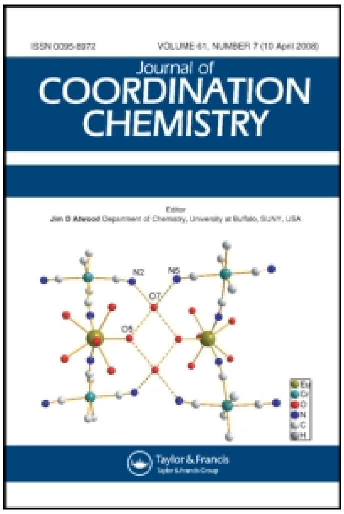

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Investigation of inorganic-organic hybrid materials containing polyoxometalate cluster anions and organic dye cations

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Investigation of inorganic–organic hybrid materials containing polyoxometalate cluster anions and organic dye cations

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Two new ionic-pair salts containing an organic dye cation, *i.e.* New Fuchsin or Pararosaniline cation, with Keggin-type POMs, $[SiW_{12}O_{40}]^{4-}$ and $[BW_{12}O_{40}]^{6-}$, have been isolated under hydrothermal conditions. $[(C_{22}H_{24}N_3)_4][SiW_{12}O_{40}]$ (**1**) and $[(C_{19}H_{18}N_3)_6][BW_{12}O_{40}]$ (**2**) have been characterized by elemental analyses, FT-IR and single crystal X-ray crystallography. Both of these complexes have strong absorption in the visible-light range due to the involvement of the organic dye and both show weak fluorescence emission.

Keywords: Organic dye; Keggin-type anions; Hybrid materials; Molecular structures; Hydrogen bonding

1. Introduction

Polyoxometalate (POM) anions are an important group of early-transition-metal-oxygen-anion clusters, which received intense investigation due to their application in catalysis, biology, magnetism, optics, medicine and green chemistry [1–7]. To further explore the potential applications, it is desirable to develop hybrid inorganic–organic materials containing optically-active organic dyes as cations. These materials could offer unprecedented properties, paving the way for novel applications [8–12]. The process of light absorbency coupled with energy/charge transfer between organic dye cations and POM anions is exciting to chemists who have envisaged the design and fabrication of sophisticated materials valuable for photocatalysis and photovoltaic applications; however, only a few reports take advantage of organic dyes [13–16] compared to the extensive research into noble metals [17–26] or cationic organic radicals [27–30]. In particular, a series of cheap organic dyes that do not contain expensive transition metals such as New Fuchsin, Basic Fuchsin (*i.e.* Pararosaniline hydrochloride), shown in scheme 1, are appealing because of

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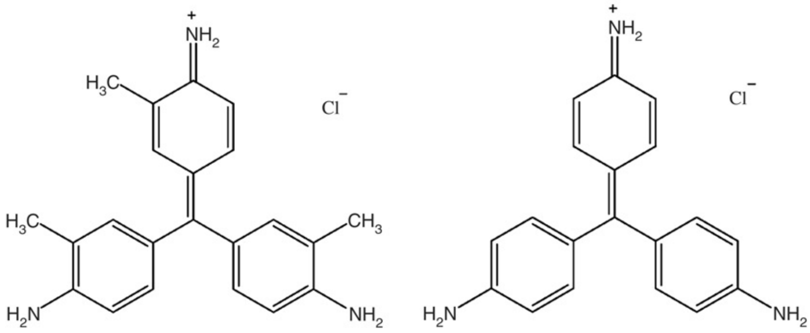

Scheme 1. Structure of New Fuchsin (left) and Basic Fuchsin (right).

several advantages: (1) The large planar conjugated π systems and intense color will enhance the potential electrical and optical properties of POM compounds; (2) The organic dyes possess significant absorption in the visible-light range and maintain the charge balance with POM anions for they only carry one positive charge; (3) Charge-assisted N–H $\cdots$ O hydrogen bonds between cations and the anion oxygen atoms will effectively facilitate formation of crystalline materials and make it possible to tune the packing structure through the design of either dye structures or POM anions. Herein, we report the synthesis of two new ionic-pair salts carrying New Fuchsin or Pararosaniline cations with Keggin POMs $[SiW_{12}O_{40}]^{4-}$, $[BW_{12}O_{40}]^{6-}$ and the initial photo-physical property investigation.

