

Direct Ion Exchange of Tris(2,2'-bipyridine)ruthenium(II) into an α -Zirconium Phosphate Framework

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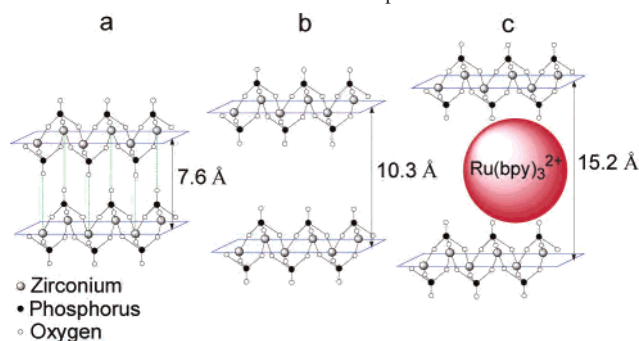
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The first direct ion exchange of a luminescent metal complex into an α -zirconium phosphate framework has been accomplished. A hydrated form of α -ZrP, with an expanded 10.3 Å interlayer distance, has been used for the intercalation of $\text{Ru}(\text{bpy})_3^{2+}$, resulting in further expansion to 15.2 Å. The $\text{Ru}(\text{bpy})_3^{2+}$ luminescence band is slightly blue-shifted. High $\text{Ru}(\text{bpy})_3^{2+}$ loadings lead to luminescence self-quenching.

The ion exchange, catalytic, photocatalytic, and intercalation chemistry of zirconium phosphates and phosphonates has become an intense area of investigation during the past two decades.¹ Zirconium bis(monohydrogen orthophosphate) monohydrate, $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, called α -zirconium phosphate (α -ZrP), is the most extensively characterized zirconium phosphate (Chart 1a).² Direct ion exchange of small ions (diameter < 2.61 Å) such as Na^+ is achieved directly by suspending α -ZrP in a solution containing sodium chloride and sodium hydroxide.³ In contrast, larger cations, such as metal complexes, can only be introduced after preintercalation of polar organic molecules, such as alcohols, glycols, and amines, which increase the interlayer separation. These expanded forms of α -ZrP greatly aid in the exchange of larger cations into the interlayer region. Another strategy to intercalate larger molecules in these materials has been the synthesis of organic derivatives (zirconium phosphonates) with expanded interlayer distances.⁴ Colón et al. used the strong ion exchanger zirconium phosphate sulfophenylphosphonate (ZrPS) to ion exchange the luminescent metal complex tris(2,2'-bipyridine)ruthenium(II), $\text{Ru}(\text{bpy})_3^{2+}$, for photophysical and photochemical studies.⁵

Chart 1. Three Different Zirconium Phosphate Phases^a



^a Idealized representation of three different zirconium phosphate phases: (a) α -ZrP, (b) expanded 10.3 Å phase, (c) $\text{Ru}(\text{bpy})_3^{2+}$ -exchanged ZrP. Hydrogen atoms and water molecules are not shown for clarity.

Direct ion exchange of $\text{Ru}(\text{bpy})_3^{2+}$ into α -zirconium phosphate (α -ZrP) has been an elusive goal for the past 20 years. Yates et al. unsuccessfully attempted the direct ion exchange of $\text{Ru}(\text{bpy})_3^{2+}$ into α -ZrP.⁶ However, these authors were able to incorporate the metal complex into the α -ZrP lattice during its crystallization and obtained a phase with a 15.9 Å interlayer distance. Vliers et al. and Kumar and Williams ion exchanged $\text{Ru}(\text{bpy})_3^{2+}$ into α -ZrP by preintercalation with hexylamine (HAZrP)⁷ and butylamine (BAZrP),⁸ respectively. The interlayer distance of the Kumar and Williams $\text{Ru}(\text{bpy})_3^{2+}$ -exchanged BAZrP was 19.5 Å, whereas Vliers et al. reported an interlayer distance of 16.3 Å. We report here a procedure for the direct ion exchange of $\text{Ru}(\text{bpy})_3^{2+}$ into an α -ZrP framework. This procedure allows for direct photochemical and photophysical studies of the interaction of luminescent molecules and quenchers within zirconium phosphates without interference from preintercalated species.

