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aLanthanoid containing phosphotungstates: Syntheses, crystal structure, electrochemistry, photoluminescence and magnetic properties

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Abstract: A series of ten mononuclear lanthanoid containing phosphotungstate clusters were synthesized by the reaction of dilacunary $[P_2W_{19}O_{69}(H_2O)]^{14-}$ with Ln(NO₃)₃.xH₂O in potassium acetate buffer (pH 4.8), leading to the formation of Peacock and Weakley type dimer $[Ln(PW_{11}O_{39})_2]^{11-}$ (Ln = Pr³⁺ (1), Nd³⁺ (2), Eu³⁺ (3), Gd³⁺ (4), Tb³⁺ (5), Dy³⁺ (6), Ho³⁺ (7), Er³⁺ (8), Tm³⁺ (9), and Yb³⁺ (10)). All isostructural molecular clusters were structurally characterized using various analytical techniques like FT-IR, ³¹P NMR spectroscopy, photoluminescence and solid state UV/vis, electrochemistry, magnetism and single crystal X-ray diffraction. The compounds crystallize as mixed potassium/caesium or potassium salt K₁₁[Ln(PW₁₁O₃₉)₂]·xH₂O $(Ln = Pr^{3+} (1a), Nd^{3+} (2a), Eu^{3+} (3a), Gd^{3+} (4a), Tb^{3+} (5a), Dy^{3+} (6a), Ho^{3+} (7a), Er^{3+} (8a), and$ $Tm^{3+}(9a)$, in the monoclinic crystal system, space group $P2_1/c$ (14) with the exception of the Gd(4a) and Ho(7a) complexes which crystallize in the triclinic system, space group P-1. The prominent effect of the paramagnetic lanthanoid ion along the group on the monolacunary Keggin unit (α -PW₁₁O₃₉) was illustrated by FT-IR and ³¹P NMR spectroscopy. This is attributed to its small size and high charge density (lanthanoid contraction). Photoluminescence of molecular clusters Eu(3a), Dy(6a) and Ho(7a) were studied at room temperature at different excitation wavelengths which shows interesting photochromic properties. The voltammetric patterns associated with the W-centers in the cluster series have enough distinct features allowing to establish a relative basicity of the reduced polyoxometalates: $\{PW11\} > Tm(9a) >$ $Eu(3a) \approx Tb(5a) \approx Ho(7a) > Gd(4a) \approx Dy(6a) \approx Er(8a)$. Among the lanthanoid cations, just the Eu^{3+} centre turned out to be electroactive, as expected. Magnetic measurement of Gd(4a) shows paramagnetic behaviour of the material.

Introduction

Polyoxometalates (POMs) chemistry, a class of inorganic metal oxygen nanoclusters, has attracted researchers worldwide in the recent years. Transition metal oxides in their high oxidation states basically form these classes of inorganic nanomolecular clusters (mainly Mo, W, V, Nb and Ta). The increasing diversity of structures isolated from a solution-based approach, either from aqueous or non-aqueous media, is notable due to the rich, unprecedented and unusual properties associated to POMs. In addition, these nanoclusters have potential applications in catalysis, molecular magnets, luminescence, and imaging in particular in the development of biomedicinal agents. Among them, the family of lanthanoid-containing POMs are of attraction due to structural flexibility, application in acid catalysis, molecular magnets, luminescence, and the development of contrast agents for magnetic resonance imaging (MRI).¹ We have witnessed the reactivity of various lacunary POMs with different lanthanoid ions, resulting in novel molecular structures with different properties.² Thus, our quest to design the synthetic strategy, using of various lacunary POMs and changing the solvent medium, the ionic strength, and the reaction conditions can lead to the isolation of more undiscovered compounds with new interesting properties of this sub family of POMs.

To date, Pope et al.'s high nuclear cerium-containing polyoxotungstoarsenate(III) and polytungstoantimonate(III) $[Ce_{16}X_{12}(H_2O)_{36}W_{148}O_{524}]^{76-}$ (X = As^{III} and Sb^{III}) reported in 1997 still remain the largest molecular tungstate clusters.³ Later, Kortz et al. reported a dimeric $[Ce_{20}Ge_{10}W_{100}O_{376}(OH)_4(H_2O)_{30}]^{56-}$ polytungstogermanate species.⁴ Recently, one of us reported on $[Ln_{16}As_{16}W_{164}O_{576}(OH)_8(H_2O)_{42}]^{80-}$ (Ln = Eu, Gd, Tb, Dy, Ho), the largest polytungstate clusters known to date in terms of tungsten centres.^{2d} However, the groups of Francesconi, Yamase, Gouzerh, Krebs, Hill, Sécheresse, Patzke,² Coronado and others are still actively working on this type of molecular clusters with different perspectives.⁵ Yet Müllers keplerate ⁶ type tungsten clusters with or without lanthanoids still remain elusive.

Peacock and Weakley type Keggin complexes, with a metal to ligand ratio (1:2) are well known since 1971.⁷ They reported the formation of (1:2) complexes on the basis of elemental analysis. Later in the year 1990, Fedotov et al. investigated the solution-based multinuclear NMR spectroscopy on Keggin type (1:2) mononuclear lanthanoid POMs $[Ln(PW_{11}O_{39})_2]^{11-}$ and proposed the structure on its basis.⁸ However, extended hybrid organic-inorganic complexes of $[Ln(PW_{11}O_{39})_2]^{11-}$ are known for few lanthanoids following a hydrothermal synthetic approach,