2. Experimental

2.1. *Materials and general procedures*

All starting materials were purchased from commercial sources and used without further purification. The IR spectra in the range 4000–400 cm^{-1} were recorded on a Perkin-Elmer Spectrum One FT–IR spectrometer. Elemental analyses were carried out by Chemical & MicroAnalytical Services Pty. Ltd., Belmont, VIC, Australia. UV-Vis spectra were recorded on a UV-1650 PC spectrophotometer. Fluorescence measurements were performed on a Varian Cary Eclipse fluorescence spectrophotometer.

2.2. *Synthesis*

2.2.1. $[(C_{22}H_{24}N_3)_4][SiW_{12}O_{40}]$ (1). $Na_4SiW_{12}O_{40}$ (0.296 g, 0.1 mmol), $[C_{22}H_{24}N_3]Cl$ (New Fuchsin, 0.146 g, 0.4 mmol) and distilled water (15.0 mL) were mixed in a Teflon-lined stainless steel autoclave (23 mL) and stirred for 15 min. The sealed vessel was heated at 180°C for seven days. After cooling to room temperature, black-purple block crystals of **1** were obtained. Yield: 0.312 g (74%). Anal. Calcd for $C_{88}H_{96}N_{12}O_{40}SiW_{12}$ (4196.06): C, 25.20; H, 2.31; N, 4.01; O, 15.25; Si, 0.67; W, 52.58%; Found: C, 25.80;

Table 1. Summary of crystal and structure refinement data for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{88}H_{96}N_{12}O_{40}SiW_{12}$	$C_{114}H_{108}BN_{18}O_{40}W_{12}$
Formula weight	4196.06	4587.19
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cells and dimensions (Å, °)		
a	13.7654(10)	12.663(2)
b	13.8842(10)	17.598(3)
c	14.9983(10)	17.604(3)
α	67.9190(10)	114.470(3)
β	89.7800(10)	103.833(3)
γ	84.2650(10)	103.970(3)
V (Å^3)	2641.2(3)	3199.6(9)
Z	1	1
D_{Calcd} (Mg m^{-3})	2.638	2.381
Abs. coeff. (mm^{-1})	13.105	10.821
Max. and min. transmission	0.275 and 0.169	0.148 and 0.089
F(000)	1930	2131
Crystal size (mm^3)	$0.16 \times 0.12 \times 0.10$	$0.30 \times 0.20 \times 0.18$
θ (°)	1.47 to 27.54	1.38 to 25.00
Limiting indices	$-17 \le h \le 11$	$-15 \le h \le 13$
	$-18 \le k \le 17$	$-20 \le k \le 18$
	$-15 \le l \le 19$	$-19 \le l \le 20$
Reflns collected/unique	16487/11504[$R_{(\text{int})} = 0.0226$]	16616/11077[$R_{(\text{int})} = 0.1529$]
Data/restraints/params	11504/0/641	11077/9/745
Goodness-of-fit on F^2	1.030	0.962
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0660$, $wR_2 = 0.1672$	$R_1 = 0.1048$, $wR_2 = 0.2654$
R indices (all data)	$R_1 = 0.0958$, $wR_2 = 0.1866$	$R_1 = 0.1462$, $wR_2 = 0.2876$

H, 2.06; N, 4.54; O, 15.63; Si, 0.69; W, 51.30%. FTIR data (cm^{-1}): 3347(s, ν(NH_2)), 3226(m, ν(NH_2)), 1630(s, δ(C=C)), 1582(vs, δ(C=C)), 1466(m, ν(CH_3)) 1362(vs, ν(NH_2)), 1334(s, ν(NH_2)), 1280(s, ν(NH_2)), 1152(s, ν(NH_2)), 968(s, ν(W–O)), 912(vs, ν(W–O)), 777(vs, ν(W–O)).