Our approach utilizes a hydrated form of α -ZrP, which instead of one water molecule per formula unit has ap-

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proximately six water molecules and an interlayer distance of ca. 10.3 Å (Chart 1b).⁹ This phase was first observed by Clearfield et al.³ and characterized by Alberti et al., who also observed a 10.4 Å phase.⁹ Kijima developed a procedure for the direct preparation of the 10.4 Å hydrated phase.¹⁰ Initial studies of this phase indicated that it exchanges some alkali and divalent metal ions more easily than the α -ZrP phase.⁹

We synthesized the 10.3 Å hydrated phase of ZrP using a procedure similar to the one that Kijima used to prepare θ -ZrP, the 10.4 Å hydrated phase.¹⁰ One volume of a 0.05 M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ aqueous solution was mixed with one volume of a 6 M H_3PO_3 aqueous solution at constant stirring and at 94 °C for 48 h. The product was obtained as a fine powder, which was analyzed by X-ray powder diffraction (XRPD). The diffraction patterns were measured in the wet sample to avoid dehydration of the material. As is common for these materials, the first order diffraction peak gives the interlayer distance that in this case was 10.3 Å (Figure 1 and Chart 1b). As first reported by Clearfield et al., upon dehydration the α -ZrP phase is obtained.³

The direct ion exchange of $\text{Ru}(\text{bpy})_3^{2+}$ was conducted in aqueous solution using various concentration ratios of the 10.3 Å hydrated phase with $\text{Ru}(\text{bpy})_3^{2+}$ at constant stirring and ambient temperature. To monitor the ion exchange process, every 24 h, an aliquot of the suspension was filtered, and a UV–vis absorbance spectrum of the filtrate solution was obtained. The ion exchange procedure was stopped when the intensity of the spectrum ceased to decrease, which took 4–5 days. The most apparent result of the ion exchange is the formation of a new phase with an expanded interlayer distance of 14.6–15.2 Å (Figure 1). The percentage of $\text{Ru}(\text{bpy})_3^{2+}$ per gram of material was calculated from the elemental analysis results.¹¹ The XRPD patterns show a tendency of sharper and better defined peaks as the $\text{Ru}(\text{bpy})_3^{2+}$ loading increased.

The diffraction patterns of the $\text{Ru}(\text{bpy})_3^{2+}$ -exchanged ZrP and the interlayer distance of 15.2 Å are in agreement with the results of Yates et al.,⁶ who obtained an interlayer distance of 15.9 Å for their $\text{Ru}(\text{bpy})_3^{2+}$ -cocrystallized ZrP material. A 16.4 Å interlayer distance can be calculated from the minimum expansion that $\text{Ru}(\text{bpy})_3^{2+}$ ions can produce^{12,13} and the thickness of an α -ZrP type layer.¹⁴ However, α -ZrP

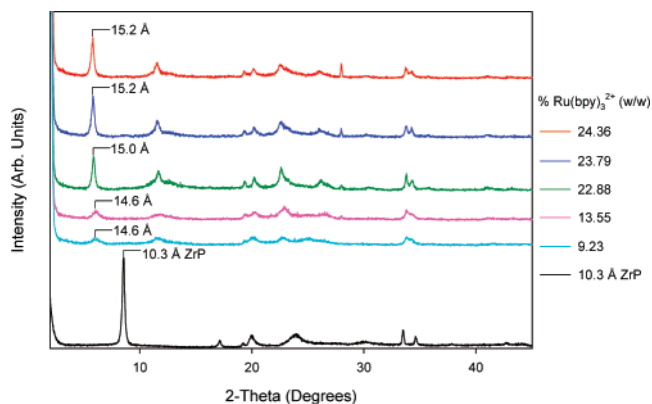


Figure 1. XRPD patterns for $\text{Ru}(\text{bpy})_3^{2+}$ -exchanged ZrP materials at various loading levels (% w/w) and the 10.3 Å phase. The interlayer distances are indicated in the first order (002) diffraction.

type layers are made of nearly perfect planes of Zr atoms having bridging O_3PO^- groups above and below each plane. Therefore, nothing precludes intercalating molecules from penetrating slightly between O_3PO^- groups, reducing the calculated interlayer distance for the intercalated material.

The cross-sectional area of $\text{Ru}(\text{bpy})_3^{2+}$ (based on its van der Waals dimensions) can be used to calculate its maximum theoretical loading within ZrP.¹² The cross-sectional area of $\text{Ru}(\text{bpy})_3^{2+}$ oriented with a C_3 axis perpendicular to the ZrP layers is 116.9 Å². Using an area per site of 0.24 nm² for ZrP-type layers,^{1a,15} we calculate 9.74 cationic sites per $\text{Ru}(\text{bpy})_3^{2+}$ molecule. Assuming that we achieve the maximum loading level in the 24.36% $\text{Ru}(\text{bpy})_3^{2+}$ sample and using elemental analysis to determine the amount of sites available, we calculate that there will be 10.18 sites per $\text{Ru}(\text{bpy})_3^{2+}$ ion if we have a pure phase. Since this experimental result is in agreement with the theoretical value, the sample with the highest loading level has reached the maximum theoretical loading level.

