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Synthesis, crystal structure and surface photo-electric property of a series of Co(II) coordination polymers and supramolecules

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ABSTRACT

Four new Co(II) coordination complexes, $[Co(o-phta)(pz)_2]_n \mathbf{1}$, $[Co(PTA)_2(Imh)_2] \cdot (HPTA) \cdot H_2O \mathbf{2}$, $\{[Co(pd-c)_2(H_2O)] \cdot (ppz) \cdot 2H_2O\}_n \mathbf{3}$, $[K_2Co_2(ox)(btec)(CH_3OH)_2]_n \mathbf{4}$, $(H_2phta = o-phthalic acid, pz = pyrazole, HPTA = p-toluic acid, ppz = piperazine, Imh = imidazole, H_2pdc = pyridine-2,5-dicarboxylic acid, H_2(ox) = oxalic acid, H_4btec = 1,2,4,5-benzenetetracarboxylic acid), were hydrothermally synthesized and characterized by X-ray single crystal diffraction, IR, UV-Vis absorption spectrum, TG analysis and elemental analysis. The surface photovoltage properties of the four Co(II) complexes were investigated by the surface photovoltage spectroscopy (SPS). The structural analyses indicate that complexes 1 and 3 are 1D coordination polymers and complex 2 is a mononuclear molecular complex. Complexes 1, 2 and 3 are connected into 2D supramolecules by hydrogen bonds, respectively. Complex 4 is a coordination polymer with 3D structure, exhibiting a 4-nodal(4,5,6,12)-connected topology with a Schläfli symbol of (4^{10})_2(4^{24}\cdot 6^{32}\cdot 8^{10})(4^{5}\cdot 6)_2$ (4⁹·6⁵·8). The results of SPS show the four complexes exhibit obvious photovoltaic responses in 300–800 nm, which indicates they all possess photo-electric conversion properties. By the comparative analysis of the SPS, it is found that structure of the complex, species of ligand and coordination micro-environment of the Co(II) ion affect the SPS. The relationships between SPS and UV-Vis absorption spectra are discussed.

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1. Introduction

The extensive studies of transition metal complexes with the ligands of aromatic carboxylic acid indicate that they possess potential applications in materials, medicine synthesis, electrochemistry, biochemistry and many other fields. Therefore, in recent years, the studies on the design, synthesis, structural analysis and property of carboxylic acid coordination polymers have been becoming a very active comprehensive subject [1–6]. Cobalt complexes aroused extensive attentions in the coordination chemistry due to the variable oxidation states and coordination geometries of cobalt ions, and cobalt complexes possess important academic significance and wide applications in magnetism, catalysis, biochemistry, etc. In the recent years, many cobalt complexes were reported. For example, Pochodylo et al. [7] reported a 2D coordination polymer $\{[Co_3(tBuip)_2 (HtBuip)_2(bpmp)] \cdot bpmp\}_n$ with ferromagnetic properties. Ma et al. [8] reported the structure of $[Co_3(NCS)_6(admtrz)_4]$ $(H_2O)_2$ $] \cdot 2H_2O$ and found that there is weak antiferromagnetic interaction between the Co(II) ions. Losse et al. [9] reported a series of cobalt complexes and studied the catalytic properties. Nas et al. [10] reported the antibacterial biological activity of the Co(II) phthalocyanine complexes. In fact, some special functions of transition metal complexes are associated with their electron behaviors. For instance, the electrons transfer between different components of complexes can cause oxidation and reduction processes, which may be correlated with catalytic function. The change of electron arrangement, coupling and exchange may give rise to different magnetic properties. The separation and transfer of photogenerated charges under light-inducement may lead to the voltage or current on the solid surface, which is photo-electric conversion. Obviously, ascertaining surface electron behaviors of complexes is very significant for deep research on properties and exploiting applications of transition metal complexes. Surface photovoltage spectroscopy (SPS) is a high sensitive detection tool and it not only relates to the charge transition process under light inducement but also reflects directly the separation and transition of photogenerated charges. This technique has been successfully applied in the study of the charge transfer in photo-stimulated surface interactions, dye sensitization processes, photo-catalysis and the process of charge transition between surfaces and inter-phases of solid materials [11-17]. Recently, our group has reported the surface electron behaviors and photo-electric conversion properties of transition metal complexes involving nickel, manganese, iron and cobalt. Some preliminary results have been obtained [18–27]. In order to compare and study photo-electric property





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of cobalt complexes with different aromatic carboxylic acid ligands, the four Co(II) coordination complexes were synthesized in this paper and the influence of ligand and structure on surface photo-electric properties was discussed by SPS.

2. Experimental

2.1. Materials and apparatus

All chemicals were of A.R. grade without further purification. Single-crystal X-ray diffraction data were collected with Bruker Smart APEX II CCD diffractometer. SPS were performed on a home-built surface photovoltage spectrophotometer in the 300–800 nm. IR spectra were recorded as KBr pellets with a JASCO FT-IR/480 spectrophotometer in the 4000–220 cm⁻¹ region and UV–Vis diffuse reflectance spectra were recorded with a JASCO V-570 UV–Vis–NIR spectrophotometer in the 200–2500 nm. The elemental analyses were detected on a PE-240C Analyzer and TLASMA-II ICP instrument. Thermogravimetric (TG) analyses were performed under N₂ atmosphere on a Perkin–Elmer Pyris Diamond TG/DTA instrument with a heating rate of 10 °C min⁻¹.