2.2.2. [$(C_{19}H_{18}N_3)_6$][$BW_{12}O_{40}$] (2). A similar procedure to that for **1** was employed with $K_5BW_{12}O_{40}$ (0.305 g, 0.1 mmol), [$C_{19}H_{18}N_3$]Cl (Pararosaniline hydrochloride, 0.162 g, 0.5 mmol) and distilled water (15.0 mL). Black-purple polyhedral crystals were obtained. Yield: 0.302 g (79% based on Pararosaniline hydrochloride). Anal. Calcd for $C_{114}H_{108}BN_{18}O_{40}W_{12}$ (4587.19): C, 29.85; H, 2.37; N, 5.50; O, 13.95; B, 0.24; W, 48.09%; Found: C, 30.20; H, 2.36; N, 5.31; O, 13.81; B, 0.25; W, 48.10%. FTIR data (cm^{-1}): 3321(m, ν(NH_2)), 3190(w, ν(NH_2)), 1629(s, δ(C=C)), 1579(vs, δ(C=C)), 1367(vs, ν(NH_2)), 1333(vs, ν(NH_2)), 1284(s, ν(NH_2)), 1165(vs, ν(NH_2)), 953(s, ν(W–O)), 853(s, δ(C–H)), 759(vs, ν(W–O)).

2.3. *X-ray crystallography*

Crystal data and details of the data collection and refinement are summarized in table 1. Crystal structures were solved using direct methods (SHELXTL V5.1 [31]) from single-crystal data collected at 130 K on a Bruker SMART/CCD area detector diffractometer fitted with Mo-Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. Structure refinements were performed using SHELX97 [32], which uses a full-matrix least-squares refinement based on F^2. All non-hydrogen atoms in **1** and **2** were refined with anisotropic thermal displacement parameters. The hydrogen atoms attached to carbon and those to nitrogen atoms were placed at geometrically estimated positions. Absorption corrections were performed using SADABS [33].

