

Synthesis, Structure, and Photoluminescence Property of a New Layered Zirconium Phosphate $[\text{Co}(\text{dien})_2][\text{Zr}_4\text{H}_8\text{P}_5\text{O}_{26}]\cdot 3\text{H}_2\text{O}$

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A new layered zirconium phosphate $[\text{Co}(\text{dien})_2][\text{Zr}_4\text{H}_8\text{P}_5\text{O}_{26}]\cdot 3\text{H}_2\text{O}$ (denoted ZrPO-CJ37) has been synthesized hydrothermally by using a racemic mixture of a chiral cobaltamine complex $\text{Co}(\text{dien})_2\text{Cl}_3$ as the template. Its structure is determined by single-crystal X-ray diffraction analysis and further characterized by X-ray powder diffraction, inductively coupled plasma, thermogravimetric, UV–vis, and photoluminescence analyses. The inorganic layer of ZrPO-CJ37 is built up from the linkage of Zr-centered octahedra and P-centered tetrahedra via vertex oxygen atoms forming a 4.6-net sheet. Its structure features the edge-sharing chains of $\text{Zr}(\text{OM})_6$ ($\text{M} = \text{P}, \text{H}$) octahedra. The cobaltamine complex cations are located in the interlayer region and interact with the host network through H bonds. ZrPO-CJ37 exhibits interesting photoluminescence in the UV–vis spectral region. The edge-sharing chains of $\text{Zr}(\text{OM})_6$ octahedra in the inorganic layer might be responsible for this unusual photoluminescence.

Introduction

Over the past few decades, by employing various alkali-metal ions or organic amines as structure-directing agents, a large number of open-framework metal phosphates have been synthesized under hydrothermal/solvothermal conditions. These open-framework metal phosphates include aluminophosphates,^{1–3} gallium phosphates,^{4–6} indium phosphates,^{7–9} zinc phosphates,^{10–12} titanium phosphates,^{13,14}

and iron phosphates,^{15,16} etc. Compared with the large number of metal phosphates mentioned above, there are a few reports on zirconium phosphates with new structures differing from the α and γ types. Such compounds are known as one-dimensional $[\text{enH}_2][\text{Zr}(\text{HPO}_4)_3]$, two-dimensional (2-D) $[\text{enH}_2]_{0.5}[\text{Zr}(\text{PO}_4)(\text{HPO}_4)]$,¹⁷ $[\text{C}_6\text{H}_{18}\text{N}_2]_{0.5}[\text{Zr}_2(\text{PO}_4)(\text{HPO}_4)_2\text{F}_2]\cdot 0.5\text{H}_2\text{O}$, and $[\text{C}_6\text{H}_{18}\text{N}_2]_{1.5}[\text{Zr}_3(\text{PO}_4)_3\text{F}_6]\cdot 1.5\text{H}_2\text{O}$,¹⁸ and three-dimensional $[(\text{enH}_2)_{0.5}][\text{Zr}_2(\text{PO}_4)_2(\text{HPO}_4)\text{F}]\cdot \text{H}_2\text{O}$,¹⁹ $[\text{C}_5\text{H}_{18}\text{N}_2]_{0.5}[\text{Zr}_3(\text{PO}_4)_3(\text{HPO}_4)\text{F}_2]\cdot 1.5\text{H}_2\text{O}$,¹⁸ and $[\text{C}_6\text{H}_{16}\text{N}_2]_{0.5}[\text{Zr}_2(\text{PO}_4)(\text{HPO}_4)_2\text{F}_2]\cdot 0.5\text{H}_2\text{O}$,²⁰ etc.