e.g. $[Cu(en)_2]_2H_8[Gd(PW_{11}O_{39})_2 \cdot (H_2en)_{0.5} \cdot 3H_2O, {[Cu(en)_2]_{1.5}[Cu(en)(2,2'-bipy)(H_2O)_n]Ce[(\alpha - 1)_{1.5}(Cu(en)_2)_{1.$ $PW_{11}O_{39}_{2}$]⁶⁻ [(Ln, n) = (Ce^{III}, 0) and (Pr^{III}, 1), {[Cu(en)_2]_2(H_2O)[Cu(en)(2,2'bipy)]Ln[(\alpha-1)_{2}(H_2O)(Cu(en)(2,2'bipy))]Ln[(\alpha-1)_{2}(H_2O $HPW_{11}O_{39}_{2}$]⁴⁻ [Ln = Gd^{III}, Tb^{III}, Er^{III}].⁹ In addition, several examples of Keggin and Wells-Dawson based lanthanoid POMs with (1:2) metal to ligand ratio have been well documented, such as $[Ce^{III}(GeW_{11}O_{39})_2]^{13}$, $[Ce^{III}(BW_{11}O_{39})_2]^{15}$, $[Ln(SiW_{11}O_{39})_2]^{13}$ (Ln = Nd^{III}, Pr^{III} and Ce^{III}) and $[Ln(\alpha_2-P_2W_{17}O_{61})_2]^{17-10}$ In the year 1991, Qu et al. reported only the synthetic methodology for the isolation of several lanthanoid POMs of the β_2 -isomer of $[Ln(SiW_{11}O_{39})_2]^{13}$ (Ln = La, Ce, Pr, Nd, Sm, Gd and Er).¹¹ Later in the year 2007, Kortz et al. structurally characterized the above chiral complex systematically for all lanthanoid series and also investigated the solution based W-NMR spectroscopy for the diamagnetic derivatives.¹² In 2004, Nogueira et al. reported on the V-shaped Ce(IV) containing phosphotungstate $[Ce_2(PW_{10}O_{38})(PW_{11}O_{39})_2]^{17}$ with two different Keggin type lacunary phosphotungstates.¹³ Nevertheless, several research groups have used different monolacunary Keggin type ions to react with lanthanoid cations in different metal to ligand ratios and reaction conditions, in order to isolate monomeric, dimeric or polymeric entities. We may mention the following examples: $[Ln(GeW_{11}O_{39})]^{5-}$ (Ln = Y and Yb), $[Ln(H_2O)(BW_{11}O_{39}H)]^{10-}$ (Ln = Ce and Nd), $[Ln(\alpha - BW_{11}O_{39})]^{12-}$ (Ln = Ce and Nd), $[{Ln(\alpha - BW_{11}O_{39})}]^{12-}$ $GeW_{11}O_{39}(H_2O)_{2}(\mu-CH_3COO)_{2}^{12}$ (Ln = Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb), $\{[Yb(SiW_{11}O_{39})(H_2O)_2]^{5-}\}_{\infty}^{2e,10}$ In the recent past we have seen that the use of dilacunary POMs with lone pair containing hetero atoms, such as $[As_2W_{19}O_{67}(H_2O)]^{14}$, resulted in unprecedented structures and new properties.^{2c,d} However, its dilacunary analog $[P_2W_{19}O_{69}(H_2O)]^{14}$ without a lone pair-containing heteroatom was not much explored. The dilacunary polyanion [P₂W₁₉O₆₉(H₂O)]¹⁴⁻ was structurally characterized by Tourné et al. It is constructed from two $[PW_9O_{34}]^{9}$ subunits that are connected by a tungsten octahedron where the axial positions are occupied by a terminal water pointing towards the centre and an oxo group pointing outside the central axis.¹⁴ This structural feature is just the opposite of the one observed in the dilacunary $[As_2W_{19}O_{67}(H_2O)]^{14}$, which was structurally characterized by Kortz et al. Thus it is quite evident that due to the presence of a lone pair on the heteroatom (As^{III}) of dilacunary $[As_2W_{19}O_{67}(H_2O)]^{14}$, the terminal water is pointed outside the central axis.¹⁵ Herein, we report the synthesis and reactivity of POMs obtained with lanthanoid cations and the dilacunary phosphotungstate $[P_2W_{19}O_{69}(H_2O)]^{14-}$.

Experimental Section

General: The dilacunary POM precursor $K_{14}[P_2W_{19}O_{69}(H_2O)]\cdot 24H_2O$ was prepared according to the literature procedure and its purity was subjected to FT-IR spectroscopy.¹⁴ All chemicals were commercially procured and were used without further purification. Fourier transform infrared (FT-IR) spectra were recorded with a Perkin-Elmer BX spectrum on KBr pellets. Thermogravimetric analyses (TGA) were performed using a TG/DTA instrument DTG-60 Shimadzu at a temperature range of 25 to 700 °C in a nitrogen atmosphere. The heating rate was maintained at 5 °C/min. TGA was performed to evaluate the number of crystal water molecules present in the synthesized compounds. Solid state UV/Vis spectra were recorded on a Thermo Scientific Evolution 300 spectrometer. Photoluminescence measurements were performed on a Fluorolog Horiba Jobin Yvon spectrometer, operated at 50 kV and 40 mA (Mo K α 1 radiation).

All the ³¹P-NMR spectra were recorded with a Jeol ECX 400P spectrometer at 400 MHz magnetic field in 9.38T field strength. Elemental analysis was performed using an ICP-AES instrument, ARCOS from M/s Spectro Germany. Magnetic measurements of only the gadolinium complex were performed on a Micro sense (EV9) magnetometer from -22 to 22 kOe applied magnetic field at room temperature. Electrochemistry was performed on an electrochemical set-up EG & G 273 A driven by a PC with the M270 software. Potentials are quoted against a saturated calomel electrode (SCE). The counter electrode was platinum gauze of large surface area. All experiments were performed at room temperature. The source, mounting and polishing of the glassy carbon (Le Carbone-Lorraine) electrodes have been described.^{20d} The glassy carbon working electrode used in cyclic voltammetry had a diameter of 3 mm. The solutions were thoroughly deaerated for at least 30 min. with pure argon and kept under a positive pressure of this gas during the experiments. The composition and pH of the media used both in the electrochemical experiments and in the stability studies by spectrophotometry were: 1M CH₃COOLi/CH₃COOH (pH 4 and 5); 0.5 M Li₂SO₄/H₂SO₄ (pH 3).

Synthesis of $K_{11}[Pr(PW_{11}O_{39})_2] \cdot 22H_2O$ (Pr-1a). 0.5656 g (0.10 mmol) of $K_{14}[P_2W_{19}O_{69}(H_2O)] \cdot 24H_2O$ was dissolved in 25 mL of potassium acetate buffer (pH 4.8) with stirring. Later 0.087 g (0.20 mmol) of Pr(NO_3)_3 \cdot 6H_2O was slowly added to the reaction mixture.