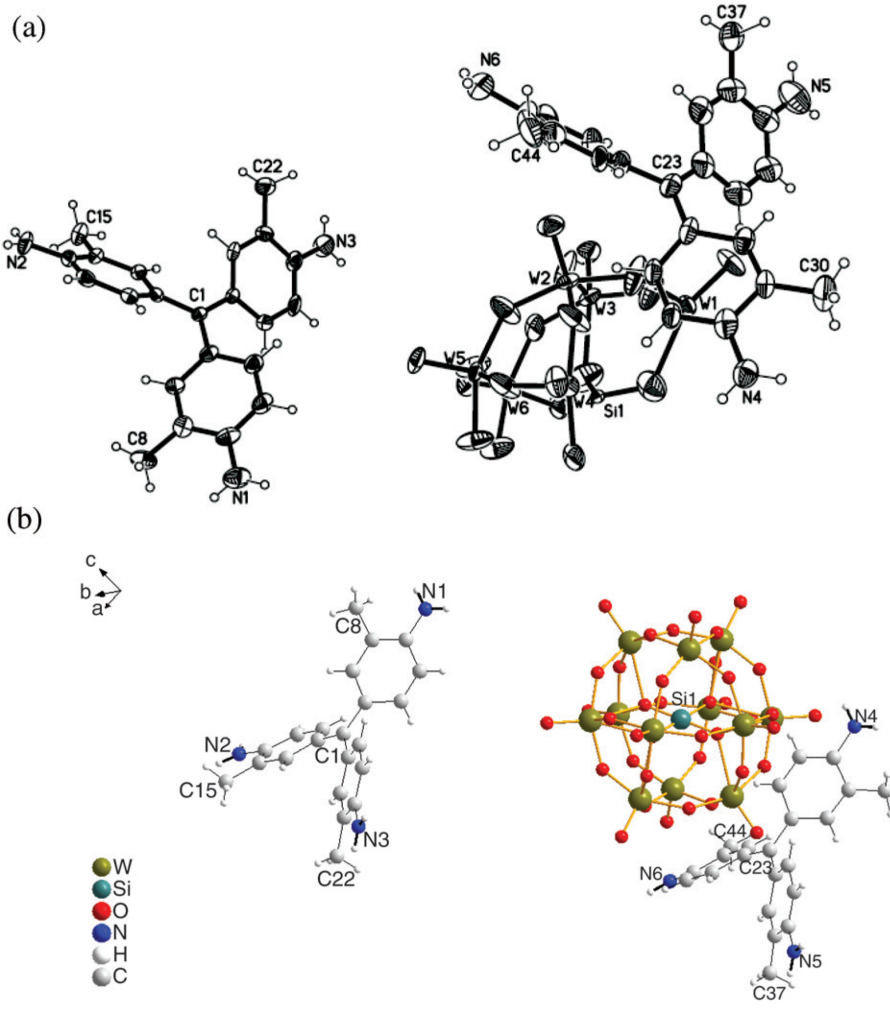

Figure 1. (a) ORTEP view with non-H atomic numbering scheme for **1**. Ellipsoids are at the 30% probability level. Selected bond lengths (Å) and angles (°): W(1)–O(1) 1.678(9), W(1)–O(6) 1.852(12), W(1)–O(2) 1.929(11),W(1)–O(16) 2.425(12), W(2)–O(3) 1.643(9), W(2)–O(7) 1.829(12), W(2)–O(2) 1.836(12), W(2)–O(4) 1.863(12), W(2)–O(8) 1.888(13), W(3)–O(5) 1.668(9), W(3)–O(20) 1.841(13), W(3)–O(6) 1.893(13), W(3)–O(4) 1.901(12), W(3)–O(17)#1 1.927(9), W(3)–O(15) 2.420(13), W(4)–O(9) 1.694(8), W(4)–O(17) 1.858(10), W(4)–O(10) 1.870(12), W(4)–O(14)#1 1.895(10), W(4)–O(7) 1.893(12), W(4)–O(15)#1 2.440(13), W(5)–O(11) 1.671(8), W(5)–O(12) 1.845(9), W(5)–O(8) 1.881(12), W(5)–O(10) 1.889(12), W(5)–O(18) 1.895(10), W(5)–O(16)#1 2.460(12), W(6)–O(13) 1.687(10), W(6)–O(19) 1.856(10), W(6)–O(14) 1.880(9), W(6)–O(12) 1.912(8), W(6)–O(20) 1.889(12), W(6)–O(16)#1 2.408(12), W(6)–O(15) 2.409(14), Si(1)–O(16) 1.541(13), Si(1)–O(15) 1.568(13), O(1)–W(1)–O(6) 103.1(5), O(1)–W(1)–O(18)#1 99.6(5), O(6)–W(1)–O(18)#1 88.3(5), O(1)–W(1)–O(19)#1 101.1(6), O(6)–W(1)–O(19)#1 155.8(5) [#1: $-x, -y+1, -z+1$]. (b) Molecular structure of $[(C_{22}H_{24}N_3)_4][SiW_{12}O_{40}]$ (**1**).

3. Results and discussion

3.1. *Structure descriptions*

$[(C_{22}H_{24}N_3)_4][SiW_{12}O_{40}]$ (**1**) and $[(C_{19}H_{18}N_3)_6][BW_{12}O_{40}]$ (**2**) were synthesized under hydrothermal conditions from New Fuchsin and $Na_4SiW_{12}O_{40}$ and Pararosaniline hydrochloride and $K_5BW_{12}O_{40}$, respectively. X-ray crystal analysis shows that $[(C_{22}H_{24}N_3)_4][SiW_{12}O_{40}]$ (**1**) crystallized in the triclinic space group $P\bar{1}$. The asymmetric unit within a cell is illustrated in figure 1(a), comprising two crystallographically