2.2. Synthesis of complexes 1, 2, 3 and 4

2.2.1. $[Co(o-phta)(pz)_2]_n$ 1

A solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.15 g, 0.50 mmol) in water (10 mL) was added to a methanol (2.5 mL) and water (7.5 mL) solution of H_2 -phta (0.20 g, 1.0 mmol), and then a methanol (5 mL) and water (5 mL) solution of pz (0.14 g, 2.0 mmol) was added into the above solution. The color of the solution turned to purple, and pH value is 5.0. The mixture was then transferred into a Teflon-lined stainless steel vessel that was sealed and heated to 160 °C for 4 days. Cooled to room temperature, purple crystals of complex 1 were collected (0.07 g; Yield, 39% based on Co). Anal. Calc. for C₁₄H₁₂N₄O₄Co: C, 46.81; H, 3.37; N, 15.60; Co, 16.41. Found: C, 46.68; H, 3.38; N, 15.53; Co, 16.20%. IR (KBr, cm⁻¹): 3202 (v_{N-H-O}) ; 3148, 3121 (v_{N-H}) ; 3073, 3014 (v_{Ar-H}) ; 2944 (v_{C-H}) ; 1604, 1559($v_{C \leftarrow C}$); 1583($v_{as(COO^{-})}$); 1399($v_{s(COO^{-})}$); 1517, 1488(δ_{N-H}); 1478, 1446(δ_{C-H}); 1167, 1142, 1085, 1070, 1047(ν_{C-C}, ν_{C-O}, ν_{C-N}); 777, 752, 706, 654, 619, 607(δ_{Ar-H}); 566, 482(ν_{Co-O}); 455, $360(v_{Co-N})$.

Table 1

Summary of data collections and structure refinements for complexes 1-4.

2.2.2. [Co(PTA)₂(Imh)₂]·(HPTA)·H₂O 2

A solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.15 g, 0.50 mmol) in water (10 mL) was added to an ethanol (5 mL) and water (10 mL) solution of HPTA (0.28 g, 2.0 mmol), and then a water (8 mL) solution of Imh (0.07 g, 1.0 mmol) was added into the above solution. The color of the solution turned to purple, and pH value is 5.0. The mixture was then transferred into a Teflon-lined stainless steel vessel that was sealed and heated to 110 °C for 5 days. Cooled to room temperature, purple crystals of complex 2 were collected (0.12 g; Yield, 40% based on Co). Anal. Calc. for C₃₀H₃₂N₄O₇Co: C, 58.16; H, 5.21; N, 9.04; Co, 9.51. Found: C, 57.90; H, 5.22; N, 9.02; Co, 9.35%. IR (KBr, cm⁻¹): 3246(v_{O-H}); 3151(v_{N-H}); 3066, 3031(v_{Ar-H}); 2957, 2920(v_{C-H}); 2860, 2626($v_{O-H\cdots O}$); 2514($v_{N-H\cdots O}$); 1678($v_{C=O}$); 1557($v_{as(COO^{-})}$); 1389($v_{s(COO^{-})}$); 1610, 1594, 1500(v_{C-C}); 1329, 1309(δ_{N-H}); 1285, 1212(δ_{C-H}); 1176, 1137, 1170(ν_{C-C} , ν_{C-O} , ν_{C-N}); 953, 849(δ_{N-H-O}); 656, 623, 756, 695(δ_{Ar-H}); 566, 526, 470(v_{CO-O}); 417, 374(v_{CO-N}).

2.2.3. { $[Co(pdc)_2(H_2O)] \cdot (ppz) \cdot 2H_2O]_n$ **3**

A solution of $CoCl_2 \cdot 6H_2O$ (0.12 g, 0.50 mmol) in water (10 mL) was added to a solution of H₂pdc (0.09 g, 0.50 mmol) and NaOH (0.08 g, 2.0 mmol) in water (10 mL), then an ethanol (5 mL) solution of ppz (0.09 g, 0.50 mmol) was added into the above solution. The color of the solution turned deep pink, and the pH value was adjusted to 6.0. Then the mixture was transferred into a Teflonlined stainless steel vessel, and the vessel was sealed and heated to 120 °C for 5 days. Cooled to room temperature, pink crystals of complex 3 were collected (0.10 g; Yield, 36% based on Co). Anal. Calc. for C₁₈H₂₂N₄O₁₁Co: C, 40.84; H, 4.19; N, 10.58; Co, 11.13. Found: C, 40.68; H, 4.20; N, 10.53; Co, 10.96%. IR (KBr, cm⁻¹): 3389(v_{О-H}); 3225(v_{N-H}); 3013 (v_{Аr-H}); 2817, 2756 (v_{С-H}); 2601, 2514, 2465(v_{O-H-O}); 1581($v_{as(COO^{-})}$); 1404($v_{s(COO^{-})}$); 1602, 1543, 1476, 1458(v_{C-C}); 1354(δ_{C-H}); 1331, 1307(δ_{N-H}); 1169, 1092, 1033(v_{C-C} , v_{C-O} , v_{C-N}); 835, 759, 690(δ_{Ar-H}); 570, 523, 453(v_{CO-O}); 415, 374(v_{Co-N}).

