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Two hybrid polyoxometalates constructed from Preyssler P_5W_{30} clusters and Schiff base exhibiting interesting third-order NLO properties†

Jie Shi,[a] Yao Xiong,[a] MengJie Zhou,[a] Lu Chen[a] and Yan Xu *[ab]

Two Preyssler P_5W_{30}-based compounds: $[Mn(H_2O)_2(DAPSC)]_2\{[Na_3(H_2O)_2Mn_{0.5}(H_2O)_4][Mn(H_2O)(DAPSC)]_2[H_3P_5W_{30}O_{110}]\}\cdot 7.5H_2O$ (**1**) and $[Co(H_2O)_2(DAPSC)]\{[Co(H_2O)_2(DAPSC)][Na_{1.5}(H_2O)_2]\}\{[Na_{0.5}(H_2O)_2Co_{0.5}(H_2O)_4][Co(H_2O)(DAPSC)]_2[H_4P_5W_{30}O_{110}]\}\cdot 6H_2O$ (**2**) modified by Schiff base 2,6-diacetylpyridine bis(semicarbazone) (DAPSC) and transition metal (TM) ions have been successfully isolated and structurally characterized by IR spectroscopy, PXRD, and single-crystal XRD. Structural analysis reveals that compound **1** is composed of a $\{[Na_3(H_2O)_2Mn_{0.5}(H_2O)_4][Mn(H_2O)(DAPSC)]_2[H_3P_5W_{30}O_{110}]\}^{4-}$ architecture (Section A), two isolated $[Mn(H_2O)_2(DAPSC)]^{2+}$ groups (Section B), and seven and a half lattice water molecules. Compounds **1–2** represent the first Preyssler-type compounds modified by Schiff base and TM ions. Additionally, the electrocatalytic and the third-order NLO properties have been investigated.

Introduction

Polyoxometalates (POMs), a peculiar subunit of discrete transition metal-oxo clusters with oxygen-rich surfaces and strong coordinating ability, are intriguing secondary building blocks for constructing various inorganic–organic hybrid materials with potential applications in catalytic reactions,[1] magnetic materials,[2] nonlinear optics,[3] materials science[4] and electrochemistry.[5] Since the distinguished Keggin-type polyoxoanion $[\alpha\text{-}PMo_{12}O_{40}]^{3-}$ was isolated,[6] POM chemistry has been rapidly developed in recent decades. In the above-mentioned area, transition metal complexes (TMCs) are commonly employed to decorate well-known POMs, for instance, Keggin-, Dawson-, Anderson- and Lindquist-type.[7] In the documented larger POM clusters, the well-known Preyssler $[P_5W_{30}O_{110}]^{15-}$ (abbreviating P_5W_{30}) anionic clusters attracted our considerable attention, which were discovered in 1970 (ref. 8) and structurally characterized through X-ray diffraction 15 years later.[9] The P_5W_{30} polyoxoanion possesses many merits: (i) the internal cavity can accommodate distinct metal cations with appropriate scale; (ii) abundant oxygen-rich surface and high stability over a large pH range of 1–10; (iii) high negative charges can capture TM cations. However, examples of selecting P_5W_{30} anion as precursor to design and synthesize of POMs with decorated or expanding configuration have seldom been documented.[10] The headmost expanding structures built on Preyssler anions and rare earth cations were successfully prepared by Wang *et al.*[11] Therefore, rational design and synthesis of charming Preyssler-type POMs modified by TMCs have been a hot area of research in recent years. The Wang[12] and Sun[13] groups reported some inorganic–organic hybrid materials based on P_5W_{30} anions and TM cations, they show moderate electrocatalytic abilities toward the reduction of NO_2^- and H_2O_2.