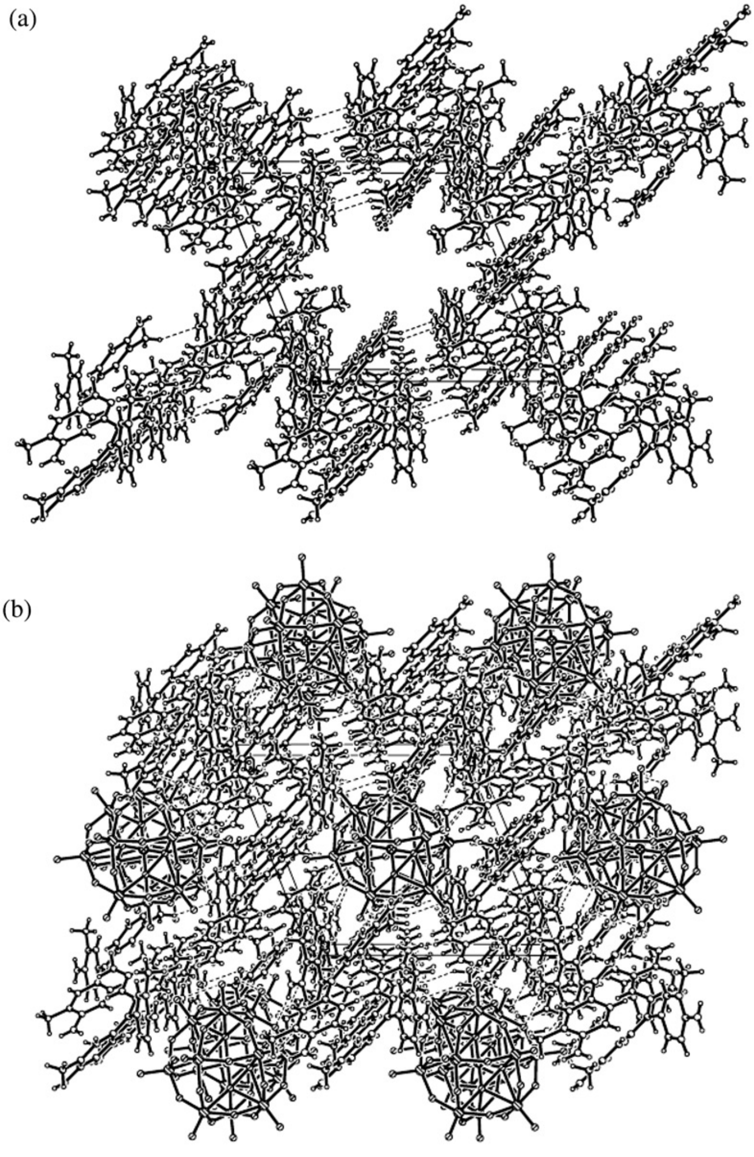

Figure 2. (a) Three-dimensional network structure formed by $C_{22}H_{24}N_3^+$ in **1**. (b) Molecule packing of **1**.

independent $C_{22}H_{24}N_3^+$ cations and one-half $[SiW_{12}O_{40}]^{4-}$. The Si1 atom is located on a center of symmetry and the overall Keggin structure was finished with symmetry operation '$-x$, $-y+1$, $-z+1$', as shown in figure 1(b). The terminal W–O bond lengths (Å) are: W(1)–O(1): 1.678(9); W(2)–O(3): 1.643(9); W(3)–O(5): 1.668(9); W(4)–O(9): 1.694(8); W(5)–O(11): 1.671(8); W(6)–O(13): 1.687(10). The bridge W–O bond lengths are in the range 1.829(12) ~ 1.929(11) Å, and the central W–O bond lengths fall within 2.408(12) ~ 2.460(12) Å. In the central SiO_4 square-planar environment, the Si–O distances are 1.568(13) Å (Si1–O15) and 1.541(13) Å (Si1–O16), similar to reported values [34–37]. In the asymmetric unit, there are two triarylcarbenium $C_{22}H_{24}N_3^+$ cations, one of which (the central carbon atom is C1) is the Δ enantiomer, while the other (the central carbon atom is C23) is the Λ enantiomer resulting in overall achiral character [38, 39]. The organic cations possess propeller blade shapes within a triangular planar geometry, for example, if the plane comprised by central carbons C1, C2, C9 and C16 is defined as the reference plane, the phenyl rings of C2~C7, C9 ~C14, C16 ~ C21 have dihedral angles of 30.9°, 31.6° and 30.3°, respectively. To our best knowledge, this is the first report of ionic-pair salts containing New Fuchsin. It should be noted that the three-dimensional network arising from the $C_{22}H_{24}N_3^+$ cations when viewed along the *a*-axis consists of cavities to accommodate the $[SiW_{12}O_{40}]^{4-}$ anions (figure 2) with the help of hydrogen bonding (N–H ··· O) between the cations and the anion surface oxygen atoms (table 2).