2.2.4. [K₂Co₂(ox)(btec)(CH₃OH)₂]_n **4**

A solution of $CoCl_2 \cdot 6H_2O$ (0.12 g, 0.50 mmol) and $K_2C_2O_4$ (0.18 g, 1.0 mmol) in water (5 mL) was added to a solution of H_4 btec (0.13 g, 0.50 mmol) in methanol (5 mL). The color of the solution turned to pink, and the pH value was adjusted to 6.0. The mixture was transferred into a Teflon-lined stainless steel

	1	2	3	4
Empirical formula	C14H12CoN4O4	C ₃₀ H ₃₂ CoN ₄ O ₇	C ₁₈ H ₂₂ CoN ₄ O ₁₁	C7H5C0KO7
Formula weight	359.21	619.53	529.33	299.14
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	ΡĪ	$P2_1/c$	$P2_1/n$
a (Å)	8.1825(19)	9.5393(17)	13.1739(15)	7.162(10)
b (Å)	16.626(4)	11.796 (2)	11.9326(13)	14.312(19)
c (Å)	11.621(3)	14.636(3)	13.7668(16)	8.066(11)
α (°)	90	76.228(2)	90	90
β (°)	101.102(3)	88.585(2)	100.455(2)	102.251(18)
γ (°)	90	77.190(2)	90	90
Volume (Å ³)	1551.4(6)	1559.1(5)	2128.2(4)	808.0(19)
Ζ	4	2	4	4
$Dc (g cm^{-3})$	1.538	1.320	1.652	2.459
F(000)	732	646	1092	596
Data/restraints/parameters	2728/0/208	5400/0/383	4013/0/307	1961/0/145
Goodness-of-fit (GOF) on F^2	1.076	1.075	1.063	1.113
Reflections collected/unique	7644/2728	7836/5400	10851/4013	4916/1961
	$R_{\rm int} = 0.0319$	$R_{\rm int} = 0.0206$	$R_{\rm int} = 0.0445$	$R_{\rm int} = 0.0440$
$R_1, wR_2 \left[I > 2\sigma(I) \right]$	0.0386, 0.1118	0.0446, 0.1257	0.0552, 0.1523	0.0740, 0.2308
R_1, wR_2 (all data)	0.0478, 0.1166	0.0564, 0.1328	0.0823, 0.1707	0.1069, 0.2676
Largest difference in peak and hole $(e^{A^{-3}})$	0.378 and -0.497	0.256 and -0.321	0.692 and -0.629	2.122 and -1.835

vessel, and the vessel was sealed and heated to 120 °C for 5 days. Cooled to room temperature, pink crystals of complex **4** were collected (0.06 g; Yield, 37% based on Co). *Anal.* Calc. for C₇H₅O₇KCo: C, 28.11; H, 1.69; Co, 19.70. Found: C, 27.98; H, 1.70; Co, 19.45%. IR (KBr, cm⁻¹): 3559(v_{O-H}); 3346(v_{OH-O}); 3049(v_{Ar-H}); 2923, 2856(v_{C-H}); 1582($v_{as(COO^-)}$); 1393($v_{s(COO^-)}$); 1626, 1496, 1436(v_{C--C}); 1335(δ_{O-H}); 1309(δ_{C-H}); 1163, 1141(v_{C-C} , v_{C-O}); 869, 814, 782, 685(δ_{Ar-H}); 587, 542, 499(v_{CO-O}); 443, 317(v_{K-O}).

2.3. Determination of crystal structure

X-ray diffraction data of complexes were collected on the Bruker APEX II CCD diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 293(2) K. Empirical absorption corrections were applied to the data. The structures were solved by the direct methods and refined by full matrix least-squares method on F^2 . All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of organic ligands were placed in calculated positions and refined isotropically with a riding model. All the structural calculations and drawings were taken out with the SHELXL-97 crystallographic software package. Further details of X-ray structural analyses were given in Table 1. Selected bond lengths and angles were summarized in Table S1 of the Supplementary Material.

3. Results and discussion

3.1. The crystal structure of $[Co(o-phta)(pz)_2]_n$ **1**

Complex **1** is a coordination polymer with 1D chain structure bridged by *o*-phta groups. The asymmetric unit consists of one Co(II) ion, one *o*-phta group and two pz molecules (Fig. 1). The



Fig. 1. The asymmetric unit of complex 1.

Co(II) ion is four-coordinate with O1 and O4A atoms from two different *o*-phta groups, N1 and N3 atoms from two different pz molecules, displaying distorted tetrahedral structure. The bond lengths of Co–O are 1.965(2) and 1.969(3) Å and those of Co–N are 2.005(3) and 2.010(3) Å. Although the two carboxyl of *o*-phta group are deprotonated, only one O atom of each COO[–] group involves in the coordination. And only one N atom of each pz molecule involves in the coordination and N atoms of –NH groups do not involve in the coordination. In the asymmetric unit, the angle between planes of two pz rings is 107.28(13)°.

In the crystal, the *o*-phta groups link $[Co(pz)_2]^{2+}$ cations into a 1D chain along the *c*-axis (Fig. 2). In the 1D chain, the carboxyl O atoms (O1 and O4) of *o*-phta group join in the connection of the chain, but uncoordinated carboxyl O atoms (O2 and O3) did not participate in the connection of the chain. The adjacent chains are linked by the hydrogen bonds (N2–H···O3, 2.876 Å) formed between the N atom (N2) of pz molecule and the uncoordinated carboxyl O atom (O3) of *o*-phta group along the *b*-axis (Fig. S1), resulting in a 2D hydrogen-bonded layer in the *bc* plane (Fig. 3).