The solution was stirred continuously at 50 °C for 30 min, followed by cooling to room temperature then filtering to remove the precipiate if formed. The addition of a 1.0 M KCl solution (1 mL) to the colorless filtrate and slow evaporation at room temperature led to rod like faint green crystals after about 4-5 weeks. Yield: 42.4% (based on $K_{14}[P_2W_{19}O_{69}(H_2O)]\cdot 24H_2O$). FT-IR(cm⁻¹): 1096(s), 1048(s), 951(s), 887(s), 836(m), 772(m), 727(m), 592(w), 512(m), 480(m). TGA was done to evaluate the number of crystal water present in the all complexes (see Figure S16). Elemental analysis (%); calcd. (found): W 63.9 (60.8), K 6.8 (6.4), P 0.98 (1.1).

Synthesis of $K_{11}[Nd(PW_{11}O_{39})_2]$ •25H₂O (Nd-2a). The above synthetic protocol was followed by using 0.0877 g (0.20 mmol) Nd(NO₃)₃·6H₂O instead of Pr(NO₃)₃·6H₂O. Plate like crystals of faint violet color were obtained after about 4-5 weeks. Yield: 43% (based on $K_{14}[P_2W_{19}O_{69}(H_2O)]$ ·24H₂O). FT-IR(cm⁻¹): 1100(s), 1048(s), 957(s), 891(s), 840(m), 772(m), 724(m), 592(w), 508(m), 482(m). Elemental analysis (%); calcd. (found): W 63.4 (61.39), K 6.7 (6.2), P 0.97 (1.1).

Synthesis of $K_{11}[Eu(PW_{11}O_{39})_2] \cdot 26H_2O$ (Eu-3a). The above synthetic protocol was followed by using 0.086 g (0.20 mmol) Eu(NO₃)₃·5H₂O instead of Pr(NO₃)₃·6H₂O. Colorless plate like crystals obtained after about 4-5 weeks. Yield: 39.2% (based were on $K_{14}[P_2W_{19}O_{69}(H_2O)]$ ·24H₂O). FT-IR(cm⁻¹): 1104(s), 1048(s), 953(s), 891(s), 838(m), 772(m), 727(m), 592(w), 512(m), 482(m). Elemental analysis (%); calcd. (found): W 63.1 (63.9), K 6.7 (6.3), P 0.97 (1.1).

Synthesis of K₁₁[Gd(PW₁₁O₃₉)₂]•32H₂O (Gd-4a). The above synthetic protocol was followed by using 0.090 g (0.20 mmol) Gd(NO₃)₃·6H₂O instead of Pr(NO₃)₃·6H₂O. Colorless needle like crystals were obtained after about 4-5 week. Yield: 46.3% (based on $K_{14}[P_2W_{19}O_{69}(H_2O)] \cdot 24H_2O)$. FT-IR(cm⁻¹) : 1104(s),1050(s), 955(s), 891(s), 842(m), 770(m), 729(m), 592(w), 512(m), 480(m). Elemental analysis (%); calcd. (found): W 62.1 (62.2), K 6.6 (6.0), P 0.95 (1.0).

Synthesis of $K_{11}[Tb(PW_{11}O_{39})_2]$ •22H₂O (Tb-5a). The above synthetic protocol was followed by using 0.087 g (0.20 mmol) Tb(NO₃)₃·5H₂O instead of Pr(NO₃)₃·6H₂O. Colorless rod like crystals were obtained after about 4-5 weeks. Yield: 44% (based on $K_{14}[P_2W_{19}O_{69}(H_2O)]$ ·24H₂O). FT-IR(cm⁻¹): 1106(s), 1050(s), 951(s), 897(s), 838(m), 774(m), 729(m), 592(w), 516(m), 472(m). Elemental analysis (%); calcd. (found): W 63.8 (61.3), K 6.8 (6.1), P 0.98 (1.1).

Synthesis of K₁₁[Dy(PW₁₁O₃₉)₂]•25H₂O (Dy-6a). The above synthetic protocol was followed by using 0.0877 g (0.20 mmol) $Dy(NO_3)_3$ ·H₂O instead of $Pr(NO_3)_3$ ·6H₂O. Colorless needle like crystals were obtained after about 4-5 weeks. Yield: 42% (based on $K_{14}[P_2W_{19}O_{69}(H_2O)]$ ·24 H_2O). FT-IR(cm⁻¹): 1106(s), 1052(s), 953(s), 891(s), 845(m), 770(m), 719(m), 594(w), 512(m), 482(m). Elemental analysis (%); calcd. (found): W 63.2 (61.32), K 6.7 (6.1), P 0.97 (1.1).

Synthesis of K₁₁[**Ho**(**PW**₁₁**O**₃₉)₂]•24**H**₂**O** (**Ho-7a**). The above synthetic protocol was followed by using 0.0882 g (0.20 mmol) Ho(NO₃)₃·5H₂O instead of Pr(NO₃)₃·6H₂O. Needle like faint yellow crystals were obtained after about 4-5 weeks. Yield: 45% (based on K₁₄[P₂W₁₉O₆₉(H₂O)]·24H₂O). FT-IR(cm⁻¹): 1110(s),1050(s), 955(s), 893(s), 842(m), 770(m), 721(m), 594(w), 518(m), 486(m). Elemental analysis (%); calcd. (found): W 63.4(63.25), K 6.7 (7.0), P 0.97 (1.1).

Synthesis of K_{11} [Er(PW₁₁O₃₉)₂]•31H₂O (Er-8a). The above synthetic protocol was followed by using 0.0886 g (0.20 mmol) Er(NO₃)₃·5H₂O instead of Pr(NO₃)₃·6H₂O. Needle like faint pink crystals were obtained after about 4-5 weeks. Yield: 47% (based on $K_{14}[P_2W_{19}O_{69}(H_2O)]$ ·24H₂O). FT-IR(cm⁻¹): 1110(s),1050(s), 955(s), 895(s), 842(m), 772(m), 724(m), 592(w), 510(m), 480(m). Elemental analysis (%); calcd. (found): W 62.1 (60.92), K 6.6 (6.24), P 0.95 (1.0).

