photoelectric phenomenon is not observed in molecular solids $[\text{Co}(\text{en})_3][\text{GeF}_6]$ and $[\text{Ni}(\text{en})_3][\text{SiF}_6]$, indicating that perfect energy band formed in metal fluoride is necessary to generate photovoltage response.

It is considered that in metal fluorides the electrons are unable to transfer from the HOMO to the LUMO energy levels upon illumination by the light of 300-380 nm. In cobaltammine complexes, even though it can be excited by the light of this wavelength, because of no perfect energy band formed, electron-hole pairs cannot be effectively separated, as a result, no photovoltage signal is generated. We believe that cooperative behaviors between discrete cobaltammine complex and metal fluoride ions through interionic interactions might be responsible for these unexpected photoelectric phenomena in these four compounds. The fact that the signal of the surface photovoltage of each compound is coincident with one of the UV/Vis adsorption transitions of the cobaltammine complex implies that a charge transfer from the excited cobaltammine complex cations to the metal fluoride anions may occur upon illumination.

In order to further investigate the charge transfer process, the relative work function (ΔWf) for the component species of **1**, **2**, and **3** are measured using the Scanning Kelvin probe. As seen in the Figure 6, each map shows the relative work function decrease when the tip scanning from metal fluorides to cobaltammine complexes. The fact that $\Delta Wf_{\text{Co}(\text{en})_3\text{Cl}_3} < \Delta Wf_{\text{K}_2\text{TiF}_6}$, $\Delta Wf_{\text{Co}(\text{chxn})_3\text{Cl}_3} < \Delta Wf_{\text{K}_2\text{ZrF}_6}$, and $\Delta Wf_{\text{Co}(\text{en})_3\text{Cl}_3} < \Delta Wf_{\text{K}_4\text{Zr}_2\text{F}_{12}}$ shown in Figure 6a, 6b, and 6c is indicative of their Fermi lever positions $E_{f_{\text{Co}(\text{en})_3\text{Cl}_3}} > E_{f_{\text{K}_2\text{TiF}_6}}$, $E_{f_{\text{Co}(\text{chxn})_3\text{Cl}_3}} > E_{f_{\text{K}_2\text{ZrF}_6}}$ and $E_{f_{\text{Co}(\text{en})_3\text{Cl}_3}} > E_{f_{\text{K}_4\text{Zr}_2\text{F}_{12}}}$, respectively.³⁰ This result proves that the photogenerated electrons in these three compounds are able to transfer from cobaltammine complex cations to metal fluoride anions energetically matched upon illumination by the light of 300-380 nm. Figure 7 shows a proposed scheme indicating the charge transfer process from the cobaltammine complex cations to metal fluoride anions. Upon photoexcitation of cobaltammine complex cations, electron-hole pairs are possibly generated in **1**. The holes are left at ground energy level (D), and photogenerated electrons transfer to higher excited state level (D*), followed by crossing the distance from cobaltammine complex cations to metal fluoride anions. These excited photogenerated electrons are

further injected into the HOMO energy level of metal fluoride anions (Ec), which energetically matches with D*. As a result, the electron-hole pairs can be separated to raise the photovoltage signal.

4. Conclusions

Employing chiral cobaltamine complex as a template, [Co(en)₃](Ti₂F₁₁) containing H-bonded assembly of discrete cobaltamine complex cations and titanium fluoride anions was successfully synthesized under solvothermal conditions. Interestingly, it exhibit novel photoelectronic effect in the near-UV region. The mechanism of this effect was determined by investigations on the relative work function for their component species with the help of Scanning Kelvin probe. The studies suggested that cooperative behaviors between discrete cobaltamine complex and metal fluoride ions through interionic interactions might be responsible for these novel photoelectric phenomena. The fact that the signal of the surface photovoltage of each compound coincidents with one of the UV/Vis absorption transitions of the cobaltamine complex implied that a charge transfer from the excited cobaltamine complex cation to the metal fluoride anion may occur upon illumination. This work will provide a route in the search for molecular solids with useful photoelectric property.

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Notes and references

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† Electronic Supplementary Information (ESI) available: the selected bond distances and bond angles are of **1**; Atomic coordinates and equivalent isotropic displacement parameters for **1**; Hydrogen bonds for **1**; SPS of cobaltamine complexes and metal fluorides. See DOI: 10.1039/b000000x/

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