Recently, by using optically pure or racemic mixtures of chiral cobaltamine complexes such as $\text{Co}(\text{en})_3\text{Cl}_3$, $\text{Co}(\text{dien})_2\text{Cl}_3$, and $\text{Co}(1, 2\text{-diaminocyclohexane})$ as the templates, our group has prepared a series of open-framework metal phosphates,^{21–24} metal oxides $[\text{Co}(\text{en})_3][\text{V}_3\text{O}_9]\cdot \text{H}_2\text{O}$ and $[\text{Co}$

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(dien)₂[V₃O₉]·H₂O,²⁵ and metal fluorides [Co(en)₃]₂(Zr₂F₁₂)-(SiF₆)·4H₂O and [Co(chxn)₃](ZrF₆)Cl·3.5H₂O with chiral characters.²⁶ Interestingly, the latter two metal fluorides containing H-bonded assemblies of each component species show unusual photoelectronic effect. In our continued research for new materials, by using a racemic mixture of a chiral cobaltamine complex Co(dien)₂Cl₃ as the template, we have successfully prepared a new layered zirconium phosphate [Co(dien)₂][Zr₄H₈P₅O₂₆]·3H₂O (denoted ZrPO-CJ37). Interestingly, it exhibits unusual photoluminescence in the UV–vis spectral region.

More recently, the synthesis of inorganic materials with luminescent property has received considerable attention.^{27–29} In particular, an unprecedented finding on the luminescent properties of open-framework metal phosphates has been reported, which provides insight into the influences of the structure of active sites on the luminescence of microporous materials.³⁰ Developing an understanding of the relationship between structure and photoluminescence is of practical and theoretical importance in the design and synthesis of new phosphor compounds.

In this work, a new layered zirconium phosphate [Co(dien)₂][Zr₄H₈P₅O₂₆]·3H₂O has been synthesized hydrothermally. Interestingly, it exhibits unusual photoluminescence in the UV–vis spectral region. The study suggests that the edge-sharing chains of Zr(OM)₆ octahedra in the inorganic layer might be responsible for this intriguing photoluminescence.

Experimental Section

1. Synthesis. In a typical synthesis, zirconium tetrachloride (ZrCl₄, 0.233 g, 1.00 mmol) was dissolved in distilled water (10 mL), followed by the addition of bis(diethylenetriamine)cobalt(III) chloride (Co(dien)₂Cl₃, 0.118 g, 0.25 mmol) and phosphoric acid (H₃PO₄, 0.159 mL, 85 wt %, 2.34 mmol) with stirring. Hydrofluoric acid (HF, 0.3 mL, 40 wt % aq, 6.00 mmol) and tetraethylorthosilicate (Si(OEt)₄, 0.20 mL, 97 wt % aq, 0.87 mmol) were then added to the above reaction mixture. After stirring for 30 min, the final reaction mixture with a pH value of ca. 1.0 was transferred into a Teflon-lined stainless steel autoclave (20 mL), heated at 140 °C for 6 days, and cooled at room temperature. The resulting product, containing orange plate-shaped crystals, was isolated by filtration, washed with deionized water, and dried in air. The phase purity of ZrPO-CJ37 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

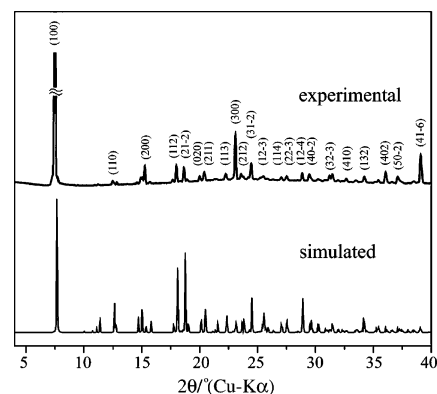


Figure 1. Experimental and simulated X-ray powder diffraction patterns for ZrPO-CJ37.

coupled plasma (ICP) analysis indicated a Zr/Co/P molar ratio of 1/0.25/1.25, in agreement with the empirical formula of [Co(dien)₂]-[Zr₄H₈P₅O₂₆]·3H₂O given by single-crystal structure analysis.