Synthesis of K₁₁[Tm(PW₁₁O₃₉)₂]•23H₂O (Tm-9a). The above synthetic protocol was followed by using 0.089 g (0.20 mmol) Tm(NO₃)₃·5H₂O instead of Pr(NO₃)₃·6H₂O. Needle like colorless crystals were obtained after about 4-5 weeks. Yield: 32.5 %(based on $K_{14}[P_2W_{19}O_{69}(H_2O)]$ ·24H₂O). FT-IR(cm⁻¹): 1110(s),1050(s), 951(s), 893(s), 842(m), 774(m), 729(m), 594(w), 516(m), 480(m). Elemental analysis (%); calcd. (found): W 63.5 (61.62), K 6.75 (6.83), P 0.97 (1.1).

Synthesis of K_{11} [Yb(PW₁₁O₃₉)₂]•28H₂O (Yb-10a). The above synthetic protocol was followed by using 0.0898 g (0.20 mmol) Yb(NO₃)₃·5H₂O instead of Pr(NO₃)₃·6H₂O. Needle like colorless crystals were obtained after about 4-5 weeks. Yield: 33.4% (based on

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K₁₄[P₂W₁₉O₆₉(H₂O)]·24H₂O). FT-IR(cm⁻¹): 1197(s), 1049(s), 951(s), 893(s), 835(m), 768(m), 718(m), 591(w), 506(m), 478(m). Elemental analysis (%); calcd. (found): W 62.6 (62.59), K 6.65 (6.13), P 0.96 (1.1).

X-ray Crystallography

A single crystal suitable for X-ray diffraction for compounds Pr^{3+} (**1a**), Nd^{3+} (**2a**), Eu^{3+} (**3a**), Gd^{3+} (**4a**), Tb^{3+} (**5a**), Dy^{3+} (**6a**), Ho^{3+} (**7a**), Er^{3+} (**8a**), and Tm^{3+} (**9a**) were mounted on a capillary tube for indexing and intensity data collection at 183(2) K on an Oxford Xcalibur CCD singlecrystal diffractometer (MoK α radiation, $\lambda = 0.71073$ Å) (see Table S1). Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the ABSCALE 3 program.²² Direct methods were used to locate the heavy metal atoms (SHELXS-97). The remaining atoms were located from successive Fourier maps (SHELXL-97).²³ Further details on the crystal structure data may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-425184 for Pr³⁺ (**1a**), CSD-425185 for Nd³⁺ (**2a**), CSD-425191 for Eu³⁺ (**3a**), CSD-425186 for Gd³⁺ (**4a**), CSD-425187 for Tb³⁺ (**5a**), CSD-425199 for Dy³⁺ (**6a**), CSD-425188 for Ho³⁺ (**7a**), CSD-425189 for Er³⁺ (**8a**), and CSD-425190 for Tm³⁺(**9a**). Disorder of cations and crystal waters are common phenomenon in polyoxometalate chemistry. For compound **Gd(4a)** and **Ho(7a)** one of the water molecule coordinated to K3 is modelled as sodium.

Emperical Formula	$GdK_{10.50}NaO_{93}P_2W_{22}$	$HoK_{10.50}NaO_{93}P_2W_{22}$
Formula weight	6185.43	6193.11
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a [Å]	12.6725(5)	12.6562(3)
b [Å]	17.6246(7)	17.5870(3)
c [Å]	19.0348(7)	19.0108(4)
α [⁰]	96.710(3)	96.812(2)
β [⁰]	96.592(3)	96.562(2)
γ [⁰]	91.847(3)	92.034(2)
V [Å ³]	4189.9(3)	4168.95(15)
Ζ	2	2
$\rho_{\text{calcd}}[\text{g cm}^{-3}]$	4.903	4.934
μ [mm ⁻¹]	31.528	31.839
Refelection	57945	56599
collected		
Unique (Rint)	13758	15080
Observed[$I > 2\sigma(I)$]		
Parameters	703	703
Gof	1.087	1.074
$R[I > 2\sigma(I)]^{[a]}$	0.0579	0.0554
Rw(all data)[b]	0.1371	0.1724

Table 1: Single crystal X-ray crystallographic data for compound Gd(4a) and Ho(7a).

[a] $R = \sum IIFoI - IFcII / \sum IFoI$. [b] $R_w = [\sum w (Fo^2 - Fc^2)^2 / \sum w (Fo^2)^2]^{1/2}$

Result and Discussion

Syntheses and Structure

The syntheses of all ten molecular complexes were undertaken following a unique reaction protocol. The potassium salts of polyanion $K_{11}[Ln(PW_{11}O_{39})_2] \cdot xH_2O$ (Ln = Pr³⁺ (1a), Nd³⁺ (2a), Eu³⁺ (3a), Gd³⁺ (4a), Tb³⁺ (5a), Dy³⁺ (6a), Ho³⁺ (7a), Er³⁺ (8a), Tm³⁺(9a), and Yb³⁺ (10a)) were synthesized in KOAc buffer (pH 4.8) on interaction of lanthanoid nitrate and potassium salts of dilacunary $[P_2W_{19}O_{69}(H_2O)]^{14-}$ in the molar ratio 2:1 under mild conditions. Single crystal X-ray diffraction analysis reveals that all the isolated polyanions are isostructural. These synthesized mid and late lanthanoid coordinated Peacock and Weakley type polytungstates represent the other examples to be structurally characterized by single crystal X-ray diffraction. The title polyanions **Pr(1a)-Yb(10a)** consist of two monolacunary α - Keggin type moiety (α -PW₁₁O₃₉) and a lanthanoid cation, where the lanthanoid cation is coordinated to the axial oxygen atoms of both the α -Keggin type moieties (α -PW₁₁O₃₉) forming a Peacock and Weakley type structure.⁷ In other words, four oxygen atoms of each α -Keggin moiety (α -PW₁₁O₃₉) are coordinated to the Ln³⁺ cation, where the Ln³⁺ cation is situated outside the pocket of the vacant site of the Keggin moiety (see Figure 1). This is attributed to the oxophilic nature of the lanthanoid cation and to

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the reactivity of the lacunary POMs, in addition to the steric hindrance of both ligands coming in close proximity. During the course of the reaction, the dilacunary polyanion $[P_2W_{19}O_{69}(H_2O)]^{14}$ underwent transformation to monolacunary $[\alpha$ -PW₁₁O₃₉]⁷. Tourné et al. proposed that the dilacunary phosphotungstates can easily transform to monolacunary Keggin type (α -PW₁₁O₃₉) in the presence of potassium ions.¹⁴ It is interesting to be noted that the reactions were carried out in KOAc buffer. Thus our observation is in accordance with the literature.¹⁴

