

PREPARATION AND PHOTOLUMINESCENCE CHARACTERIZATION OF $\text{Ru}(\text{bipy})_3^{2+}$ INTERCALATED $\text{Cd}_2\text{P}_2\text{S}_6$

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Abstract—Single crystals and powders of the layered, wide bandgap semiconductor, $\text{Cd}_2\text{P}_2\text{S}_6$, have been intercalated with $\text{Ru}(\text{bipy})_3^{2+}$ by a cation exchange mechanism. Cation vacancies are created in the lattice to compensate for the charge of the intercalated ions. The photoluminescence spectrum of the intercalated material has been examined over the temperature range 1.8–77 K and compared with the photoluminescence properties of the host lattice and the free intercalate. Analysis of the spectra indicates that only weak interactions exist between the intercalate and the host lattice. The polarization of the photoluminescence suggests that the $\text{Ru}(\text{bipy})_3^{2+}$ ions are partially oriented with their C_3 symmetry axes perpendicular to the host lattice layers.

Keywords: Photoluminescence, intercalation, lamella or layered solid, spectra, ruthenium, organometallic.

INTRODUCTION

The transition metal chalcogenophosphates are broad-band semiconductors with the general chemical formula $\text{M}_2\text{P}_2\text{X}_6$ (M = transition metal, X = S, Se). They crystallize with the layered structure [1] illustrated schematically in Fig. 1. Because the three-atom-thick repeating layers are held together only by weak van der Waals (vdW) interactions, it is possible to introduce a variety of atoms, ions or molecules into the vdW interstices to form intercalation compounds of the chalcogenophosphate lattice [2]. We have endeavored to exploit the solid-state chemistry of the chalcogenophosphates to prepare new materials with novel photochemical or electroluminescent properties. Such behaviour could arise, for example, by combining the large photoexcitation cross-section and exciton mobility of the semiconducting lattice with the high quantum efficiency for photochemistry or photoluminescence of an appropriate intercalate. This paper describes the preparation and optical properties of the intercalation compound $\text{Cd}_2\text{P}_2\text{S}_6$ with $\text{Ru}(\text{bipy})_3^{2+}$.

$\text{Ru}(\text{bipy})_3^{2+}$ is an interesting intercalate both because of its high photoluminescence yield and its ability to photochemically reduce water. Indeed, the photochemical activity of some $\text{Ru}(\text{bipy})_3^{2+}$ intercalated silicates has been examined already [3]. The photochemical reaction cycle requires both the

$\text{Ru}(\text{bipy})_3^{2+}$ photocatalyst and a metal cation redox catalyst [4]. The efficiency of H_2O oxidation is improved if the reduced form of the metal catalyst can be prevented from acting as a reducing agent for $\text{Ru}(\text{bipy})_3^{2+}$. The heterogeneous environment of the layered silicates improved the reaction efficiency, possibly by increasing the average distance between the Ru complex, located in an interstitial region, and the reducing metal, located in intralamellar sites.

The substitution of a wide bandgap, layered, semiconducting host lattice ($\text{Cd}_2\text{P}_2\text{S}_6$) for the insulating silicate lattice offers improved excitation cross-sections and other potential advantages. Unfortunately, the intercalation of an ionic species, common in silicate lattices, is generally not possible in the more covalent chalcogenide materials. The $\text{M}_2\text{P}_2\text{S}_6$ family of materials, however, is unique in its ability to intercalate cations by an exchange reaction and thus is singularly suitable for the present study.

EXPERIMENTAL

Sample preparation

The $\text{Cd}_2\text{P}_2\text{S}_6$ used in this work was synthesized by procedures described in detail elsewhere [1]. Intercalated samples were prepared by a variety of methods, both as powders and large single crystals. It is necessary to employ fairly large single crystals for optical polarization measurements.

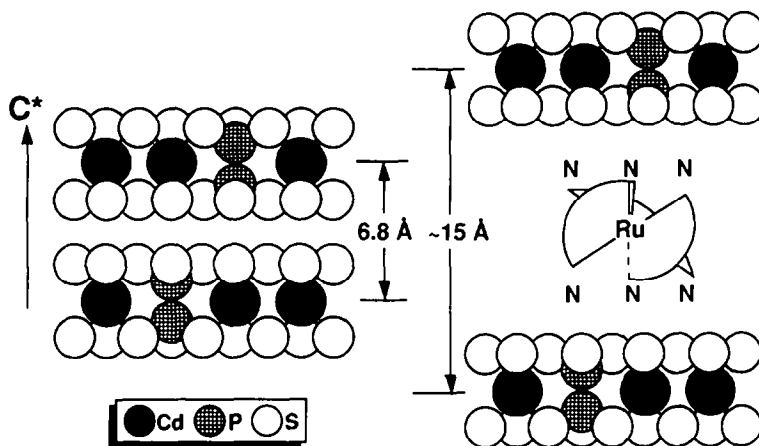
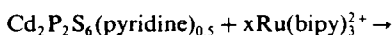