3.2. The crystal structure of [Co(PTA)₂(Imh)₂]·(HPTA)·H₂O 2

Complex **2** is a mononuclear molecular complex (Fig. 4). It consists of one Co(II) ion, two PTA groups, two Imh molecules, one free HPTA molecule and one lattice water molecule. The Co(II) ion is four-coordinate with two N atoms (N1 and N3) from two different Imh molecules and two O atoms (O1 and O3) from two different PTA groups, forming a distorted tetrahedral geometry. The bond lengths of Co–O are 1.963(2) and 1.972(2) Å and those of Co–N are 1.992(2) and 1.993(3) Å.

In the crystal, the adjacent molecules are linked by a lot of hydrogen bonds (N–H···O and O–H···O) as follows: the hydrogen bond (N2–H···O2, 2.788 Å) between N atom of Imh and O atom of PTA, the hydrogen bond (N4–H···O5, 2.966 Å) between N atom of Imh and O atom of free HPTA, the hydrogen bond (O6–H···O7, 2.571 Å) between O atom of free HPTA and O atom of lattice water, the hydrogen bond (O7–H···O4, 2.757 Å, O7–H···O2, 2.733 Å) between O atom of lattice water and O atom (O2 and O4) of PTA. Those hydrogen bonds connect the molecules along the *b*-axis, forming a hydrogen-bonded 1D chain (Fig. S2). Simultaneously, the adjacent 1D chains are further connected by hydrogen bonds (N4–H···O5, 2.966 Å, O6–H···O7, 2.571 Å, O7–H···O4, 2.757 Å, O

3.3. The crystal structure of $\{[Co(pdc)_2(H_2O)] \cdot (ppz) \cdot 2H_2O\}_n$ 3

Complex **3** is a coordination polymer bridged by pdc^{2-} with 1 D structure. The asymmetric unit comprises one Co(II) ion, two pdc^{2-} , one coordinated water molecule, one free ppz molecule



Fig. 2. The 1D infinite chain of complex 1 along c-axis.



Fig. 3. The 2D hydrogen-bonded layer of complex **1** on *bc* plane.



Fig. 4. Molecular structure of complex 2.

and two lattice water molecules (Fig. 6). The central Co(II) ion is six-coordinate with two N atoms and two O atoms from two different pdc²⁻, one O atom from the coordinated water molecule, another O atom from a pdc²⁻ forming a slightly distorted octahedral geometry (Fig. 7). The equatorial plane is made up of O3, N3, O1 and N4 atoms, and the axial position is occupied by O8 and O9 atoms. The bond lengths of Co-O are 2.058(3)-2.132(3) Å and those of Co-N are 2.137(4) and 2.138(3) Å. The two pdc^{2–} anions bond to Co(II) ions in two different coordination modes. The first one is that the pyridine N atom together with its neighboring one O atom of COO^- group of pdc^{2-} anion chelate one Co(II) ion, and the other COO⁻ group coordinates to another Co(II) ion in the type of unidentate coordination (Fig. S4). In the second one, only the N atom and its neighboring COO⁻ group coordinate to one Co(II) ion, but the other carboxyl does not join in the coordination (Fig. S5).

In the crystal, firstly, the Co(II) ions are linked by pdc^{2-} groups adopting the first coordination mode to form a 1D chain along the *b*-axis (Fig. 8). The adjacent 1D chains are linked by the hydrogen bonds (09–H···07, 2.690 Å, 09–H···05, 2.636 Å) formed between coordinated water molecules and uncoordinated carboxyl O atoms of two pdc^{2-} along the *c*-axis. As a result, a 2D hydrogen-bonded layer is formed in the *bc* plane (Fig. 9).

3.4. The crystal structure of $[K_2Co_2(ox)(btec)(CH_3OH)_2]_n$ **4**

Complex **4** is a coordination polymer bridged by $btec^{4-}$ and ox²⁻ groups with 3D structure. The asymmetric unit consists of one Co(II) ion, one K(I) ion, one-second of ox²⁻, one-second of btec^{4–} and one methanol molecule (Fig. 10). The central Co(II) ion is six-coordinate with four O atoms from four different btec^{4–} and two O atoms from one ox²⁻, forming a slightly distorted octahedral geometry (Fig. S6). O1A, O3A, O5 and O6A atoms construct the equatorial plane and O2 and O4A atoms occupy the axial position. The bond lengths of Co-O are 2.176(5)-2.240(5) Å. The K(I) ion is seven-coordinate with two O atoms from one $btec^{4-}$ group. one O atom from another btec^{4–} group, two O atoms from two ox^{2-} group and left two O atoms from two methanol molecules (Fig. S7). The bond lengths of K-O are 1.866(11)-3.248(6) Å. The coordination mode of K(I) is rare. The Co(II) and K(I) ions are bridged by btec⁴⁻ and ox²⁻ groups (Fig. 11). The btec⁴⁻ is all deprotonated, and its eight O atoms all participate in coordination to connect eight Co(II) ions and four K(I) ions (Fig. S8). Four O atoms of ox²⁻ all involve in the coordination, bridging two Co(II) ions and four K(I) ions (Fig. S9).

In the crystal, the K(I) and Co(II) ions are connected into a 1D chain by the btec^{4–} group along the c-axis (Fig. S10). The adjacent 1D chains are connected by the ox^{2-} groups along *b*-axis, so a 2D layer is formed in the *bc* plane (Fig. 12).