Schiff bases are a significant class of organic ligands and have been studied widely. Polydentate Schiff base ligands are capable of combining various metals through imine nitrogen, hydroxyl and carbonyl groups, it will alter the electron structure and improve the catalytic performance. The documented on POMs decorated by Schiff base are relatively rare,[14] while the hybrid polyoxometalate constructed P_5W_{30} and Schiff base ligands has not been prepared. On account of the solubility and steric-hindrance effects, we selected DAPSC as conjugated organic ligand. Owing to DAPSC possesses more coordination sites and a weaker conjugated effect, it was good candidate for decorating POMs to establish inorganic–organic hybrid materials. Herein, we have successfully obtained two unprecedented Preyssler P_5W_{30} modified by planar Schiff base, formulated as $[Mn(H_2O)_2(DAPSC)]_2\{[Na_3(H_2O)_2Mn_{0.5}(H_2O)_4][Mn(H_2O)(DAPSC)]_2[H_3P_5W_{30}O_{110}]\}\cdot 7.5H_2O$ (**1**) and $[Co(H_2O)_2(DAPSC)]\{[Co(H_2O)_2(DAPSC)][Na_{1.5}(H_2O)_2]\}\{[Na_{0.5}(H_2O)_2Co_{0.5}(H_2O)_4][Co(H_2O)(DAPSC)]_2[H_4P_5W_{30}O_{110}]\}\cdot 6H_2O$ (**2**), respectively. Additionally, the electrochemical properties and electrocatalytic

[a]*College of Chemistry and Chemical Engineering, State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing 210009, PR China. E-mail: yanxu@njtech.edu.cn*

[b]*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, PR China*

† Electronic supplementary information (ESI) available: Summary of selected bond lengths and angles; table of hydrogen bond lengths and bond angles; IR, XRD, TG and coordination modes of **1** and **2**. CCDC reference numbers: 1562173 (**1**) and 1562174 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7ra12165b

activities of both compounds were investigated. The molecular 2PA cross section σ of compounds **1–2** were 888 GM and 707 GM, which manifests that the Schiff base in the modified Preyssler polyoxoanions will strengthen the third-order NLO responses.

Experimental section

Materials and physical methods

$(NH_4)_{14}NaP_5W_{30}O_{110}\cdot31H_2O$ was synthesized according to the literature.[15] DAPSC was isolated applying a previous approach.[16] All other chemical reagents and solvents were purchased commerically and used without further purification. Elemental analysis (C, H, and N) was carried out on a PerkinElmer 2400 CHN elemental analyzer. FTIR spectra were measured in the range of 400–4000 cm^{-1} on a FTIR-8900 IR spectrometer using KBr pellets. TG analyses were recorded on a Pekin-Elmer Pyris Diamond TG analyzer. PXRD data were measured on a Bruker D8X diffractometer with graphite monochromatized Cu Kα radiation (λ = 0.154 nm) at room temperature. Two-photon absorption (2PA) cross-sections were gained by using a Chameleon II femtosecond laser pulse and a Ti:95 sapphire system (680–1080 nm) with 80 MHz repetition rate and a 140 fs pulse duration. Electrochemical measurements were conducted on a CHI760 electrochemical workstation. A conventional three-electrode system was utilized. A Ag/AgCl (3 mol L^{-1}, KCl) and Pt foil were used as the counter electrode and reference electrode. The working electrode was a modified glassy carbon electrode (GCE).

Preparation of $[Mn(H_2O)_2(DAPSC)]_2\{[Na_3(H_2O)_2Mn_{0.5}(H_2O)_4][Mn(H_2O)(DAPSC)]_2[H_3P_5W_{30}O_{110}]\}\cdot7.5H_2O$ (1)

A mixture of $(NH_4)_{14}NaP_5W_{30}O_{110}\cdot31H_2O$ (0.2 g, 0.024 mmol), DAPSC (0.02 g, 0.073 mmol), $MnCl_2\cdot4H_2O$ (0.099 g, 0.5 mmol) and 10 mL distilled water and stirred for 30 min at ambient temperature. The resulting suspension was transformed into 25 mL Teflon-lined stainless-steel autoclave and heated at 120 °C for 72 h. After the autoclave cooled over 12 h to room temperature, the orange strip crystals were isolated and washed with distilled water in 40% yield (based on Mn). Anal. calcd. (Found) for $C_{44}H_{102}Mn_{4.5}N_{28}Na_3O_{137.5}P_5W_{30}$: C, 5.74 (5.85); H, 1.12 (1.24); N, 4.26 (4.37)%. IR (KBr) of compound **1** (cm^{-1}): 3416(w), 1663(s), 1163(s), 1085(m), 934(w), 910(m), 796(s), 755(w).