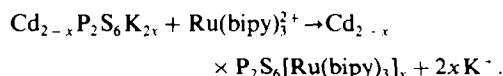
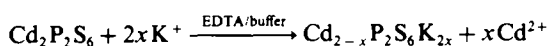
Fig. 1. The layered structure of $M_2P_2S_6$ crystals and the $Ru(bipy)_3^{2+}$ intercalated lattice.

Intercalated *single crystals* were prepared by immersing crystals of $Cd_2P_2S_6(pyridine)_{0.5}$ in a 1 M solution of $Ru(bipy)_3Cl_2$ in a 50% by volume pyridine in water solvent for 3 days at room temperature. The pyridine–water solvent has been employed previously for the intercalation of large organometallic cations into $M_2P_2S_6$ lattices [5]. The reaction mechanism is thought to involve the intercalation of $Ru(bipy)_3^{2+}$ cations into the vdw region as the Cd^{2+} cations complexed by pyridine are displaced from the lattice.



The $Cd(py)_n^{2+}$ complex is quite stable ($K = 18.6$ for $n = 2$) [6, 7] and its formation assists in the creation of lattice metal vacancies to compensate the charge of the intercalate. Chemical analysis of the product indicated the following typical elemental composition: %C = 8.36, %Cd = 38.51, %N = 0.606, %H = 0.03, %Ru = 0.95, %S = 37.55 and %P = 10.988. The composition is consistent with formulation of the product as $Cd_{1.86}P_2S_6[Ru(bipy)_3]_{0.15}$ (referred to as I hereafter). Approximately 0.1 wt.% of pyridine and 3 wt.% of water from the solvent remain in the lattice. X-ray diffraction data using the CuK_α radiation reveal that the basal plane spacing of the product is 14.7 Å, close to the value found in $Mn_{2-x}P_2S_6[Ru(bipy)_3]_x$ [8].

A higher degree of intercalation could be achieved if crystalline powders of the host lattice were used as a starting material, and a stronger complexing agent (EDTA) was employed in place of pyridine. Intercalated powders were prepared by insertion of $Ru(bipy)_3^{2+}$ in two steps.



A potassium intercalate was first synthesized by reacting $Cd_2P_2S_6$ (≈ 100 mg) with an aqueous 0.1 M EDTA solution (≈ 10 ml) containing KCl (≈ 1 g), $NaHCO_3$ (≈ 0.1 g) and Na_2CO_3 (≈ 0.1 g). In a basic medium, EDTA assists in the removal of intralayer Cd^{2+} ions. The potassium intercalate was treated with 10 ml of an aqueous ≈ 0.17 M solution of $Ru(bipy)_3Cl_2$ for 3 days at $\approx 60^\circ C$. As some unexchanged potassium intercalate was still present, the latter was filtered and treated with additional $Ru(bipy)_3Cl_2$ solution. The red powder obtained was then filtered, washed several times with water and dried under vacuum. Elemental analysis of the intercalate yielded the following weight percentages: %C = 12.95, %H = 0.63, %N = 2.93, %S = 31.42, %P = 9.90, %Cd = 29.48, %Ru = 3.23 and %K = 1.7. The composition is consistent with a formulation of the product as $Cd_{1.64}P_2S_6[Ru(bipy)_3]_{0.2}K_{0.24}$ (referred to as II hereafter). An X-ray powder diffractogram of the intercalate exhibited sharp {001} and {002} reflections from which the basal spacing was determined to be 15.3 Å.

Finally, infrared spectra of II exhibited the same bands as $Ru(bipy)_3Cl_2$. In addition, the host lattice PS_3 asymmetric stretch, which occurs at 570 cm^{-1} in $Cd_2P_2S_6$, was split into two components at 605 cm^{-1} and 555 cm^{-1} , as invariably observed in the $M_2P_2S_6$ intercalates containing intralamellar metal vacancies [10].