The Co(II) ions are also connected into 1D double chain by the carboxyl O atoms of btec^{4–} groups by monodentate mode along the *a*axis (Fig. 13). As a result, a 3D structure is formed for 4 (Fig. 14). From the topological view, in the 3D framework structure of complex 4, the btec⁴⁻ ligand connecting eight Co(II) ions and four K(I) ions can be considered as a 12-connected node, ox²⁻ ligand as a 6-connected node, the Co(II) ion as a 5-connected node, the K(I) ion as a 4-connected node, respectively. As a result, the framework of 4 can be reduced to a 4-nodal(4.5.6.12)-connected topology with a Schläfli symbol of $(4^{10})_2(4^{24} \cdot 6^{32} \cdot 8^{10})(4^5 \cdot 6)_2(4^9 \cdot 6^5 \cdot 8)$ (Fig. 15 and Fig. S11). For comparison and more clarity, in the 3D framework neglecting K(I) ion, the btec ligand can be regarded as an 8-connected node, ox ligand as a 2-connected node, Co(II) ion as a 5-connected node. Therefore, the framework of 4 becomes a 3-nodal (2,5,8)-connected net with a Schläfli symbol of $(4^{12} \cdot 6^{12} \cdot 8^4)(4^8 \cdot 6^2)_2(4)$ (Fig. 16 and Fig. S12), which, to the best of our knowledge, is a new topology type.



Fig. 5. The 2D hydrogen-bonded layer of complex 2 on ab plane.



Fig. 6. The asymmetric unit of complex 3.

3.5. The analysis and assignment of SPS and UV–Vis spectra of complexes

Seen from the UV–Vis absorption spectra of the four complexes (Figs. 17b–20b), there are some wide and strong absorption bands. These absorption bands nearly cover the entire UV–Vis region, and the energies of the bands are in the range of bandgap energy of semiconductor, so they can be seen as broad semiconductors. In this paper, energy-band theory of semiconductor and crystal field theory were combined to analyze and assign the SPS, *i.e.*, 2s and 2p orbitals of direct coordinated atoms (O or N) form valence band, meanwhile conjugated π orbitals of the ligands also belong to valence band. Empty 4s and 4p orbitals of central metal ions as well as π^* orbitals of ligands form conduction band and 3d orbitals of the central metal ions are considered as impurity levels. The transition from valence band to conduction band is called band-to-

band transition (or sub-gap transition), while the electron transition between d orbitals of central metal ions is called impurity transition.

3.5.1. The analysis and assignment of SPS and UV–Vis spectra of $[Co(o-phta)(pz)_2]_n$ **1**

In the SPS of complex 1 (Fig. 17a), there is a wide and strong response band with many overlapped bands within 300-800 nm. Treated by program ORIGIN 7.0, the response band can be divided into four response bands (λ_{max} = 339, 375, 450, and 618 nm). In the complex 1, the coordination micro-environment of Co(II) ions is distorted T_d geometry with CoN₂O₂ coordination mode, so the response bands can be assigned as follows: the strong responses at λ_{max} = 339 and 375 nm are assigned to the band-to-band transition arising from ligand-to-metal charge transfer transition (LMCT). Because there are different direct coordinated atoms (O and N) and their electronegativity is different in the complex 1, the two LMCT responses can be assigned to the $O \rightarrow Co$ and $N \rightarrow Co$ transitions, respectively. The response bands (λ_{max} = 450 and 618 nm) are assigned to the impurity transition responses corresponding to the $d \rightarrow d^*$ transitions of Co(II) ions $({}^4A_2 \rightarrow {}^4T_1(P) \text{ and } {}^4A_2 \rightarrow {}^4T_1(F))$. Another $d \rightarrow d^*$ transition of Co(II) ions $({}^4A_2 \rightarrow {}^4T_2)$ should appear in the near infrared region and it beyonds the measurement scope of SPS (300-800 nm), so it can not be observed.

There are six absorption bands in the UV–Vis absorption spectrum of complex **1** (Fig. 17b and Fig. S13). The band ($\lambda_{max} = 258$ nm) is assigned to $\pi \rightarrow \pi^*$ transition of the ligand. The bands ($\lambda_{max} = 294$ and 330 nm) are assigned to the LMCT (O \rightarrow Co and N \rightarrow Co). The bands at $\lambda_{max} = 520$ and 572 nm are assigned to the d \rightarrow d* transitions of Co(II) ions (${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$, ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(F)$), and the band at $\lambda_{max} = 1130$ nm is assigned to another d \rightarrow d* transition of Co(II) ions (${}^{4}A_{2} \rightarrow {}^{4}T_{2}$) in the near infrared region. There is a good corresponding relationship between SPS and UV–Vis spectra.

3.5.2. The analysis and assignment of SPS and UV–Vis spectra of [Co(PTA)₂(Imh)₂]-(HPTA)·H₂O **2**

There is a wide and strong response band with many overlapped peaks in the SPS of complex **2** within 300–800 nm (Fig. 18a). Treated by program ORIGIN 7.0, the response band can



Fig. 7. The coordination environment of Co(II) ion in complex 3.



Fig. 8. The 1D infinite chain of complex 3 along *b*-axis.



Fig. 9. The 2D hydrogen-bonded layer of complex 3 on *bc* plane.