The coordination environment of the lanthanoid in the title polyanions shows a square antiprismatic geometry for eight coordinated lanthanoid cations. In order to evaluate the effect of lanthanoids on the geometry of the heteroatom (PO₄ group), all the bond lengths and bond angles of the PO₄ group were closely examined. The P-O bond lengths were in the range of 1.50(2) to 1.574(14) Å, whereas the bond angles of O-P-O ranged from 107.5(2) to 111.6(11)°. Similar bond lengths and bond angles were observed for monolacunary (α -PW₁₁O₃₉). Most of the molecular clusters crystallize in the monoclinic crystal system and *P*2₁/*c* space group (see Table S1) except the gadolinium and holmium derivatives, which fall in the triclinic system and space group P-1 (Table 1). We have hardly noticed any structural change in the polyanion crystallizing from different crystal systems or in the coordination environment of the lanthanoid cations. Such observation was also reported by May et al. for the Mo-complexes [Ln(PMo₁₁O₃₉)2]^{11-.16}

Generally, the average bond lengths of Ln-O follow a decreasing trend across the series i.e. upon increasing the atomic number (see Table S2). Such trend was reflected in our current studies along the lanthanoid series (see Figure 2).

Bond valence sum calculation¹⁷ was performed for all the polyanions, and none of the oxygens of the monolacunary α -Keggin moiety (α -PW₁₁O₃₉) were mono or diprotonated. In addition, no bridging oxygens Ln-O(W) were protonated. Thus the net charge of the polyanion $[Ln(PW_{11}O_{39})_2]^{11-}$ was calculated to be -11.



Fig. 1 Ball and stick diagram of polyanion $[Ln(PW_{11}O_{39})_2]^{11-}$ $(Ln = Pr^{3+}(1), Nd^{3+}(2), Eu^{3+}(3), Gd^{3+}(4), Tb^{3+}(5), Dy^{3+}, (6), Ho^{3+}(7), Er^{3+}(8), and Tm^{3+}(9))$. Color code for the octants: red: lanthanoid; blue: oxygen; green: tungsten; pink ball: phosphorus.

Moreover, we carried out a rational synthesis by reacting Ln^{3+} metal salts with the potassium salt of the monolacunary $[\alpha-PW_{11}O_{39}]^{7-}$ polyanion in KOAc buffer (pH 4.8) in a 1:2 metal to ligand molar ratio. We were successful in obtaining all the complexes and single crystals suitable for Xray diffraction was obtained for Pr^{3+} and Nd^{3+} complexes. FT-IR spectra recorded on KBr pellets shows the *"fingerprint"* signature of polyoxophosphotungstate matched well with the title polyanions of Pr^{3+} and Nd^{3+} complexes (see Figure S5).



Fig. 2 Change in the average bond lengths Ln-O (Å) in the polyanion clusters $[Ln(PW_{11}O_{39})_2]^{11-}$ (Ln = Pr³⁺ (1), Nd³⁺ (2), Eu³⁺ (3), Gd³⁺ (4), Tb³⁺ (5), Dy³⁺ (6), Ho³⁺ (7), Er³⁺ (8), and Tm³⁺(9)) with the atomic number of the lanthanoids.

FT-IR Spectroscopy

FT-IR spectra of all the isolated compounds **Pr(1a)-Yb(10a)** showed moreover identical stretching frequencies, suggesting that the molecular complexes are isostructural. In the parent Keggin ion $[\alpha$ -PW₁₂O₄₀]³⁻, there are four characteristic asymmetric vibrations, axial $v_{as}(P-O_a)$, terminal $v_{as}(W-O_t)$, corner shared $v_{as}(W-O_b)$, and edge shared $v_{as}(W-O_c)$ representing the *"finger-print"* signature of the polytungsten framework. The axial $v_{as}(P-O)$ band of the heterogroup (PO₄) is situated in the range 1040–1100 cm⁻¹, whereas the terminal $v_{as}(W-O_t)$ is seen in the range 900–950 cm⁻¹, and the other two bands corner shared $v_{as}(W-O_b)$ and edge shared $v_{as}(W-O_c)$ are observed in the range of 800 – 730 cm⁻¹. In all polyanions, the band of $v_{as}(P-O_a)$ is splitted into two at about 1100 and 1050 cm⁻¹, which signifies a change in symmetry due to loss of one tungsten octahedra { α -PW₁₁O₃₉} from the parent ion.¹⁶ Similarly, the characteristic bands in the region 950-955 cm⁻¹, 890-895 cm⁻¹ and 835–720 cm⁻¹ are assigned to the terminal $v_{as}(W-O_t)$, the corner shared $v_{as}(W-O_b)$ and the edge shared $v_{as}(W-O_c)$ stretching frequencies of the polyanion in a complex. Moreover, there is no change in the terminal $v_{as}(W-O_c)$

 O_t) stretching frequency in all polyanions, indicating that there are hardly any interactions of the cations located outside the polyanion. It is interesting to note the gradual change in the edge sharing v_{as} (W–O_c) frequency, which can be attributed to the effect of lanthanoid contraction along the series (see Figure S3 and Table S4). ^{16,18}