Preparation of $[Co(H_2O)_2(DAPSC)]\{[Co(H_2O)_2(DAPSC)][Na_{1.5}(H_2O)_2]\}\{[Na_{0.5}(H_2O)_2Co_{0.5}(H_2O)_4][Co(H_2O)(DAPSC)]_2[H_4P_5W_{30}O_{110}]\}\cdot6H_2O$ (2)

A mixture of $(NH_4)_{14}NaP_5W_{30}O_{110}\cdot31H_2O$ (0.2 g, 0.024 mmol), DAPSC (0.02 g, 0.073 mmol) and $CoCl_2\cdot6H_2O$ (0.1189 g, 0.5 mmol) was dissolved in sodium acetate buffer (10 mL, 0.5 mol L^{-1}, pH = 4.0) and stirred for 100 min at room temperature. The resulting suspension was sealed in 25 mL Teflon-lined stainless-steel autoclave and kept at 120 °C for 72 h. After being cooled to room temperature, the red block crystals were obtained and washed with distilled water in 45% yield (based on Co). Anal. calcd. (Found) for $C_{44}H_{104}Co_{4.5}N_{28}Na_2O_{138}P_5W_{30}$: C, 5.74 (5.89); H, 1.14 (1.35); N, 4.26 (4.35)%. IR (KBr) of compound **2** (cm^{-1}): 3422(w), 1665(s), 1161(s), 1075(m), 934(w), 915(m), 792(s), 751(w).

Table 1 Crystal data for compounds **1–2**

Compounds	1	2
Formula	$C_{44}H_{102}Mn_{4.5}N_{28}$-$Na_3O_{137.5}P_5W_{30}$	$C_{44}H_{104}Co_{4.5}N_{28}$-$Na_2O_{138}P_5W_{30}$
Fw	9210.08	9215.06
T (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	18.523(4)	18.672(6)
b (Å)	19.013(4)	19.068(6)
c (Å)	28.923(6)	28.995(9)
α (°)	80.663(3)	81.025(4)
β (°)	79.162(3)	78.083(4)
γ (°)	74.784(3)	73.649(4)
V (Å^3)	9585(3)	9639(5)
Z	2	2
D_c (Mg m^{-3})	3.191	3.173
μ/mm^{-1}	18.352	18.339
F(000)	8205	8203
θ range (°)	0.722–25.025	0.722–25.025
Limiting indices	$-21 \le h \le 22$	$-22 \le h \le 22$
	$-22 \le k \le 21$	$-22 \le k \le 22$
	$-33 \le l \le 34$	$-34 \le l \le 33$
Reflections collected/unique/R_{int}	68 738/33 477/0.0975	68 277/33 529/0.0586
Data/restraints/parameters	33 477/516/2301	33 529/1100/2320
GOF	1.035	1.077
$R_1{}^a$, w$R_2{}^b$ [$I > 2\sigma(I)$]	0.0623, 0.1593	0.0691, 0.1809
R_1, wR_2 (all data)	0.0974, 0.1798	0.0963, 0.1946

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = \Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]^{1/2}$.

X-ray crystallography

X-ray analyses data for **1–2** were performed on a Bruker Apex II CCD diffractometer at 296 K, with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). Structures was solved by direct methods and refined by full-matrix least-squares using SHELXL-2014 crystallographic software package. The non-hydrogen atoms were refined anisotropically. CCDC 1562173 and 1562174.† All the crystallographic information for **1–2** are listed in Table 1. Selected bond lengths and angles for **1–2** are listed in Tables S2–S5.†

Results and discussion

Synthesis

Over the past few years, hydrothermal method has been proved to be a cogent approach in preparation of metal and Schiff base decorated Preyssler P_5W_{30} polyoxoanion. During a conventional hydrothermal method, numerous elements can impact on the nucleation and crystal development of final products, for example, initial reactant, reactant concentration, solvents, reaction time, pH values, and reaction temperature. It is a remarkable fact that the selection appropriate precursors and solvent is vital to the success of this kind of reactions. Namely, the chosen solvent as well as organic and inorganic subunits should be favored to each other. Thus we use buffer solution, which offers a moderate pH environment for TM, Schiff base and POMs. The experimental PXRD patterns of the bulk products of compounds **1–2** are consistent with the simulated ones calculated from X-ray single-crystal diffraction (Fig. S1 and S2†), which indicates the phase purity of the two compounds. The intensity difference between experimental and simulation PXRD patterns may be ascribed to the variation in the preferred orientation of the powder sample during measurements. The bond valence calculations[17] suggest that the valence of Mn and Co atoms in compounds **1** and **2** are both in +2.