Photoluminescence spectra

Photoluminescence (PL) spectra of I and II were recorded over the temperature range 77–1.8 K. Samples were placed in a Janis 10DT cryostat and cooled by helium gas or direct immersion in the liquid. Temperatures below 4.2 K were obtained by pumping on the liquid helium bath.

Excitation energies were selected with a combination of filters that selectively passed the output of a high-pressure 1 KW Xenon arc lamp. Simultaneous broadband excitation of both host lattice and intercalate was achieved by the combination of a Ni/CoSO₄ solution and a Corning 7-54 filter that together transmit between 40,000 and 30,300 cm⁻¹. Selective excitation of the intercalate was provided by filtering with the combination of a CuSO₄ solution and a Corning 7-59 filter that transmitted energies below the host lattice band edge between 30,300 cm⁻¹ and 23,000 cm⁻¹. The PL was filtered with a Corning 3-75 glass filter to remove scattered excitation wavelengths, dispersed with a grating monochromator and detected with a cooled RCA 7102 photomultiplier tube.

Since crystals of I were aligned with their *c**-crystallographic axes (stacking axis), either parallel or perpendicular to the direction of excitation. The polarization measurements were carried out by direct excitation of the Ru(bipy)₃²⁺ metal-ligand, charge-transfer transition with unpolarized light. The polarization of the PL was determined with a Polaroid sheet analyzer oriented parallel and perpendicular to the direction of excitation as illustrated in Fig. 4.

RESULTS AND DISCUSSION

Intercalation mechanism

The mechanism of intercalation of M₂P₂X₆ compounds has been discussed extensively in the literature [2, 10–12]. It is likely that several mechanisms exist and that the mechanism followed depends upon the particular lattice and the intercalate. It has been established that large cations can be intercalated via synthetic routes leading to intralamellar metal defi-

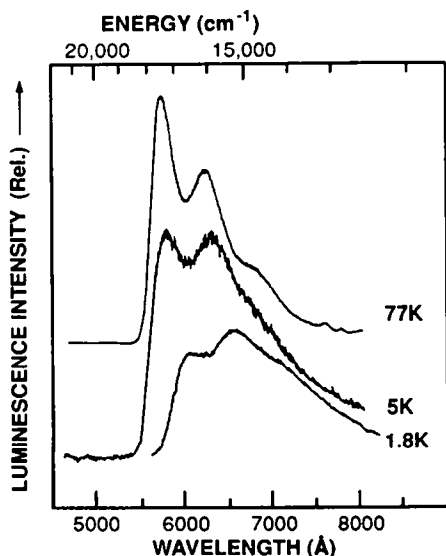


Fig. 2. Emission spectra of Ru(bipy)₃²⁺ intercalated Cd₂P₂S₆ crystals, recorded at different temperatures as labeled in the figure.

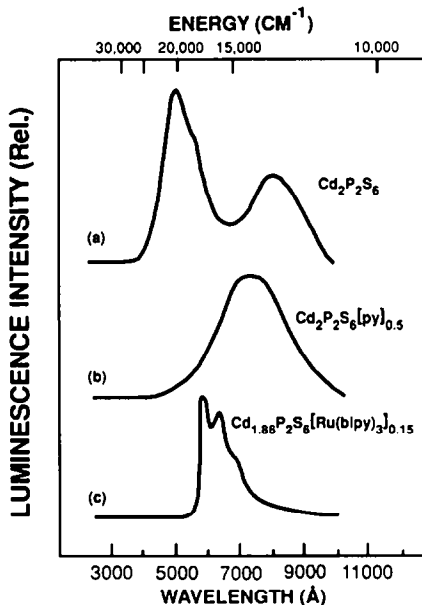


Fig. 3. A comparison of the photoluminescence spectra of (a) Cd₂P₂S₆, (b) Cd₂P₂S₆(py)_{0.5} and (c) Cd_{1.88}P₂S₆[Ru(bipy)₃²⁺]_{0.15}, at 4.2 K.

cient products with the general formula M_{2-x}P₂S₆-(cation)_x, for a dipositive cation. The chemical analyses of I and II indicate that intercalation of Cd₂P₂S₆ by Ru(bipy)₃²⁺ proceeds by this mechanism. Because of the large size of the cation and the magnitude of the basal expansion observed we infer that the intercalated cations are located in the vdW interstices (see Fig. 1).