UV-visible Spectroscopy

UV/vis spectra of the compounds Pr(1a), Nd(2a), Dy(6a), Ho(7a), and Er(8a) were recorded in solid state. The spectrum of Pr(1a) shows five broad peaks at 449, 474, 489, 589 and 598 nm which can be ascribed to ${}^{3}H_{4} \rightarrow {}^{3}P_{2}$, ${}^{3}H_{4} \rightarrow {}^{3}P_{1}$, ${}^{3}H_{4} \rightarrow {}^{3}P_{0}$, and ${}^{3}H_{4} \rightarrow {}^{1}D_{2}$ transitions of the Pr^{3+} ion, respectively (see Figure 3).^{19e} In the spectrum of Nd(2a), five broad high intense peaks were observed in addition to splitting of the peaks. The peaks at 525, 586, 751, 803, and 871 nm correspond to ${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$, ${}^{4}I_{9/2} \rightarrow {}^{4}F_{3/2}$, ${}^{4}I_{9/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}I_{9/2} \rightarrow {}^{4}I_{13/2}$ and ${}^{4}I_{9/2} \rightarrow {}^{4}I_{11/2}$ transitions of the Nd^{3+} ion.¹⁹ (see Figure S6) Compound **Dy**(6a) shows three weak absorption peaks in the visible region at 429, 454 and 479 nm and two highly intense peaks were prominently visible at about 758 and 808 nm in the near-IR region. Peaks are assigned to ${}^{6}H_{15/2} \rightarrow {}^{4}F_{9/2}$, ${}^{6}H_{15/2} \rightarrow {}^{4}I_{15/2}$, ${}^{6}\text{H}_{15/2} \rightarrow {}^{4}\text{G}_{11/2}$, ${}^{6}\text{H}_{15/2} \rightarrow {}^{6}\text{F}_{3/2}$ and ${}^{6}\text{H}_{15/2} \rightarrow {}^{6}\text{F}_{5/2}$ transitions of the Dy³⁺ ion, which is in accordance with our earlier studies (see Figure S7).¹⁹ For the **Ho(7a)** compound, the peaks at 418, 453, 469, 474, 486, and 539-543 nm can be ascribed to ${}^{5}I_{8} \rightarrow {}^{5}G_{5}$, ${}^{5}I_{8} \rightarrow {}^{5}F_{1}$, ${}^{5}G_{6}$, ${}^{5}I_{8} \rightarrow {}^{3}K_{8}$, ${}^{5}I_{8} \rightarrow {}^{5}F_{2}$, ${}^{5}I_{8} \rightarrow {}^{5}F_{2} \rightarrow {}^{5$ ${}^{5}F_{3}$, ${}^{5}I_{8} \rightarrow {}^{5}F_{4}$ and ${}^{5}S_{2}$ transitions of the Ho³⁺ ion (see Figure S8).¹⁹ Likewise, for polyanion (**Er**-8a) the absorption bands were seen in the region 380-655 nm, with sharp intensities at 380, 408, 451, 489, 523, 544, and 655 nm which can be assigned to ${}^{4}I_{15/2} \rightarrow {}^{4}F_{5/2}$, ${}^{4}F_{3/2}$, ${}^{4}I_{15/2} \rightarrow {}^{2}G_{9/2}$, ${}^{2}F_{9/2}$, ${}^{2}\text{H}_{9/2}$, ${}^{4}\text{I}_{15/2} \rightarrow {}^{4}\text{F}_{7/2}$ and ${}^{4}\text{I}_{15/2} \rightarrow {}^{2}\text{H}_{11/2}$ transitions of the Er³⁺ ion, respectively (see Figure S9).¹⁹ Similar observations were made for Pr^{3+} and Er^{3+} in the complex $K_{1,3}Na_{3,2}H_{6,5}[L Ln(PW_{11}O_{39})_2] \cdot 8.3L$ - proline $\cdot 21 \cdot 5H_2O$ (Ln = Pr^{III} and Er^{III}).^{19e}



Electrochemistry

The electrochemistry of compounds Eu(3a) - Tm(9a) and of the monolacunary $[\alpha-PW_{11}O_{39}]^7$ -{PW11} polyanion was carried out in several aqueous media (see Table S10). The stabilities of these compounds in aqueous solutions were assessed by monitoring their respective UV/vis spectra. A complementary cross-check of their stabilities was obtained by cyclic voltammetry (CV). Compounds Eu(3a) - Tm(9a) were tested in a LiOAc buffer at pH 4, a medium where they are stable as revealed by UV-visible spectrophotometry. Similarly to {PW11} (whose response due to the W-centres is described below), the voltammograms of Eu(3a) and Tm(9a) are composed of two successive couples, Eu(3a) having the most negative second reduction wave of the series at -0.934 V, and Tm(9a) having the most positive first reduction wave of the series, peaking at -0.794 V and a second clearly defined reduction wave at -0.920 V (see Figure 4).



Fig. 4 Comparison of the cyclic voltammograms obtained from solutions of conc. 2×10^{-4} M for **Eu(3a)** and **Tm(9a)**, and 4×10^{-4} M for {PW11}, in 1 M LiCH₃COO/CH₃COOH, pH = 4.0, at 10 mV.s⁻¹.

The linear dependence of the peak currents on the square root of the scan rate proves that the redox waves are diffusion-controlled (see Figure S11). The reduction wave of **Eu(3a)** just mentioned is more intense than that of **Tm(9a)**, and has a pre-wave shoulder at \approx -0.834 V. This current increase is attributed to the reduction of Eu³⁺ within the POM. Indeed, this lanthanide cation gives rise to a broad, poorly-defined reduction wave peaking at -0.950 V when free in solution (see Figure 5).



Fig. 5 Comparison of the cyclic voltammograms obtained from solutions of conc. 4×10^{-4} M for {PW11}, 8×10^{-4} M for Eu³⁺ and 2×10^{-4} M for **Eu(3a)**, in 1 M LiCH₃COO/CH₃COOH, pH = 4.0, at 10 mV.s⁻¹.

If there is no drastic change in its reduction potential when bound to {**PW11**}, this supplementary electron transfer process will enhance the most negative reduction wave when compared to a POM with an electrochemically silent lanthanide cation. This is further supported by the fact that the voltammogram of a solution of a 1:2 ratio of Eu³⁺ and {**PW11**} prepared *in situ* for the same concentrations shows also a current enhancement at the same potential domain. Upon re-oxidation, both **Eu(3a)** and **Tm(9a)** exhibit two waves, the ones of the latter, which peak at -0.818 V and -0.692 V, being cathodically shifted with respect to the ones of the former, at -0.806 V and -0.634 V. In Figure 4, these voltammograms are compared to the curve obtained with {**PW11**} at double concentration, since there are two monolacunary moieties per lanthanoid-containing POM. Two reversible waves were observed before the solvent discharge (not shown), their reduction peak potentials, E_{pc} , and formal redox potentials, $E^{0'}$, being at -0.714 and -0.676 V for the first couple and at -0.842 and -0.814 V for the second couple (see Table S10). These waves are attributed to the tungsten centres, since apart from the latter and the Eu-containing one, no other metal centres among the present compounds are expected to give

rise to an electrochemical response in our experimental conditions.^{20a} In the acetate medium (pH 4), CV revealed the same general pattern for compounds Gd(4a) - Er(8a), which consists of voltammograms exhibiting a reduction wave beyond -0.900 V preceded by a less well-defined reduction wave, which are matched by two re-oxidation waves on the anodic side (see Figure S12 and Table S10). It is clear that the waves are better separated in the cases of {**PW11**} and **Tm(9a**). In the latter case, the separation was further improved upon increasing the pH, the potential difference between the two reduction waves increasing from 0.124 V at pH 3.0 up to 0.134 V at pH 5.0. Also, these waves cathodically shift upon increasing the pH by an amount comprised between 0.046 and 0.080 V per decade (see Figure 6 and Table S10),