2. Characterization. X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). ICP analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. A Perkin-Elmer TGA 7 unit was used to carry out the thermogravimetric analysis (TGA) in air with a heating rate of 10 °C /min. The UV–vis absorption spectrum was recorded on a Perkin-Elmer Lambda 20 UV–vis spectrometer using BaSO₄ pellet and measured in a scattering geometry. The luminescent property was measured on a Perkin-Elmer LS55 spectrometer. The slit width for both excitation and emission measurements was 5 nm. The powdered sample was placed in the quartz cell for the photoluminescence spectrum measurement. The magic-angle-spinning NMR spectra were recorded on a Varian Infinity Plus-400 spectrometer. The ³¹P NMR spectrum was taken at 161.9 MHz with a spinning rate of 11 kHz. Chemical shifts were referenced to 85% H₃PO₄. The recycle delay time was 60 s.

3. Structural Determination. A suitable single crystal with dimensions of 0.2 × 0.2 × 0.08 mm³ was selected for single-crystal X-ray diffraction analysis. The intensity data were collected on a Rigaku R-Axis RAPID IP diffractometer by oscillation scans using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Cell refinement and data reduction were accomplished with the *RAPID AUTO* program. The structure was solved in the space group *P2/c* by direct methods and refined on *F*² by full-matrix least squares using *SHELXL97*.³¹ No absorption correction was applied. The heaviest atoms of Zr, Co, and P were easily located, and O, C, and N atoms were subsequently located in the difference Fourier maps. H atoms attached to the terminal Zr–O and P–O groups, and parts of the cobaltamine complex cations were placed geometrically and refined using a riding model. H atoms associated with water molecules were not added. It was noted that the C(2) atom of the Co(dien)₂³⁺ cation was positionally disordered. The low-temperature X-ray study has been made at 80 K, but there was no improvement for the disorder of C(2) atom in the structure. All non-hydrogen atoms were refined anisotropically. Crystal data and refinement parameters for the structure determination are presented in Table 1. The selected bond distances and bond angles are presented in the Supporting Information Table 2s. CCDC publication no. 622251 contains the supplementary crystallographic data for this paper.

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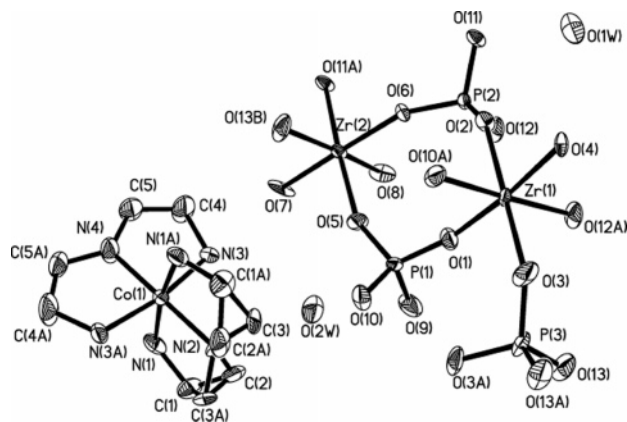


Figure 2. ORTEP view (50%) for ZrPO-CJ37.