Fig. 10. The asymmetric unit of complex 4.

be divided into four response bands. In the complex **2**, the coordination micro-environment and coordination mode of Co(II) is similar to those of complex **1**. The strong responses at $\lambda_{max} = 357$ and 385 nm are assigned to the band-to-band transition based on LMCT. Because there are different direct coordinated atoms (O and N) with different electronegativity, the two LMCT response bands can be assigned to the O \rightarrow Co and N \rightarrow Co transitions, respectively. The response bands ($\lambda_{max} = 501$ and 649 nm) are assigned to the impurity transition responses corresponding to the d \rightarrow d* transitions of Co(II) ions (${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$ and ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(F)$). Another d \rightarrow d* response band should appear in the near infrared region.

There are six absorption bands in the UV–Vis absorption spectrum of complex **2** (Fig. 18b and Figs. S14 and S17). The band $(\lambda_{\text{max}} = 262 \text{ nm})$ is assigned to $\pi \rightarrow \pi^*$ transition of the ligand. The



Fig. 11. The coordination environment of K(I) and Co(II) ions in complex 4.



Fig. 12. The 2D layer of complex 4 on bc plane.



Fig. 13. The 1D infinite chain of complex 4 along *a*-axis.



Fig. 14. The 3D infinite structure of complex 4.

bands (λ_{max} = 276 and 304 nm) are assigned to the LMCT (O \rightarrow Co and N \rightarrow Co). The bands at λ_{max} = 524 and 557 nm are assigned to the d \rightarrow d* transitions of Co(II) ions (${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$, ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(F)$), and the band at λ_{max} = 1134 nm is assigned to another d \rightarrow d* transition of Co(II) ions (${}^{4}A_{2} \rightarrow {}^{4}T_{2}$) in the near infrared region. There is a corresponding relationship between the SPS and UV–Vis spectra in complex **2**.

It is noted that the wide $d \rightarrow d^*$ response bands are extended to 700 nm and present splitting in the SPS of complexes **1** and **2**, which arise because the Co(II) ions in the complexes **1** and **2** are distorted T_d (CoN₂O₂) geometry. The decrease of symmetry of coordination micro-environment of Co(II) ion results in the widening and splitting of $d \rightarrow d^*$ response bands.

3.5.3. The analysis and assignment of SPS and UV–Vis spectra of ${[Co(pdc)_2(H_2O)] \cdot (ppz) \cdot 2H_2O}_n$ **3**

There is a wide and strong response band with many overlapped peaks in the SPS of complex **3** within 300–800 nm (Fig. 19a). Treated

by program ORIGIN 7.0, the response band can be divided into four response bands. The two response bands ($\lambda_{max} = 348$ and 387 nm) are assigned to the band-to-band transition responses based on LMCT. Because there are different direct coordinate atoms (O and N) with different electronegativity, the two LMCT response bands can be assigned to the O \rightarrow Co and N \rightarrow Co transitions, respectively. The response bands ($\lambda_{max} = 453$ and 548 nm) are assigned to the impurity transition responses corresponding to the d \rightarrow d* transitions of Co(II) ions (${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}$, ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$). In the complex **3**, the Co(II) ion is six-coordinate with the coordination mode of CoN₂O₄ and the distorted octahedral geometry. Therefore, the energy of d \rightarrow d* response bands in complex **3** is higher than that in complexes **1** and **2**. However, the lowering in symmetry from a regular O_h to distorted O_h (CoN₂O₄) results in the splitting of the d \rightarrow d* response bands in the **3**.

There are six absorption bands in the UV–Vis absorption spectrum of complex **3** (Fig. 19b and Fig. S15). The band $(\lambda_{\text{max}} = 256 \text{ nm})$ is assigned to $\pi \rightarrow \pi^*$ transition of the ligand. The



Fig. 15. The 4-nodal (4,5,6,12)-connected topology of complex **4** (red: btec node; cyan: ox node; blue: Co node; green: K node).



Fig. 16. The 3-nodal (2,5,8) connected topology of complex **4** (K(1) node is omitted for clarity; red: btec node; cyan: ox node; blue: Co node).

bands (λ_{max} = 334 and 352 nm) are assigned to the LMCT (O \rightarrow Co and N \rightarrow Co). The bands at λ_{max} = 456, 518, and 1172 nm are assigned to the d \rightarrow d^{*} transitions of Co(II) ions (⁴T_{1g}(F) \rightarrow ⁴A_{2g}, ⁴T_{1g}(F) \rightarrow ⁴T

3.5.4. The analysis and assignment of SPS and UV–Vis spectra of $[K_2Co_2(ox)(btec)(CH_3OH)_2]_n$ **4**

There is a wide and strong response band with several overlapped peaks in the SPS of complex **4** within 300–800 nm



Fig. 17a. SPS of complex 1.



Fig. 17b. UV-Vis spectrum of complex 1.



Fig. 18a. SPS of complex 2.

(Fig. 20a). Treated by program ORIGIN 7.0, the response band can be divided into three response bands. The strong response at λ_{max} = 339 nm is assigned to the band-to-band transition based



Fig. 19a. SPS of complex 3.



Fig. 19b. UV-Vis spectrum of complex 3.

on LMCT of $O \rightarrow Co$. The response bands ($\lambda_{max} = 457$ and 536 nm) are assigned to the impurity transitions between d orbitals of $Co(II)(d^7)$ ions, which are corresponded to the $d \rightarrow d^*$ transitions



of Co(II) ions $({}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}, {}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$. In the complex **4**, the coordination mode of Co(II) is CoO₆ with octahedral geometry. Therefore, there is only one response band of LMCT (O \rightarrow Co) in the SPS, and the two d \rightarrow d* transition response bands are not split.