Fig. 6 Comparison of the cyclic voltammograms obtained from solution of conc. 2×10^{-4} M of **Tm(9a)** in different media at pH values 3.0, 4.0 and 5.0, at 10 mV.s⁻¹.

implying that reduction is coupled to proton uptake. The graphs of $E^{0^{2}}=f(pH)$ for Tm(9a) at pH values comprised between 3 and 5 are straight lines with slopes close or equal to -60mV/pH, meaning that the transfer of n electrons is coupled to the uptake of n protons. If we assume that each wave involves 4 electrons, then 4 protons take part in the process as well. When less well-

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defined waves are observed, an electrochemical-electrochemical (ECE) or an electrochemical-electrochemical-chemical (EEC) type process is favored, which is the case for the other compounds of the series, Eu(3a) - Er(8a). In addition, peak potential shifts are related to the basicity of the reduced forms of the POMs, in the sense that a cathodic shift implies a less favorable proton uptake upon reduction, and therefore a lower basicity.^{20b} Hence, the compounds in the series may be classified in the following sequence of decreasing basicity: $\{PW11\} >$ $Tm(9a) > Eu(3a) \approx Tb(5a) \approx Ho(7a) > Gd(4a) \approx Dy(6a) \approx Er(8a)$ (Table S10). Controlled potential coulometry was carried out in a pH 5 medium with solutions of Tm(9) at -1.06 V, and then re-oxidation was performed at +0.500 V. Even if the expected number of electrons involved per molecule of POM is 8^{20c}, we obtained 8.6, a slightly higher value. During electrolysis, the current reached an apparent steady state, indicative of the existence of another redox process, most likely hydrogen evolution being catalyzed by the POM. The blue color of the solutions after the reduction steps revealed that the POM had been at least partially reduced, as confirmed by spectrophotometry due to the presence of absorption bands at 600 and 940 nm. These and the blue color of the solutions, disappeared after the re-oxidation step, but the charge passed in the system upon re-oxidation corresponded to 80% of that passed during reduction, again hinting at the interference of another redox process upon reduction. CV carried out at the end of the experiment revealed that the compounds remained stable, and so the behavior observed in controlled potential coulometry cannot be attributed to their decomposition.

Thus, electrochemistry revealed a general trend within the lanthanide series, consisting of two couples on the negative side of the potential vs. SCE. **Eu(3a)** exhibited a larger current on the most negative process, possibly due to the redox involvement of its Eu^{3+} centre, while **Tm(9a)** showed well defined waves, a phenomenon further enhanced upon increasing the pH.

Photoluminescence Spectroscopy

Photoluminescence (PL) spectra of the molecular complexes Pr(1a)-Yb(10a) were investigated at room temperature. We were successful in recording emission spectra for complexes Eu(3a), Dy(6a) (see Figure 7) and Ho(7a). The PL of the Eu(3a) complex was measured on excitation at 460 nm which shows red photoluminescence. The spectra displayed five peaks, of which only four were sharp and intense. The emission peaks were observed at wavelengths 582, 596, 616, 652 and 704 nm which can be assigned to ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 0, 1, 2, 3, 4) excited to respective ground state of the Eu³⁺ ion. A weak shoulder at 582 nm corresponds to the transition from ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ which is symmetry forbidden, and it also signifies that the compound Eu(3a) favours high symmetry. The transition ${}^{5}D_{0} \rightarrow {}^{7}F_{1,3}$ at 596 and 652 nm represents magnetic-dipole transition and its intensity is correlated to the influence of the crystal field strength of the ligand on the Eu³⁺ ion. The other dipole transition, known as electric dipole transition, is responsible for the emission ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 2, 4) which is extremely sensible to the nature of chemical bonds in the proximity of the Eu³⁺ ion. Nevertheless, these transitions are of high intensity, and that of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition increases as the site symmetry of Eu³⁺ ion decreases. Therefore, the intensity ratio $I({}^{5}D_{0} \rightarrow {}^{7}F_{2})/I({}^{5}D_{0} \rightarrow {}^{7}F_{1})$ is often used to determine the coordination state and site symmetry of the rare earth ions. In the complex, the ratio was determined to be about 2.4, signifying the low symmetry coordination environment.^{19c,21c,d} For the **Dy(6a)** molecular cluster, the ground state term for Dy³⁺ ion ([Xe]4f⁹) is ⁶H_{15/2}. On excitation at 370 nm, two sharp highly intense emission bands were observed at 480 and 576 nm, corresponding to ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ (blue emission) and ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ (yellow emission). Similar observations were also encountered in our earlier studies.^{19a} In addition, transition ${}^{4}F_{9/2} \rightarrow {}^{6}H_{11/2}$ was also seen at 661 nm.^{21a,b} For the **Ho(7a)** molecular cluster, (see Figure S13) the ground state term for Ho^{3+} ion ([Xe]4f¹⁰) is ⁵I₈. The compound was excited at a wavelength of 410 nm, and four emission transitions were seen with broadening in emission bands at 464, 548 (shoulder), 575 and 660 nm. The emission bands can be ascribed to the transitions ${}^{3}F_{2} \rightarrow {}^{5}I_{8}$, ${}^{3}G_{5} \rightarrow {}^{5}I_{6}$, ${}^{5}S_{2} \rightarrow {}^{5}I_{8}$ and ${}^{3}G_{5} \rightarrow {}^{5}I_{4}$, respectively.^{21e,f}





Fig. 7 Solid state photoluminescence spectra of (a) Eu(3a) and (b) Dy(6a) POMs measured at room temperature on excitation at wavelengths of 460 and 370 nm.