Table 1. Crystal Data and Structure Refinement for [Co(dien)₂][Zr₄H₈P₅O₂₆]·3H₂O

empirical formula	C ₈ H ₄₀ CoN ₆ O ₂₉ P ₅ Zr ₄	
fw	1263.12	
<i>T</i> (K)	273(2)	
wavelength (Å)	0.71073	
cryst syst, space group	monoclinic, <i>P2/c</i>	
unit cell dimens		
	<i>a</i> = 12.1149(11) Å	α = 90°
	<i>b</i> = 8.8183(8) Å	β = 107.997(2)°
	<i>c</i> = 17.3298(16) Å	γ = 90°
<i>V</i> (Å ³)	1760.8(3)	
<i>Z</i> , calculated density (Mg/m ³)	2, 2.382	
abs coeff (mm ⁻¹)	1.944	
<i>F</i> (000)	1248	
cryst size (mm)	0.2 × 0.2 × 0.08	
θ range for data collection (deg)	1.77–27.81	
limiting indices	−15 ≤ <i>h</i> ≤ 15, −11 ≤ <i>k</i> ≤ 7, −22 ≤ <i>l</i> ≤ 22	
reflins collected/unique	10204/3747 [<i>R</i> (int) = 0.0586]	
completeness to θ = 27.48° (%)	89.8	
refinement method	full-matrix least squares on <i>F</i> ²	
data/restraints/params	3747/12/255	
GOF on <i>F</i> ²	0.992	
final <i>R</i> indices [I > 2 σ (I)]	<i>R</i> ₁ = 0.0514, <i>R</i> ₂ = 0.0991	
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0838, <i>R</i> ₂ = 0.1097	
largest diff peak and hole	0.991 and −0.677 e [−] Å ^{−3}	

Results and Discussion

1. Structure and Characterization. Single-crystal X-ray diffraction analysis indicates that ZrPO-CJ37 crystallizes in the monoclinic space group of *P2/c* (No. 13) with the formula [Co(dien)₂][Zr₄H₈P₅O₂₆]·3H₂O. Each asymmetric unit (Figure 2) contains two crystallographically distinct Zr atoms and three distinct P atoms. Both Zr atoms are coordinated by six oxygen atoms to form distinct Zr(1)O₅(OH) and Zr(2)-O₄(OH)₂ octahedra, with the Zr–O_{bridging} and the terminal Zr–OH distances in the range of 2.029(5)–2.092(4) Å and 1.981(4)–1.987(5) Å, respectively. The O–Zr–O angles are in the range of 84.4(2)–178.8(2)°. Both P(1) and P(2) atoms are tetrahedrally coordinated by oxygen atoms, forming P(1)-O₃(OH) and P(2)O₄ tetrahedra, with the P–O_{bridging} distances in the range of 1.513(5)–1.529(4) Å and the terminal P–OH

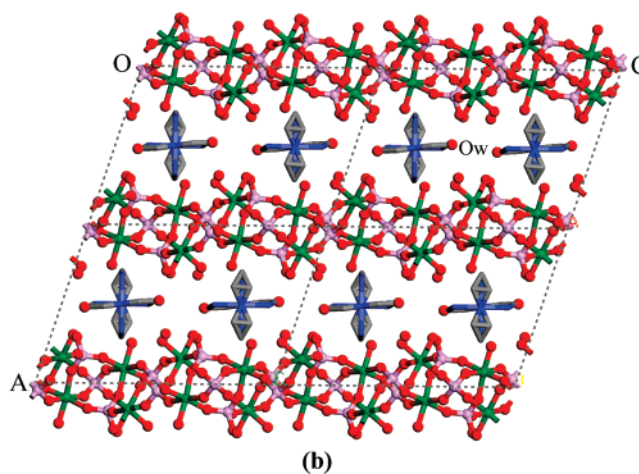
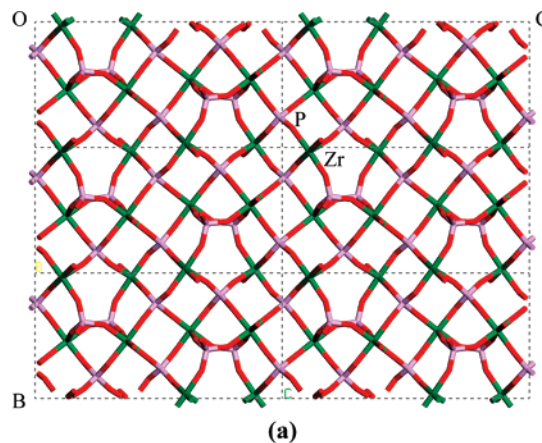


Figure 3. (a) View of 4.6-net sheet structure parallel to the *bc** plane in ZrPO-CJ37. (b) Packing of the inorganic sheets in an AAAA sequence along the [100] direction.

distance of 1.553(5) Å. A P(3) atom lying on the 2-fold axis is in the tetrahedral environment to make four P–O–Zr linkages, and the P–O distances are in the range of 1.520(5)–1.536(5) Å. The asymmetric unit also contains two water molecules and one unique Co atom on the 2-fold axis. The C(2) atom of the Co(dien)³⁺ cation is disordered over two sites, with 50% occupancy.