500

Wavelength/nm

Fig. 20b. UV-Vis spectrum of complex 4.

600

700

800

There are five absorption bands in the UV–Vis absorption spectrum of complex **4** (Fig. 20b and Fig. S16). The band $(\lambda_{max} = 260 \text{ nm})$ is assigned to $\pi \rightarrow \pi^*$ transition of the ligand. The bands $(\lambda_{max} = 320 \text{ nm})$ are assigned to the LMCT ($O \rightarrow Co$). The bands at $\lambda_{max} = 486$, 560, and 1154 nm are assigned to the d \rightarrow d* transitions of Co(II) ions (${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}$, ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$, ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}$). The SPS and the UV–Vis is also basically same.

3.6. Comparison and analyses of SPS of complexes

300

400

- (1) There are obvious photovoltage response bands in the SPS of complexes 1–4, which indicates that they all possess certain photo-electric conversion properties. But the changes of structure, the coordination micro-environment and the coordination number of central metal ion can lead to the difference of the intensity and width of the SPS response bands.
- (2) The SPS are associated with the UV-Vis absorption spectra. And the number and the relative intensity of the response bands in SPS are similar to those of the absorption bands in UV-Vis spectra except limit of measurement scope of SPS.

- (3) The species and number of direct coordination atoms of complexes directly affect the results of the SPS. Firstly, the different direct coordination atoms with different electronegativity result in the splitting of the band-to-band responses bands based on LMCT. Secondly, the different species of direct coordination atoms can decrease the symmetry of coordination environment of the central metal ions, leading to the splitting, shifting and broadening of $d \rightarrow d^*$ impurity response bands. For example, there is one species of coordinated atoms (*i.e.*, O atom) in complex **4**, so there is one LMCT response band and the $d \rightarrow d^*$ transition response bands are not split and broadened. However, in the other three complexes, the coordination modes of Co(II) ions are $CoN_2O_2(1)$, $CoN_2O_2(2)$ and $CoN_2O_4(3)$, respectively. So there are two LMCT response bands ($O \rightarrow Co$ and $N \rightarrow Co$), and the splitting and broadening of the two $d \rightarrow d^*$ response bands are observed in SPS of complexes 1-3.
- (4) The different coordination numbers of Co(II) (d⁷) ions lead to the different symmetries of coordination environments, which causes the d \rightarrow d* transition response obviously different. The Co(II) ion is four-coordinate ($\sim T_d$ geometry) in complexes **1** and **2**, and the d \rightarrow d* transition response bands are red shifted than those in complexes **3** and **4** (six-coordinate, $\sim O_h$ geometry). This arises because the energy difference between d orbitals in T_d field (Δ_t) are less than that in O_h field (Δ_o). The phenomenon is obvious in both of SPS and UV–Vis spectra.
- (5) It is worthy of attention that if the Co(II) ion is four-coordinate and the species of direct coordination atom is not unique, the $d \rightarrow d^*$ transition response bands will show red-shifting, splitting and widening. This is very beneficial for improving the photo-electric conversion efficiency due to expanding the utilizing scope of visible-light.

3.7. TG analyses

The thermogravimetric analyses of complexes **1–4** were performed under N₂ atmosphere for numerous single crystal samples in the temperature 25–900 °C (Fig. 21). The TG data show that polymers **1**, **3** and **4** are stable before 200 °C, displaying a good thermal stability. But, complex **2** begins to decompose at 100 °C, which shows that its thermal stability is not good like that of polymers **1**, **3** and **4**. This may be because complex **2** is not a coordination polymer. The TG curve of polymer **1** shows that it is stable up to 220 °C, and then loses weight from 220 to 300 °C (obsd. 37.01%,



Fig. 21. The TG curves of complexes 1-4.

calcd. 37.90%), corresponding to the removal of two organic pz molecules. The second weight loss of 42.4% (calcd. 45.69%) in the temperature range of 300-700 °C can be assigned to the release of o-phta ligand. The TG curve of polymer 3 shows two steps of weight loss. It first loses the coordinated and lattice water molecules in the temperature range of 100–160 °C (obsd. 10.75%; calcd. 10.21%). Subsequently, a plateau region is observed from 160 to 300 °C. It keeps losing weight from 300 to 750 °C, ascribing to the removal of ppz and bdc molecules. For polymer 4, it is thermally stable up to 100 °C. Above this temperature, the TG curve exhibits two weight-loss stages. The first weight loss of 10.13% between 100 and 300 °C is attributable to loss of the methanol molecules (calcd. 10.71%). The second weight loss occurred from 300 to 500 °C, attributed to the decomposition of organic ligand and the collapsion of the structure [28]. From the observed weight loss (29.78%), it corresponds to loss of the four CO₂ molecules from decomposition of btec⁴⁻ ligands (calcd. 29.42%), therefore, the latter step of weight loss mainly is decomposition of organic ligand and release of CO₂.

4. Conclusions

Four Co(II) coordination complexes were synthesized and structures were determined by single-crystal X-ray diffraction. The photo-electric properties were discussed by SPS. By comparison and analysis, it is obvious: (1) Four complexes can be seen as broad semiconductors and they all possess certain photo-electric conversion ability. (2) The change of structure of complexes, the species and number of direct coordination atoms and the symmetry of coordination environment of the central metal affect the response bands of SPS. (3) The decrease of symmetry of coordination environment of the central metal can lead to shifting, splitting and widening of the response bands of SPS. This is favorable for improving the photo-electric conversion efficiency and extending the utilization scope of the visible-light.