Description of the structures

Crystal structure of 1. X-ray single-crystal structural analysis shows that complex **1** crystallizes in triclinic $P\bar{1}$ space group. As shown in Fig. 1, its asymmetric structural unit contains a $\{[Na_3(H_2O)_2Mn_{0.5}(H_2O)_4][Mn(H_2O)(DAPSC)]_2[H_3P_5W_{30}O_{110}]\}^{4-}$ architecture (Section A), two isolated $[Mn(H_2O)_2(DAPSC)]^{2+}$ TMC cations (Section B), seven and a half lattice water molecules. The Preyssler-type P_5W_{30} polyoxoanion comprises five PW_6 units, 30 μ_1-O and 60 μ_2-O atoms spread on the shell. The P_5W_{30} anion owns a perfect 5-fold symmetry axis. In a mirror plane includes five P atoms perpendicular to this axis. All of 30 W atoms in the P_5W_{30} shell are located on four parallel planes perpendicular to the center axis: each of the external and internal planes includes 5 and 10 W atoms (Fig. S11†). All W centers are connected with 6 O atoms, exhibiting a WO_6 octahedron geometry.[9] Two $[Mn(H_2O)_2(DAPSC)]^{2+}$ fragments are bonded to the Preyssler P_5W_{30} anion by Mn–O bonds to form an interesting framework in Section A. Both Mn1 and Mn3 are heptacoordinated and display distorted pentagonal bipyramid geometry $\{MnN_3O_4\}$ coordination modes (Fig. S9†). The coordination geometries of Mn1 and Mn3 are defined by three N atoms and two oxygen atoms from a DAPSC ligand. The other two oxygen atoms, one from coordinated water molecule and the other from the Preyssler P_5W_{30} anion, respectively. It is noteworthy that all nonhydrogen atoms of each $[Mn(H_2O)_2(DAPSC)]^{2+}$ unit are almost planar in Section A.

Compared with other polyoxometalates modified by Schiff bases, this is the first Preyssler P_5W_{30} polyoxoanion decorated by Schiff base ligand. In Section A, the occupancies of Na2 and Na4 are both 75%, Na3 at half occupancy. The polyoxoanion connect to another P_5W_{30} cluster by means of Mn2, Na3 and O atoms, which forms a amusing dimer configuration (Fig. 2). Additionally, the two free $[Mn(H_2O)_2(DAPSC)]^{2+}$ coordination cations (Section B) are regarded as counter ions to sustain balance of charge. Mn4 and Mn5 are in hepta-coordinated MnN_3O_4 pentagonal bipyramid environment, the axial two oxygen atoms are both from two coordinated water molecules. The Mn–N bond and the Mn–O bond lengths are in the range of 2.25(2)–2.33(2) and 2.129(16)–2.27(2) Å. The aforementioned values are in agreement with those observed in other known Mn-contained complexes.[18]

It is notable that compound **1** possesses hydrogen bonds between the neighboring clusters, which extremely reinforces the whole structural stability. By means of hydrogen bonds and electrostatic interaction, the adjacent Preyssler-type $\{P_5W_{30}\}$ polyoxoanion and the $[Mn(H_2O)(DAPSC)]^{2+}$ cations alternately connect with each other to give a 3D supramolecular network (Fig. 3).

Crystal structure of 2. The crystallographic analysis reveals that compounds **1** and **2** are isomorphic. Their structure, bond lengths and angles, and water molecules are slightly distinct. The basic structural unit contain a $\{[Na_{0.5}(H_2O)_2Co_{0.5}(H_2O)_4][Co(H_2O)(DAPSC)]_2[H_4P_5W_{30}O_{110}]\}^{5.5-}$ structure (Section A), two isolated coordination cations: $[Co(H_2O)_2(DAPSC)]^{2+}$ (Section B) and $\{[Co(H_2O)_2(DAPSC)][Na_{1.5}(H_2O)_2]\}^{3.5+}$ (Section C), and six lattice water molecules (Fig. 4). In Section C, Na1 atom has a tetracoordinated geometry, which is defined by two water molecules and two oxygen atoms from one DAPSC ligand. Na2 and Na3 atoms are at half occupancy. The coordination mode of Co ions are shown in Fig. S10.† The Co–N bond and the Co–O