As seen in Figure 3a, the linkage of Zr-centered octahedra and P-centered tetrahedra via vertex oxygen atoms forms a 2-D sheet containing four and six rings (denoted 4.6-net). The inorganic sheets stack in an AAAA sequence along the [100] direction, with the cobaltammine complex cations and H₂O molecules residing in the interlayer regions (Figure 3b). The cobaltammine complex cations interact with the terminal OH groups in the inorganic framework and H₂O molecules through H bonds, with the N(O)···O separations of 2.786(7)–3.124(13) Å. It is worth noting that the inorganic layer can be viewed as being composed of the edge-sharing chains of Zr(OM)₆ (M = P, H) octahedra along the [010] direction; as seen in Figure 4, the zirconium atom acts as the octahedra center and the M atom acts as the octahedra vertex.

TGA shows three weight loss steps between 50 and 1200 °C (Supporting Information, Figure 1s). The first weight loss of 4.32 wt % from 50 to 250 °C corresponds to the loss of three water molecules (calcd 4.28 wt %). The second

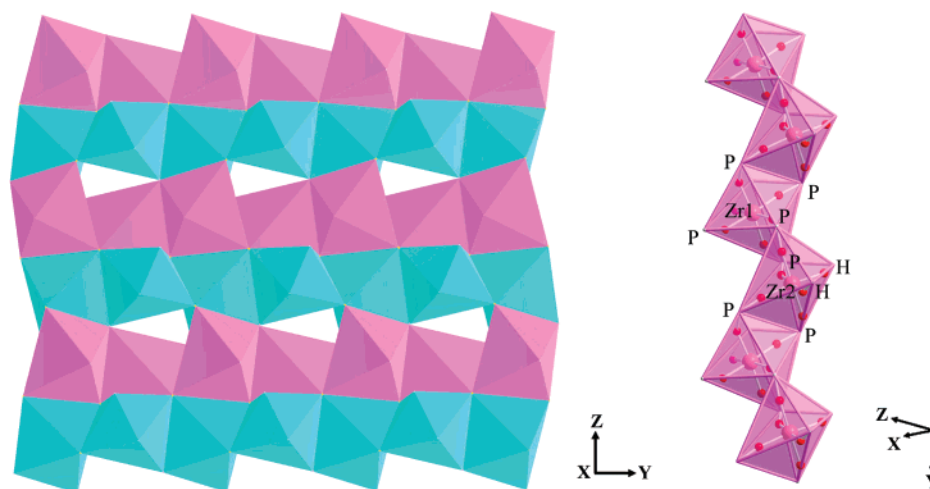


Figure 4. Inorganic layer composed of the edge-sharing chains of $Zr(OM)_6$ ($M = P, H$) octahedra along the [010] direction (octahedra center, Zr atoms; vertex, M atom).

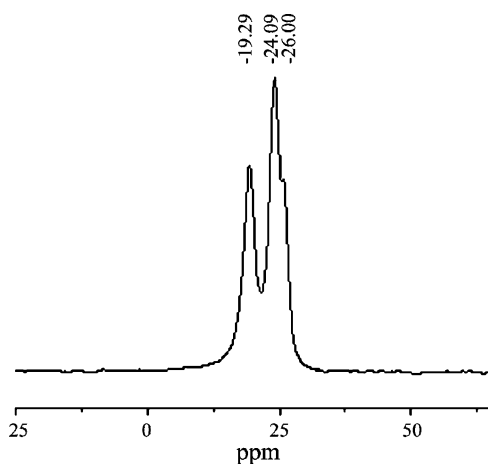


Figure 5. ^{31}P MAS NMR spectroscopy of ZrPO-CJ37.