In contrast to **1**, which undergoes no redox change, $[BW_{12}O_{40}]^{5-}$ has been reduced to $\left[BW_{11}^{VI}W_{1}^{V}O_{40}\right]^{6-}$ under hydrothermal conditions to form $[(C_{19}H_{18}N_3)_6][BW_{12}O_{40}]$ (**2**). Its asymmetric unit within a cell is illustrated in figure 3(a), comprising three crystallographically independent $C_{19}H_{18}N_3^+$ cations and one-half $[BW_{12}O_{40}]^{6-}$. As shown in figure 3(b), in the central distorted square-planar BO_4, the B–O distances [1.445(18) ~ 1.748(17) Å] and O–B–O angle [104.3(9)°] somewhat deviate from values reported in the literature [27, 30]. Similar to **1**, the packing of the pararosaniline cations provides cavities to accommodate the $[BW_{12}O_{40}]^{6-}$ anions and allows formation of multiple charge-assisted hydrogen bonds N–H ··· O between the cation $-NH_2$ and the anion oxygens (figure 4, table 2).

Table 2. Hydrogen bonds parameters in **1** and **2** (with H ··· A < r(A) + 2.000 Å and ∠DHA >110°).

D–H	d(D–H)	d(H ··· A)	∠DHA	d(D ··· A)	A
Complex **1**					
N2–H2A	0.88	2.47	164	3.32(1)	O6 $[x+1, y, z+1]$
N6–H6A	0.88	2.54	174	3.42(2)	O12 $[-x+1, -y+1, -z+1]$
Complex **2**					
N1–H1A	0.88	2.56	150	3.35(3)	O7 $[-x+1, -y, -z+1]$
N2–H2A	0.88	2.01	169	2.88(2)	O12 $[-x, -y+1, -z+1]$
N2–H2B	0.88	2.09	155	2.91(2)	O5
N3–H3A	0.88	2.64	160	3.48(2)	O8 $[-x, -y, -z+1]$
N4–H4A	0.88	1.98	170	2.85(2)	O14 $[-x+1, -y+1, -z+2]$
N4–H4B	0.88	2.13	156	2.95(2)	O3 $[x+1, y, z+1]$
N5–H5B	0.88	2.59	144	3.34(3)	O9 $[-x+2, -y+1, -z+1]$
N7–H7A	0.88	2.00	173	2.87(2)	O4 $[x+1, y+1, z]$
N7–H7B	0.88	2.18	154	2.99(2)	O13 $[-x+1, -y+2, -z+1]$
N8–H8A	0.88	2.64	129	3.27(2)	O1 $[-x, -y+1, -z]$
N9–H9B	0.88	2.61	147	3.38(3)	O10 $[-x+1, -y+1, -z]$

3.2. *UV-Vis measurements*

From the viewpoint of introducing organic cationic dyes as more efficient visible-light energy transfer agents for POMs, New Fuchsin possesses a significant absorption band centered at 563 nm and a less strong band at 298 nm. The UV-Vis spectrum of **1** is shown in figure 5(a) and apart from the band at 563 nm, which originated from New Fuchsin, a doublet at 298 nm and 262 nm was observed suggesting that within the UV range, New Fuchsin and $SiW_{12}O_{40}^{4-}$ (262 nm) absorb together.