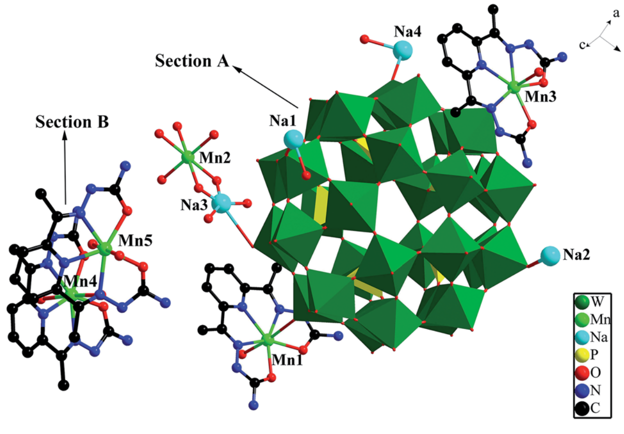

Fig. 1 The asymmetric unit of compound **1**. Color codes: PO_4, yellow tetrahedra WO_6, green octahedra; W, green; Mn, bright green; Na, turquoise; P, pink; O, red; N, bule; C, black. (All the hydrogen atoms and free water molecules have been omitted for clarity).

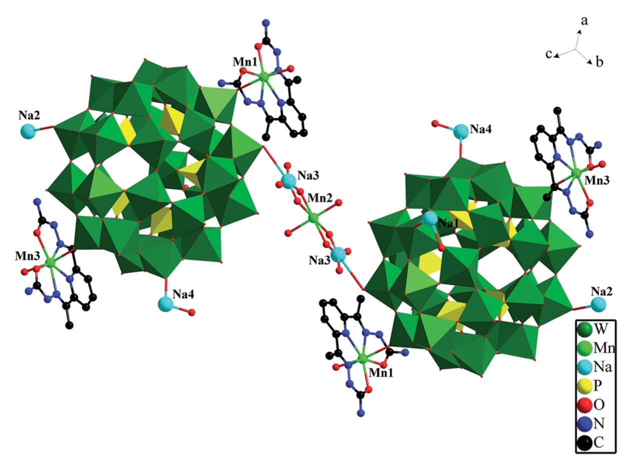

Fig. 2 The dimer of compound **1**.

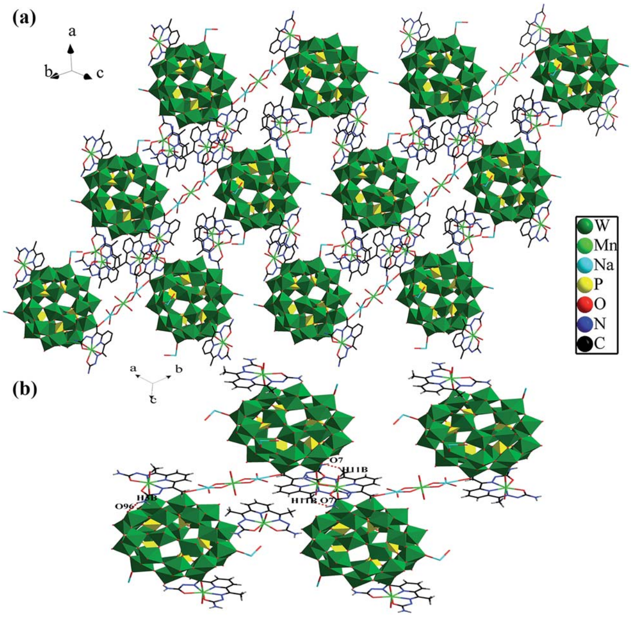

Fig. 3 (a) Polyhedral and stick representation of 3D supramolecular framework of compound **1**, (b) the hydrogen-bonding interactions in compound **1**.