weight loss of 10.7 wt % between 250 and 500 °C is attributed to the loss of hydroxyl groups in the framework (calcd 10.8 wt %), which can be confirmed by the fact that the $-OH$ absorption bands around 3520 and 1612 cm^{-1} ³² are absent in the IR spectrum when ZrPO-CJ37 is calcined at 500 °C (Supporting Information, Figure 2s). The third weight loss of 14.6 wt % from 500 to 1200 °C corresponds to the decomposition of the cobaltamine complex (calcd 14.7 wt %) in the product. XRD studies indicated that the final product upon calcination above 1200 °C is a mixture of ZrO_2 , CoO , and $Zr_2O(PO_4)_2$.³³

As seen in Figure 5, ^{31}P MAS NMR spectroscopy shows two sharp resonance lines at -19.29 and -24.09 ppm, respectively. The signal at -24.09 ppm with one shoulder at -26.00 ppm indicates that it is the superposition of two lines with close chemical shifts. The three ^{31}P signals are in agreement with the three crystallographically distinct P sites in the structure and are characteristic of the tetrahedral phosphate sites.³⁴

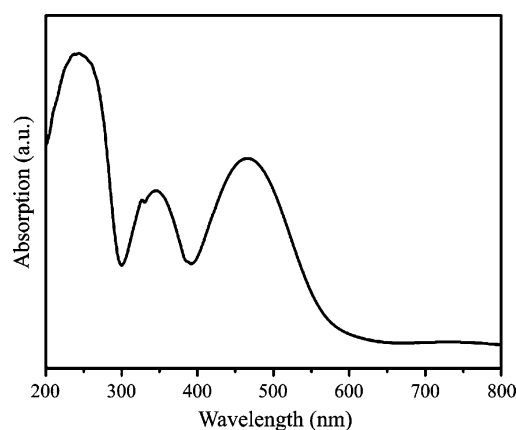


Figure 6. UV-vis absorption spectrum of ZrPO-CJ37.

The UV-vis absorption spectrum of ZrPO-CJ37 shows three bands with maxima at approximately 243, 345, and 466 nm (Figure 6). The two bands at 345 and 466 nm are d-d transitions characteristic of $Co(dien)_2^{3+}$ cations.³⁵ The band at 243 nm is assigned as a ligand-to-metal charge transfer from the oxygen to the zirconium center.³⁶

2. Luminescent Property. The photoluminescence (PL) spectrum for ZrPO-CJ37 excited at 243 nm shows wide and distinct emission bands at 300, 380–430, and 450–600 nm (Figure 7a). This is scarcely observed in the known zirconium phosphates.³⁷ A previous study shows that the photoluminescence of $K_2Hf_{1-x}Zr_x(PO_4)_2$ and $KHf_{2(1-x)}Zr_{2x}(PO_4)_3$ ³⁸ is ascribed to oxygen-to-zirconium charge transfer within the $Zr(PO_4)_6$ subunits. This octahedral $Zr(PO_4)_6$ moiety appears to be an important structural element for efficient luminescence. It is believed that the luminescence for ZrPO-CJ37 might be due to the charge transfer from oxygen to zirconium in the octahedral $Zr(OM)_6$ moiety of the edge-sharing chains. Because its luminescence is described as a self-activated charge-transfer mechanism, it is possible that a shorter