The dependence of the interlayer distance on loading level is a result of the ordered packing of the $\text{Ru}(\text{bpy})_3^{2+}$ -exchanged cations with increased loading. When $\text{Ru}(\text{bpy})_3^{2+}$ is ion exchanged into 10.3 Å ZrP, it acts as a wedge. At higher loading, more $\text{Ru}(\text{bpy})_3^{2+}$ cations serve as pillars keeping the ZrP layers apart and avoiding imperfections on the ZrP stacking. That is reflected in the XRPD patterns as a tendency to sharper and more defined peaks, especially on the 002 diffraction, as the $\text{Ru}(\text{bpy})_3^{2+}$ loading increases (Figure 1).¹⁵

Figure 2 shows the luminescence spectra of $\text{Ru}(\text{bpy})_3^{2+}$ -exchanged ZrP powders suspended in water (0.08% w/w) and of 1.60×10^{-5} M solution. The spectra resemble the one in aqueous solution with a small blue shift of λ_{max} from 598 nm in aqueous solution to 592 nm in the exchanged material. The result indicates that the microenvironment that the $\text{Ru}(\text{bpy})_3^{2+}$ complex probes in the interlayer region is polar due to the highly hydrated state of the ZrP. This blue shift is consistent with the rigidochromic effect,¹⁶ due to a more rigid environment in the interlayer region of the exchanged material.

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(14) We can calculate the minimum distance that a $\text{Ru}(\text{bpy})_3^{2+}$ ion should separate ZrP layers on the basis of the $\text{Ru}(\text{bpy})_3^{2+}$ crystalline structure.¹² The minimum distance that $\text{Ru}(\text{bpy})_3^{2+}$ ions can separate ZrP layers is obtained if their C_3 axes are normal to the 002 planes, giving an interlayer distance of 9.8 Å. Since the thickness of an α -ZrP type layer is 6.6 Å, adding the expansion produced by the $\text{Ru}(\text{bpy})_3^{2+}$ ions would give an expected interlayer distance for $\text{Ru}(\text{bpy})_3^{2+}$ -exchanged ZrP of 16.4 Å.

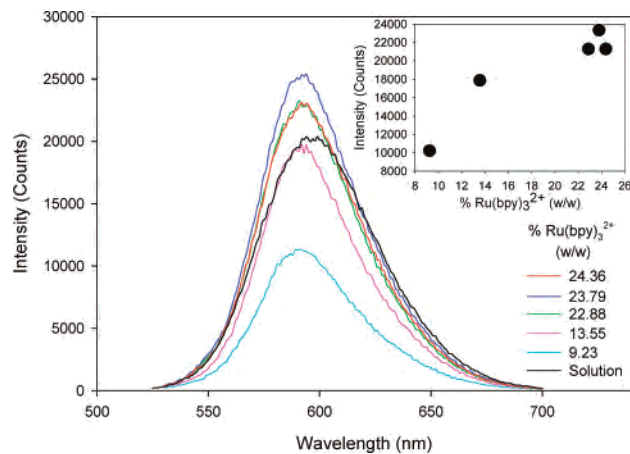


Figure 2. Luminescence spectra of aqueous suspensions of Ru(bpy)₃²⁺-exchanged ZrP at different Ru(bpy)₃²⁺ loading levels and of a 1.60×10^{-5} M Ru(bpy)₃²⁺ aqueous solution. Inset shows the luminescence intensity at λ_{\max} vs %Ru(bpy)₃²⁺ (w/w). The luminescence spectra of the suspensions were taken with a slit aperture of 0.25 mm, whereas the luminescence in solution was taken with a slit aperture of 1.25 mm.

The inset in Figure 2 shows that the luminescence intensity of Ru(bpy)₃²⁺-exchanged ZrP increases with an increase in Ru(bpy)₃²⁺ loading level until it levels off. This result is consistent with self-quenching. Preliminary luminescence lifetime measurements show a decrease in the luminescence lifetime as the loading level increases,¹⁷ probably by a catalyzed deactivation of the excited state through collisions

with neighboring ground-state Ru(bpy)₃²⁺ complexes.⁵ A complete elucidation of the role of excited-state quenching reactions within directly ion exchanged ZrP requires quenching experiments with other molecules that deactivate the Ru(bpy)₃²⁺ excited state. We are currently pursuing such investigations, and the results will be reported in a future publication.

In conclusion, we have performed the first direct ion exchange of Ru(bpy)₃²⁺ into an α -ZrP framework, that avoids the incorporation of Ru(bpy)₃²⁺ during a highly reactive synthetic procedure for preparing α -ZrP.⁶ In addition, we have avoided having Ru(bpy)₃²⁺ coexchanged with alkylamines within α -ZrP,^{7,8} which promotes a rigid and hydrophobic microenvironment in the interlayer space. Our method provides a rigid but hydrophilic environment which allows the encapsulation of Ru(bpy)₃²⁺ and similar complexes without affecting significantly its luminescent properties.

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Supporting Information Available: Details of the synthesis of the 10.3 Å ZrP phase, intercalation procedure for the preparation of the different Ru(bpy)₃²⁺-exchanged ZrP materials, and elemental analysis results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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