Photoluminescence spectrum

The PL spectrum of I is shown in Fig. 2 and is identical in all important features to that of II. The photoluminescence could be stimulated either by direct excitation of I below the bandgap energy of Cd₂P₂S₆ ($E_G \approx 25,000$ cm⁻¹) or by excitation above the band edge into delocalized conduction band states of the host lattice. In the latter event, the intercalate photoluminescence must originate from rapid energy transfer from the lattice layers to the intercalate in the vdW interstitial space. The absence of luminescence from the host lattice or intercalated solvent, is consistent with rapid energy transfer from Cd₂P₂S₆ to Ru(bipy)₃²⁺ states lying below the conduction band edge.

The PL spectrum of I is compared with that of Cd₂P₂S₆(py)_{0.5} and Cd₂P₂S₆ in Fig. 3. It is similar in its appearance to that of Ru(bipy)₃²⁺ cation in a variety of crystalline and glassy solvent matrices [13]. At all temperatures, the PL spectra of I exhibited a regular vibronic progression with spacing of ≈ 1400 cm⁻¹. As the temperature was lowered from 4.2 K to 1.8 K the PL intensity decreased and the high temperature spectrum with its origin band at 17,420 cm⁻¹ band was replaced by a low temperature spectrum with an origin at 16,920 cm⁻¹. This be-

behaviour is characteristic of $\text{Ru}(\text{bipy})_3^{2+}$ and is due to a temperature dependent distribution of population among close lying excited states [14–18] whose individual electronic origins fall within the highest energy band in the PL spectrum.

Intercalate–lattice interaction

The similarity of the spectrum to that of the unintercalated cation suggests that the electronic structure of the cation is relatively unaffected by insertion into the host lattice. Qualitative indications of the effect of the host lattice upon the intercalate may be obtained from the spectral shift and changes in vibrational intervals. We observe, for example, the highest energy luminescence band at $17,420\text{ cm}^{-1}$, red-shifted $\approx 480\text{ cm}^{-1}$ relative to the corresponding band in the spectrum of $\text{Ru}(\text{bipy})_3^{2+}$ in glassy matrices. A similar shift has been observed in substituted Ru complexes such as $\text{Ru}(4,4'\text{-Me}_2\text{bipy})_3^{2+}$ and $\text{Ru}[(\text{bipy})_m(\text{phen})_n]^{2+}$ ($m+n=3$) and has been attributed to steric effects [19, 20]. It is possible that steric constraint within the vdW gap induces the red shift in the present case. Other small modifications of the PL spectrum were observed, indicative of weak host–guest interaction. For example, the vibronic progression interval increases from $\approx 1300\text{ cm}^{-1}$ to $\approx 1400\text{ cm}^{-1}$ upon intercalation. The vibronic origin is red-shifted $\approx 410\text{ cm}^{-1}$ in the unintercalated $\text{Ru}(\text{bipy})_3^{2+}$ and $\approx 500\text{ cm}^{-1}$ in the intercalated lattice.

We anticipate that the two-dimensional interstitial spaces of the intercalated host lattice may cause ordering of the intercalate. If the orientation of the intercalate is established by *intercalate–lattice* interactions, a special relationship may be established between the crystallographic and intercalate symmetry axis. In particular, we consider the orientations in which the unique molecular axis $C_3(Z)$ adopts an orientation parallel or perpendicular to the stacking axis c^* as shown in Fig. 4. We prefer the $Z\parallel c^*$ model for the following reason. Lattice energy is minimized if the intercalate is located in the vdW gap, proximate to the lattice cation vacancies created by the intercalation process. The Cd^{2+} vacancies are located in planes above and below the vdW gap and the orientation with $Z\parallel c^*$ establishes the same relationship between the octahedral anionic lattice vacancies and the $\text{Ru}(\text{bipy})_3^{2+}$ ion as is found between the $\text{Ru}(\text{bipy})_3^{2+}$ cation and the octahedral PF_6^- anions in the crystal $[\text{Ru}(\text{bipy})_3][\text{PF}_6]_2$.