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Appendix A. Supplementary material

CCDC 830390, 830391, 830392 and 830393 contain the supplementary crystallographic data for complexes **1**, **2**, **3** and **4**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif, or email: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.09.040.

References

- D. Aiello, R. Aiello, F. Testa, T. Martino, I. Aiello, M.L. Deda, M. Ghedini, J. Photochem. Photobio. A 201 (2009) 81.
- [2] K. Yu, Z.C. Gu, R.N. Ji, L.L. Lou, S.X. Liu, Tetrahedron 65 (2009) 305.
- [3] B.J. Jung, N.J. Tremblay, M.L. Yeh, H.E. Katz, Chem. Mater. 23 (2011) 568.
- [4] V.K. Garripelli, J.K. Kim, S. Son, W.J. Kim, M.A. Repka, S. Jo, Acta Biomater. 7 (2011) 1984.
- [5] J.S. Pap, B. Kripli, T. Váradi, M. Giorgi, J. Kaizer, G. Speier, J. Inorg. Biochem. 105 (2011) 911.
- [6] D.M. Griffith, B. Szőcs, T. Keogh, K.Y. Suponitsky, E. Farkas, P. Buglyó, C.J. Marmion, J. Inorg. Biochem. 105 (2011) 763.
- [7] A.L. Pochodylo, R.L. LaDuca, Inorg. Chem. Commun. 14 (2011) 722.
- [8] Q. Ma, M.L. Zhu, L.P. Lu, S.S. Feng, J.Z. Yan, Inorg. Chim. Acta 370 (2011) 102.
- [9] S. Losse, J.G. Vos, S. Rau, Coord. Chem. Rev. 254 (2010) 2492
- [10] A. Nas, E.Ç. Kaya, H. Kantekin, A. Sökmen, V. Çakır, J. Organomet. Chem. 696 (2011) 1659.

- [11] Q. Hou, X. Xu, T. Guo, X.H. Zeng, S.L. Luo, L.T. Yang, Eur. Polym. J. 46 (2010) 2365.
- [12] G.J. Zhao, Y.J. He, C. He, H.J. Fan, Y. Zhao, Y.F. Li, Sol. Energy Mater. Sol. Cells 95 (2011) 704.
- [13] J.A. Mikroyannidis, D.V. Tsagkournos, P. Balraju, G.D. Sharma, J. Power, Sources 196 (2011) 2364.
- [14] M. Rusu, S. Wiesner, R. Würz, S. Lehmann, S. Doka-Yamigno, A. Meeder, D.F. Marrón, M. Bär, V. Koteski, H.E. Mahnke, E. Arushanov, J. Beckmann, K. Höhn, W. Fritsch, W. Bohne, P. Schubert-Bischoff, M. Heuken, A. Jäger-Waldau, A. Rumberg, T. Schedel-Niedrig, Sol. Energy Mater. Sol. Cells 95 (2011) 1555.
- [15] G.J. Yang, C.J. Li, S.Q. Fan, J.C. Gao, Surf. Coat. Technol. 205 (2011) 3205.
- [16] A. Mathew, G.M. Rao, N. Munichandraiah, Mater. Chem. Phys. 127 (2011) 95.
- [17] J.Y. Lee, M.H. Choi, S.W. Heo, D.K. Moon, Synth. Met. 161 (2011) 1.
- [18] L.P. Sun, S.Y. Niu, J. Jin, G.D. Yang, L. Ye, Eur. J. Inorg. Chem. (2006) 5130.
- [19] L.P. Sun, S.Y. Niu, J. Jin, G.D. Yang, L. Ye, Inorg. Chem. Commun. 9 (2006) 679.

- [20] L. Li, S.Y. Niu, Z.F. Shi, L.C. Gong, J. Jin, Y.X. Chi, Y.H. Xing, Polyhedron 30 (2011) 976.
- [21] L. Zhang, S.Y. Niu, J. Jin, L.P. Sun, G.D. Yang, L. Ye, Inorg. Chim. Acta 362 (2009) 1448.
- [22] L. Zhang, S.Y. Niu, J. Jin, L.P. Sun, Chin. Sci. Bull. 53 (2008) 339.
- [23] Z.F. Shi, J. Jin, L.M. Zhao, P. Chen, S.Y. Niu, Chin. Sci. Bull. 55 (2010) 124.
- [24] L. Li, J. Jin, Z.F. Shi, L.M. Zhao, J.C. Liu, Y.H. Xing, S.Y. Niu, Inorg. Chim. Acta 363 (2010) 748.
- [25] Z.F. Shi, L. Li, S.Y. Niu, J. Jin, Y.X. Chi, L. Zhang, J.C. Liu, Y.H. Xing, Inorg. Chim. Acta 368 (2011) 101.
- [26] L. Li, S.Y. Niu, J. Jin, Q. Meng, Y.X. Chi, Y.H. Xing, G.N. Zhang, J. Solid State Chem. 184 (2011) 1279.
- [27] L. Li, S.Y. Niu, D. Li, J. Jin, Y.X. Chi, Y.H. Xing, Inorg. Chem. Commun. 14 (2011) 993.
- [28] E.J. Jung, U.K. Lee, B.K. Koo, Inorg. Chim. Acta 361 (2008) 2962.