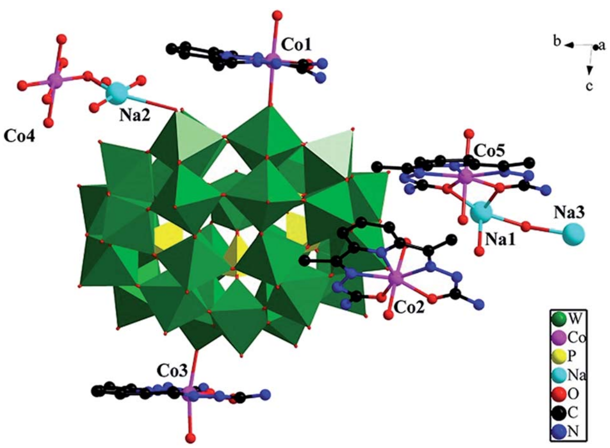

Fig. 4 The asymmetric unit of compound **2**. Color codes: PO_4, yellow tetrahedra WO_6, green octahedra; W, green; Co, pink; P, yellow; Na, turquoise; O, red; C, black; N, bule. (All the hydrogen atoms and crystallization water molecules have been omitted for clarity).

bond lengths are in the range of 2.16(2)–2.23(3) and 2.114(16)–2.40(5) Å. The aforementioned values are in accordance with those observed for known Co-contained complexes.[19] Co4 ion is hexa-coordinated with a distorted octahedral coordination geometry defined by six oxygen atoms from four water molecules (the occupancies of O27W and O30W are both 50%). The coordination modes of Co1, Co3 and Co4, Co5 are similar to Mn1 and Mn4. Sun groups reported two hybrid M–O cluster (1α and 1β),[20] the Co ions are six-coordinated and display octahedral geometry $\{CoN_2O_4\}$ coordination modes. Each P_5W_{30} unit is linked to adjacent clusters through double O–Co–O bridges in 1α and a single O–Co–O bridge in 1β to form 2D and 3D frameworks. Comparing with above-mentioned two complexes, compounds **1–2** are greatly different. The Co ions (except for Co4) are in seven-coordinated CoN_3O_4 pentagonal bipyramid environment. The P_5W_{30} anion is linked to one neighbor through a single O–Na–O–Co–O–Na–O bridge form a amusing dimer (Fig. 5). Similar to compound **1**, compound **2** exhibits 3D supramolecular framework by strong hydrogen-bonding interactions (Fig. S12†).

IR spectra

The IR spectra of **1–2** were recorded varies from 400 to 4000 cm^{-1} with KBr pellets (Fig. S3 and S4†). In IR spectra, characteristic vibration patterns of the P_5W_{30} anions, namely, $\nu(P–O_a)$, $\nu(W–O_{terminal})$, $\nu(W–O_{b/c})$, ($O_{b/c}$: corner and edge-shared oxygen atoms) appear at 1163 and 1085, 934 and 916, and 796 and 755 cm^{-1} for **1**; 1161 and 1075, 934 and 915, and 792 and 751 cm^{-1} for **2**, respectively.

Thermogravimetric (TG) analysis

In the cause of examine the thermostabilities of compounds **1–2**, thermogravimetric analyses were investigated in N_2 atmosphere. The TG curves of both compounds show some similarities in the range of 25–800 °C (Fig. S5 and S6†). Both compounds illustrate a consecutive weight-loss process, and the observed entire weight losses are 16.68% and 16.18% for compounds **1** and **2**, respectively, which correspond to the loss of all water molecules and the decomposition of the DAPSC ligands.

Voltammetric behavior of 1 and 2-GCEs

A naphthol-modified glassy carbon electrode (GCE) was prepared as working electrode to study the electrochemical behaviors of compounds **1–2** in 1 mol L^{-1} sulfuric acid aqueous solution at different scanning speed. As depicted in Fig. 6a and b, from 0 to −800 mV, three pairs of reversible redox peaks related to redox reactions are explored for **1** and **2**-GCE. The average peak potentials $E_{1/2} = 0.5(E_{pa} + E_{pc})$ of I/I′, II/II′, and III/III′ are −0.300, −0.496, and −0.687 V for **1**-GCE as well as −0.314, −0.504, and −0.658 V for **2**-GCE. Two pairs of reversible

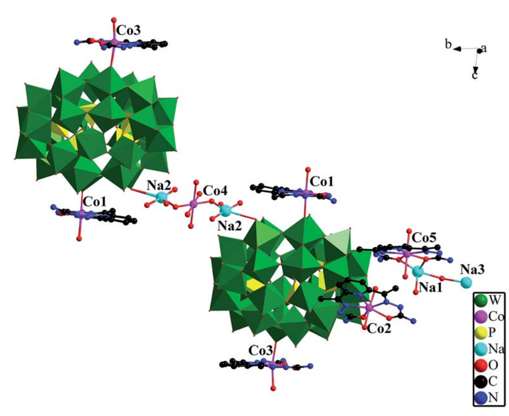

Fig. 5 The dimer of compound **2**.