³¹P-NMR Spectroscopy

The ³¹P NMR spectra for compounds **Pr(1a)-Yb(10a)** were recorded at a 400 MHz magnetic field at 298 K. All the samples were prepared by redissolving the isolated crystals in D₂O. ³¹P NMR spectra of the molecular complexes **Pr(1a)-Yb(10a)** show only one peak which signifies that both phosphorous atoms are magnetically equivalent. The parent monolacunary Keggin ion (α -PW₁₁O₃₉) shows a single peak at -11.6 ppm. The large variation in the NMR shifts (see Table 2) shows the influence of the paramagnetic property of the lanthanoid ions on the heteroatom (see Figure 8). Fedotov et al. extensively studied the NMR behaviour of such complexes and proposed the structures based on multinuclear NMR spectroscopy.⁸ Our results are quite different for **Tb(5a)**, **Ho(7a)**, **Er(8a)**, and **Tm(9a)** from the observation of Fedotov et al. which we believe may be due to impurities (see Table 2). However, our results for the Eu(3a) complex are in accordance with the observation of Francesconi et al.

Later May et al. studied the ³¹P NMR spectroscopy of the polyanion $[Ln(PMo_{11}O_{39})_2]^{11-}$ (Ln = La^{3+} , Ce³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, Yb³⁺, and Lu³⁺) both in aqueous medium and in the solid state, and also characterized them by single crystal X-ray analysis. At room temperature, ³¹P–NMR of both the polyanions $[Ln(PMo_{11}O_{39})_2]^{11-}$ (Ln = Tm³⁺ and Yb³⁺) shows two peaks¹⁶, whereas for the tungstophosphate cluster only one peak was observed, signifying the existence of only one conformer in solution. We were unsuccessful in recording the gadolinium and dysprosium analogues, which we believe may be due to a more pronounced paramagnetic behaviour of the lanthanoid ions (see Figure S14).

Table 2. ³¹P NMR data of the molecular cluster $[Ln(PW_{11}O_{39})_2]^{11}$

Ln^{III}	δ ³¹ P (ppm)	$\delta^{31}P (ppm)^8$
Pr	-12.98	-14.6
Nd	-24.40	-24.2
Eu	0.67	-1.2
Tb	-199.5	-223
Но	-115.4	-109
Er	62.7	61.4
Tm	220.2	217
Yb	30.7	32

Magnetism

The magnetic properties of the Gd(4a) polyanion were investigated on a Micro sense (EV9) vibrating sample magnetometer in an applied magnetic field range of -22 to 22 kOe at room temperature. The ground state electronic configuration of Gd^{3+} ion is [Xe]4f⁷ which has a spin only magnetic moment of 7.93 µ_B. Measurement of magnetization as a function of the applied magnetic field exhibits the paramagnetic properties of the compound. The magnetic moment calculated from the data was about 7.75 μ_B , which resembles to the Gd³⁺ ion (see Figure S15). Such phenomenon earlier observed for dimeric species was our $Na_{4}K_{8}[{Gd(CH_{3}COO)GeW_{11}O_{39}(H_{2}O)}_{2}] \times H_{2}O$, showing no-exchange interaction among the gadolinium centers.^{2e}.



Fig. 8³¹P NMR spectrum of Ln-POM (Ln = Pr(1a), Nd(2a), Eu(3a), and Yb(10a)) re-dissolved in D₂O solvent.

Conclusions

A series of ten isostructural Peacock and Weakley type lanthanoid containing phosphotungstates $[Ln(PW_{11}O_{39})_2]^{11-}$ (Ln = Pr³⁺ (1), Nd³⁺ (2), Eu³⁺ (3), Gd³⁺ (4), Tb³⁺ (5), Dy³⁺ (6), Ho³⁺ (7), Er³⁺ (8), Tm³⁺(9), and Yb³⁺ (10)) was synthesized using dilacunary phosphotungstate $[P_2W_{19}O_{69}(H_2O)]^{14-}$ in KOAc buffer following a single step process. The polyanions were structurally characterized by single crystal X-ray diffraction in two different space groups $P2_1/c$ or P-1, FT-IR, photoluminescence, UV/vis, and ³¹P-NMR spectroscopy. The presence of potassium ion in the reaction medium plays a vital role in structure directing as well as in the transformation of dilacunary $[P_2W_{19}O_{69}(H_2O)]^{14-}$ to monolacunary $[PW_{11}O_{39}]^{7-}$. The decrease in the average bond length of Ln-O followed the general trend across the lanthanoid series. The effect of lanthanoids on the polyanion across the series was evident from both FT-IR and ³¹P NMR spectroscopy. In addition, ³¹P-NMR spectroscopy shows that the compounds were stable

in aqueous medium. Electrochemistry shows a general trend of two reversible couples attributed to the W-centres within the POM series. **Eu(3a)** exhibits an enhanced reduction current on the second reduction wave due to Eu^{3+} being electroactive in the cluster. Also, the influence of the lanthanide cation in the relative basicity of the reduced POMs in the series led to the following sequence: {**PW11**} > **Tm(9a)** > **Eu(3a)** \approx **Tb(5a)** \approx **Ho(7a)** > **Gd(4a)** \approx **Dy(6a)** \approx **Er(8a)**. The molecular clusters **Eu(3a)**, **Dy(6a)**, and **Ho(7a)** show highly intense photoluminescence at room temperature. Room temperature magnetic measurement of the compound **Gd(4a)** reveals paramagnetic properties of the material. Synthesis of lanthanoid complexes from dilacunary [P₂W₁₉O₆₉(H₂O)]¹⁴⁻ following other reaction parameters are under progress in our research laboratory, and we have isolated several other complexes which will be reported elsewhere.

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Notes and references

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Graphical Abstract

A series of Peacock and Weakley type dimer $[Ln(PW_{11}O_{39})_2]^{11-}$ (Ln = Pr³⁺ (1), Nd³⁺ (2), Eu³⁺ (3), Gd³⁺ (4), Tb³⁺ (5), Dy³⁺ (6), Ho³⁺ (7), Er³⁺ (8), Tm³⁺ (9), and Yb³⁺ (10)) was synthesized in one pot reaction with high yield using di-lacunary ligand $[P_2W_{19}O_{69}(H_2O)]^{14-}$ in KOAc buffer. All the molecular cluster were structurally characterized and its photoluminescence shows interesting photochromic effect at room temperature.