Luminescence polarization and intercalate orientation

We have attempted to infer the intercalate orientation from luminescence polarization measurements conducted on a number of crystal samples of I. In order to accomplish this, it is necessary to know the polarization of both the absorption and emission of $\text{Ru}(\text{bipy})_3^{2+}$ and to assume that these properties are not altered by intercalation. There exists relative unanimity concerning the nature of the absorption

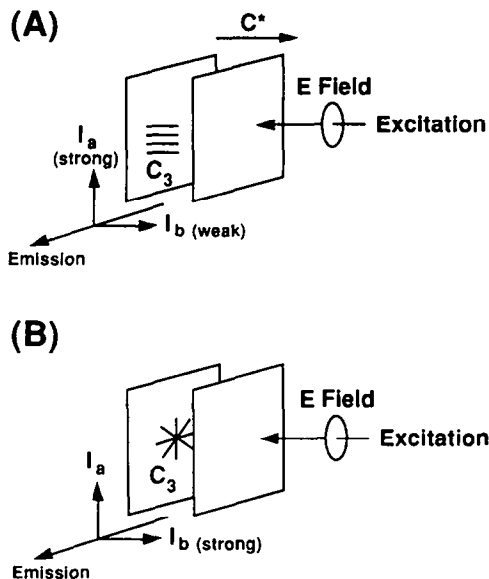


Fig. 4. Schematic diagram of the polarization measurement geometry. The host lattice is represented by the coplanar plates, the Ru complex C_3 symmetry axis is represented by the straight lines. In (A) the C_3 axis is parallel to the c^* and in (B) the C_3 axis is perpendicular to c^* .

oscillator. Krausz [21] has recently commented on the variety of spectroscopic experiments yielding evidence on the nature of the excited states of $\text{Ru}(\text{bipy})_3^{2+}$, noting that in all cases the dominant absorption intensity is in the XY plane. However, considerable disagreement exists concerning the nature of the emission oscillator.

Luminescence polarization measurements were reported by Fujita and Kobayashi [22], who examined $\text{Ru}(\text{bipy})_3^{2+}$ in EPA glassy solution at 77 K. The luminescence polarization was found to be generally consistent with planar absorption and luminescence oscillators; quantum chemical arguments suggested that the oscillator lay in the XY plane. However, the polarization ratio $P = 0.23$ obtained with excitation near $21,300\text{ cm}^{-1}$ deviated considerably from the value expected for strictly planar oscillators (0.14), indicating linear oscillator behaviour in this region. The linear oscillator could arise through a solvent induced symmetry breaking the degeneracy of a planar oscillator.

In 1982 Carlin and DeArmond [23] reported evidence for symmetry reduction in excited states of $\text{Ru}(\text{bipy})_3^{2+}$, rejecting solvent interactions as the cause and invoking a model in which the electronic excitation is initially localized on a single ligand. Using arguments derived in part from the polarization behaviour of asymmetrically substituted Ru^{2+} complexes, it was proposed that better agreement with the polarization data could be obtained with a linear Y -oscillator model. The localization model was further employed to interpret the time-resolved polarization ratio behaviour reported by Myrick *et al.* [24] in 1987. The initially high polarization ($\approx 0.24\text{--}0.37$

depending upon the solvent), more characteristic of a linear oscillator, was observed to approach the steady-state value of 0.23 at times greater than ≈ 10 ns. However, Krausz [25] reported results from a similar study that found no time variation of the polarization ratio, but instead a generally good agreement with the *XY* planar oscillator model employed by Fujita and Kobayashi.

The ambiguity in the polarization of the emission oscillator does not influence conclusions concerning the orientation of the intercalate in the present work, since *both* the *XY*-planar and *Y*-linear emission oscillator models yield identical predictions for ordering in a two-dimensional space (see Table 1). We adopt Albrecht's [26] general notation for a space fixed coordinate system **a**, **b** and **c** and a molecule-fixed axis system **x**, **y** and **z**, defined with respect to the space fixed axes by the Euler angles ϕ , Θ and Φ [27]. Experiments were conducted with light incident along **b** with intensity p polarized parallel to **a** and $(1-p)$ polarized parallel to **c**. The luminescence was viewed along **c** and the polarization measured parallel to **a** and **b**. The geometry of the photoluminescence polarization measurement is shown in Fig. 4.

Equations for the luminescence intensity polarized parallel to the **a**, **b** and **c** are given by Albrecht and Simpson [28]. In order to use these relations to compute the luminescence intensity for oscillators ordered, for example, with $Z \perp \mathbf{b}$, we must average over $0 \leq \Theta \leq \pi$, $0 \leq \Phi \leq 2\pi$ with $\phi = 0$ using

$$\int_0^{2\pi} d\Phi \int_0^{\pi} d\Theta. \quad (1)$$

The results for randomly ordered linear and planar oscillators given by Albrecht and Simpson are obtained by extending the average over $0 \leq \phi \leq 2\pi$ using

$$\int_0^{2\pi} d\phi \int_0^{2\pi} d\Phi \int_0^{\pi} \sin\Theta d\Theta. \quad (2)$$

The luminescence polarization ratio viewed along **c** is defined as

$$P_{ab} = (I_a - I_b)/(I_a + I_b), \quad (3)$$

where I_a and I_b are, respectively, the PL intensities polarized parallel to the **a** and **b** axes (see Fig. 4).