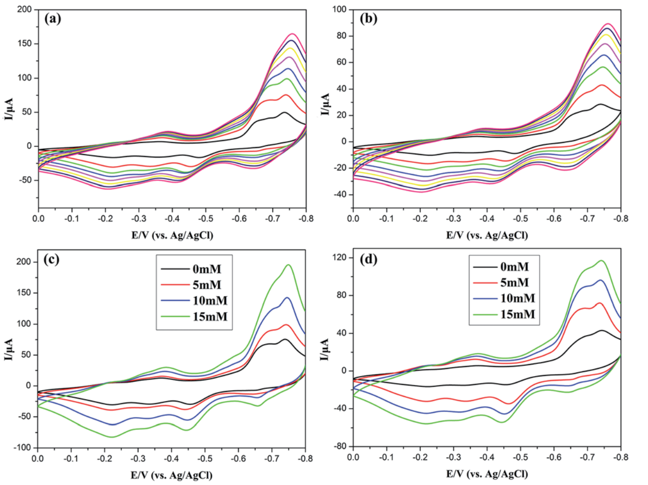

Fig. 6 (a, b) Cyclic voltammograms of the **1**-, and **2**-GCEs in 1 mol L^{-1} sulfuric acid aqueous solution at distinct scanning speeds (from inside to outside: 50, 100, 150, 200, 250, 300, 350, 400 mV s^{-1}). (c, d) Cyclic voltammograms of the **1**-, and **2**-GCEs in 1 mol L^{-1} sulfuric acid aqueous solution containing H_2O_2 in different concentration with a scanning speed of 100 mV s^{-1}.

redox peaks I/I′ and II/II′ correspond to two successive double electron processes of the modified P_5W_{30} polyoxoanion.[10b,13,21] The cyclic voltammetry behavior of **1** and **2**-GCEs were recorded at changing scan rates. The cathodic peak potentials move to the minus orientation and the homologous anodic peak potentials move toward the positive orientation with enhancing scanning rates, which indicates that the redox process of **1** and **2**-GCEs are surface-controlled.[22]

Electrocatalytic properties of 1 and 2-GCEs for the reduction of H_2O_2

POMs have been widely employed as electrocatalysts for the reduction of H_2O_2. Fig. 6c and d reveal **1** and **2**-GCEs show good electrocatalytic activities on the reduction of H_2O_2 in 1 M H_2SO_4 aqueous solution with the potential changing from 0 mV to −800 mV. With the increase of the concentration of H_2O_2 from 0.0 to 15.0 mmol L^{-1}, the reduction peak currents increase clearly while the corresponding oxidation peak currents remarkably reduced, which indicates that the **1** and **2**-GCEs have good electrocatalytic ability for the reduction of H_2O_2.

Nonlinear optical properties

DAPSC is an outstanding conjugated polydentate ligand, and the incorporation of POMs with Schiff base may be able to enhance the NLO response. Herein, we explored the electronic spectra of both compounds in DMF solution with concentration of 1.0×10^{-4} mol L^{-1} at ambient temperature. The 2PA coefficient β and 2PA cross section of σ were calculated by the open-aperture Z-scan method with a femtosecond laser pulse and Ti:95 sapphire system.[23] Fig. 7 and 8 reveal the open-aperture Z-scan data of **1–2**. The red empty circles are the test data and the black solid line on behalf of the theoretical fitting line modified by the equations:[24]