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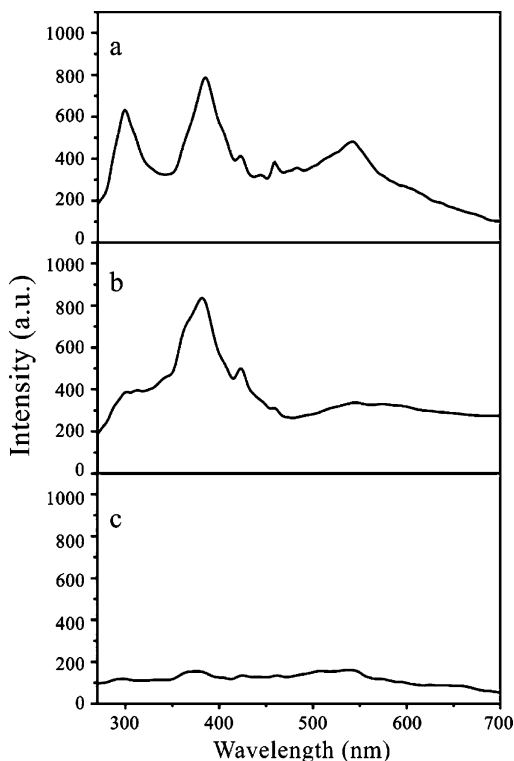


Figure 7. Photoluminescence spectra of the as-prepared sample of ZrPO-CJ37 (a) and the sample calcined at 500 °C (b) and 1200 °C in air (c) ($\lambda_{\text{ex}} = 243$ nm, slit (Ex), 5.0 mm; and slit (Em), 5.0 mm).

distance between the luminescent Zr^{4+} cations facilitates energy transfer from the oxygen ligands and encourages significant electronic reorganization.³⁹ Moreover, we found that the known zirconium phosphates, which are not composed of the edge-sharing chains of the $\text{Zr}(\text{OM})_6$ octahedra, did not exhibit luminescence.

The complicated coordination environment of the luminescent center for zirconium in ZrPO-CJ37 might lead to different Stokes shifts and consequently result in the wide and distinct luminescence emission in the UV–vis spectral region. As is known, the Stokes shifts increase with the decrease of the electronegativity of adjacent or subadjacent coordinated atoms to the luminescent center atom.⁴⁰ Therefore, the emission bands at 300 nm and in the regions of

380–600 nm might be due to the charge transfer from oxygen to zirconium in Zr–O–H and Zr–O–P linkages, respectively. Figure 7 shows the photoluminescence spectra of the as-prepared sample of ZrPO-CJ37 and the sample calcined at 500 and 1200 °C. The wavelengths of the excitation light are all 243 nm. It is worth noting that, in contrast to Figure 7a, the intensities of the emission bands around 300 nm and in the region of 450–600 nm decrease remarkably in Figure 7b. It might be caused by the change of luminescence environment for Zr–O–H and part of the Zr–O–P linkages with the loss of hydroxyls at 500 °C. As seen in Figure 7c, the fact that all the emission bands almost vanish might be explained by the structure transformation of ZrPO-CJ37 with $\text{Zr}(\text{OM})_6$ octahedra to $\text{Zr}_2\text{O}(\text{PO}_4)_2$, with ZrO_7 pentagonal bipyramids in geometry,³³ when ZrPO-CJ37 is calcined at 1200 °C. These results in Figure 7 not only present the influences of crystal structure on the photoluminescence but also further confirm the analyses of the emission bands in Figure 7a.

Conclusions

$[\text{Co}(\text{dien})_2][\text{Zr}_4\text{H}_8\text{P}_5\text{O}_{26}] \cdot 3\text{H}_2\text{O}$ is the first zirconium phosphate templated by a metal complex. The linkage of Zr-centered octahedra and P-centered tetrahedra forms the 2-D layered structure. The cobaltamine complex cations are accommodated in the interlayer region. It exhibits interesting photoluminescence in the UV–vis spectral region, which is ascribed to an oxygen-to-zirconium charge transfer within the octahedral $\text{Zr}(\text{OM})_6$ moiety of the edge-sharing chains, and may be influenced by the complicated coordination environments of the luminescent center of zirconium. The successful synthesis of ZrPO-CJ37 and the discovery of its unusual optical property will be helpful for the search of new materials with useful luminescent properties.

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Supporting Information Available: One PDF and one CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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