Using the appropriately averaged intensities, the results assembled in Table 1 were obtained for randomly and partially ordered linear and planar oscillators.

After correction for the polarizing and depolarizing effects of the optical apparatus, the experimental value of the polarization was $P_{ab} = 0.34 \pm 0.02$, obtained with unpolarized excitation ($p = 1/2$). This value is about 4.5 times greater than predicted for the randomly oriented intercalate and we conclude that the Ru(bipy)₃²⁺ molecular axes cannot be randomly organized in the vdW gap. However, the experimental result is not in agreement with the value predicted for any *XY* oscillator model, but rather falls between the values for an ordered ensemble with $Z \perp \mathbf{b}$ and $Z \parallel \mathbf{b}$.

The observed polarization may result from a mixture of two or more special orientations. If a fraction (f) of the intercalate has structure α and the remaining $(1-f)$ structure β , then the predicted polarization is:

$$P = fP^\alpha + (1-f)P^\beta, \quad (4)$$

where P^α and P^β are the predicted polarizations for the α structure and the β structure, respectively. The polarization ratio for a mixture of intercalate oriented with $Z \parallel \mathbf{b}$ ($P_{ab}^\alpha = 1$) and intercalate randomly oriented ($P_{ab}^\beta = 1/13$) yields $f = 0.29$. For a mixture of intercalate oriented with $Z \parallel \mathbf{b}$ ($P_{ab}^\alpha = 1$) and $Z \perp \mathbf{b}$ ($P_{ab}^\beta = -1/3$), the experimental polarization value is consistent with $f = 0.51$.

The experimental polarization is in good agreement with that predicted for randomly oriented linear oscillators. However, the bulk of experimental evidence gathered on the polarization properties of Ru(bipy)₃²⁺ luminescence is not consistent with a predominately linear absorption oscillator.

CONCLUSION

We have prepared Ru(bipy)₃²⁺ intercalated Cd₂P₂S₆. The material is strongly photoluminescent and exhibits rapid energy transfer from the photoexcited host lattice to the intercalate. The photophysical behaviour of Ru(bipy)₃²⁺ is little changed by intercalation into Cd₂P₂S₆. The polarization ratio is consistent with partial orientation of the intercalate in the vdW gap. The value of the polarization ratio requires

Table 1. Polarization ratios for randomly and partially oriented oscillators

Oscillator		Orientation	Polarization ratio			
EX	EM		$(p = 1/2)$		$(p = 1)$	
			P_{ab}	P_{ac}	P_{ab}	P_{ac}
<i>XY</i>	<i>XY</i>	Random	1/13	0	1/7	1/7
<i>Z</i>	<i>Z</i>	Random	1/3	0	1/2	1/2
<i>XY</i>	<i>XY</i>	$Z \parallel \mathbf{b}$	1	0	1	0
<i>XY</i>	<i>XY</i>	$Z \perp \mathbf{b}$	-1/3	0	-1/7	1/2
<i>Z</i>	<i>Z</i>	$Z \perp \mathbf{b}$	1	0	1	1/2
<i>XY</i>	<i>Y</i>	$Z \parallel \mathbf{b}$	-1/3	0	-1/7	0

that at least 3/10 of the intercalate be oriented with the $C_3(Z)$ symmetry axis perpendicular to the host lattice layers.

Based upon the results obtained, it may prove possible to produce a water photo-oxidation cycle similar to the one already demonstrated for intercalated silicates, but using $\text{Ru}(\text{bipy})_3^{2+}$ intercalated $\text{M}_2\text{P}_2\text{S}_6$ host lattices with M^{2+} chosen to be a suitable redox catalyst. Work is in progress to examine the effect of M^{2+} (or M^{3+}) reducing ions in inter- and intralamellar positions.

Finally, we note that transparent, intercalated host lattices may be generally useful for the examination of the absorption and emission spectra of highly absorbing cations. The large single crystals may be easily cleaved to almost arbitrarily thin sections and the intercalated ions frequently exhibit a large degree of ordering. The vdW region will often accommodate ions with a wide range of size and geometries while excluding neutral solvents not directly associated in solvation.

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