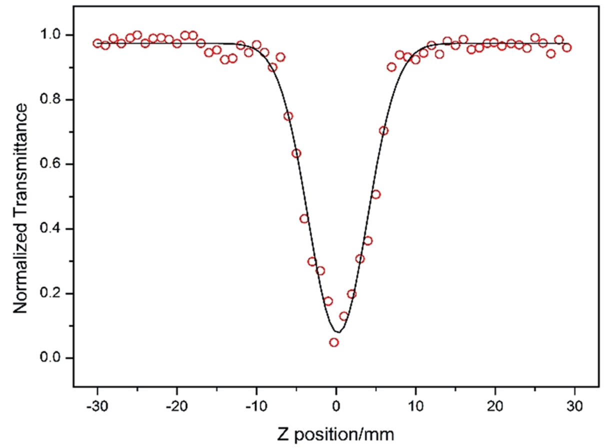

Fig. 7 Z-scan data for compound **1** in DMF at 1.0×10^{-4} mol L^{-1} measured by open aperture Z-scan method.

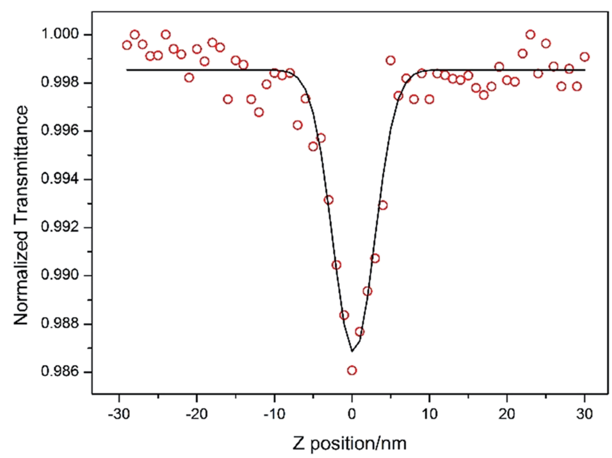

Fig. 8 Z-scan data for compound **2** in DMF at 1.0×10^{-4} mol L^{-1} measured by open aperture Z-scan method.

$$T(z, s=1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}} \quad \text{for} \ |q_0| < 1 \tag{1}$$

$$q_0(z) = \frac{\beta I_0 L_{\text{eff}}}{1 + z^2/{z_0}^2} \tag{2}$$

here, $z_0 = \pi{\omega_0}^2/\lambda$ is the diffraction distance of the beam, In which ω_0 is the spot size at focus, λ is wave length of the beam, z is sample position. I_0 is the input intensity at the focus $z = 0$, $L_{\text{eff}} = (1 - e^{-\alpha L})/\alpha$ is the effective length, where α is the linear absorption coefficient, L is the sample length. By using the above equations, we inference that the 2PA absorption coefficient β is calculated as 0.002099 cm GW^{-1} and 0.001715 cm GW^{-1} for **1–2**, respectively. Furthermore, the molecular 2PA cross-section σ could be determined by the subjacent formula:

$$\sigma N_A d \times 10^{-3} = h\nu\beta \tag{3}$$

where h, ν, N_A, and d are the Planck constant, frequency of input intensity, the Avogadro's constant, and is the concentration of the compound, respectively. According to formula (3), the molecular 2PA cross-section σ of both compounds were computed as 888 GM and 707 GM (1 GM = 10^{-50} cm^4 per photon). It is well known that the modified π-electron delocalization in the framework leaded to the third-order nonlinear optics response. But so far the investigation of POMs in the area of nonlinear optical materials basically concentrate on the well-known Keggin- and Dawson-type polyoxoanions.[25] As far as we know, two compounds have bigger molecular TPA cross section σ comparing with other reported NLO materials.[26] The third-order NLO properties of two compounds manifest that POMs modified by Schiff base lead to a powerful NLO response, and could be promising candidates for making NLO materials.

Conclusions

In conclusion, two novel based on Preyssler P_5W_{30} compounds modified by Schiff base and TM ions were synthesized under hydrothermal conditions. The cyclic voltammograms of both compounds have been studied. Both compounds show better electrocatalytic activities toward the reduction of H_2O_2. Moreover, the both compounds have moderate molecular 2PA cross section σ, hence they own potential applications in NLO materials. The successful isolation of compounds **1–2** can provide new synthetic strategy for the construct of distinct POMs-based inorganic–organic hybrid materials by means of combining diverse flexible organic molecules. Further work in this area will be focused on preparing Preyssler-based compounds with fascinating structure and rich physicochemical properties.

Conflicts of interest

There are no conflicts to declare.

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