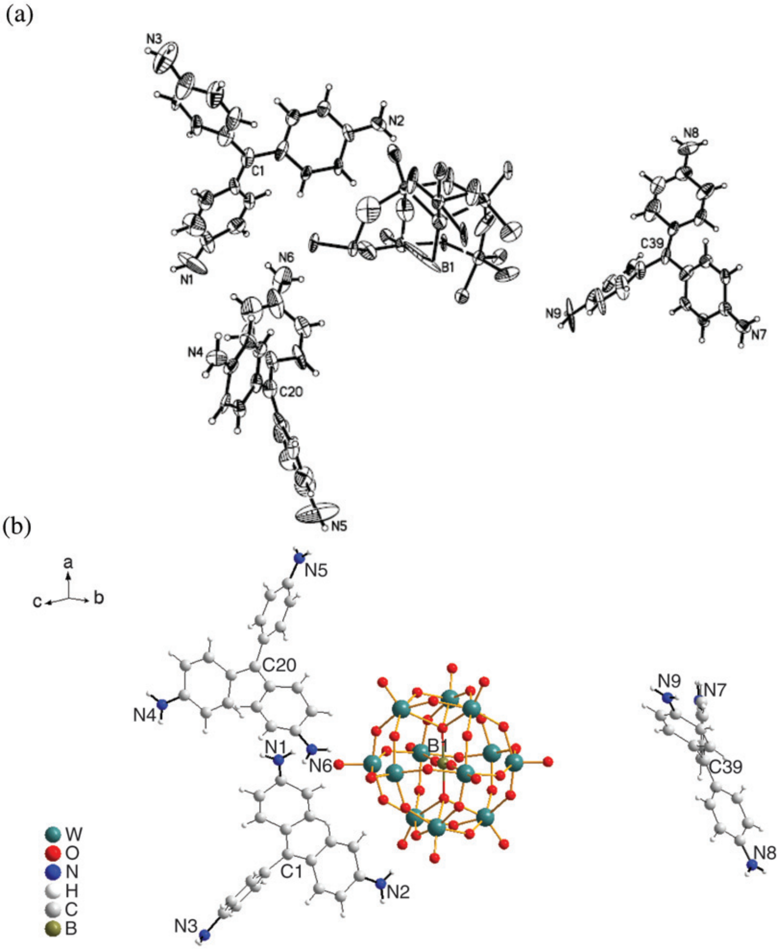

Figure 3. (a) ORTEP view with non-H atomic numbering scheme for **2**. Ellipsoids are at the 30% probability level. Selected bond lengths (Å) and angles (°): W(1)–O(1) 1.705(10), W(1)–O(2) 1.795(18), W(1)–O(20)#1 1.853(16), W(1)–O(8) 1.855(18), W(1)–O(10) 1.900(19), W(1)–O(16) 2.366(15), W(2)–O(4) 1.635(12), W(2)–O(6) 1.81(2), W(2)–O(5) 1.903(15), W(2)–O(3) 1.932(19), W(2)–O(2) 1.881(19), W(2)–O(15) 2.295(14), W(3)–O(7) 1.725(11), W(3)–O(19)#1 1.801(16), W(3)–O(6) 1.881(19), W(3)–O(8) 1.882(17), W(3)–O(18)#1 1.906(13), W(4)–O(9) 1.674(13), W(4)–O(11) 1.846(19), W(4)–O(10) 1.876(15), W(4)–O(18) 1.876(13), W(4)–O(17) 1.877(15), W(5)–O(12) 1.650(13), W(5)–O(13) 1.851(17), W(5)–O(3) 1.865(15), W(5)–O(19) 1.887(14), W(5)–O(11) 1.873(19), W(5)–O(15) 2.293(19), W(6)–O(14) 1.661(15), W(6)–O(17)#1 1.836(17), W(6)–O(20) 1.868(15), W(6)–O(13) 1.908(19), W(6)–O(5) 1.941(13), W(6)–O(15) 2.251(18), O(15)–B(1) 1.748(17), O(16)–B(1) 1.445(18), O(1)–W(1)–O(2) 102.7(7), O(1)–W(1)–O(20)#1 102.6(7), O(2)–W(1)–O(20)#1 154.8(7), O(1)–W(1)–O(8) 102.1(6), O(2)–W(1)–O(8) 88.1(8) [#1: $-x+1, -y+1, -z+1$]. (b) Molecular structure of **2**.

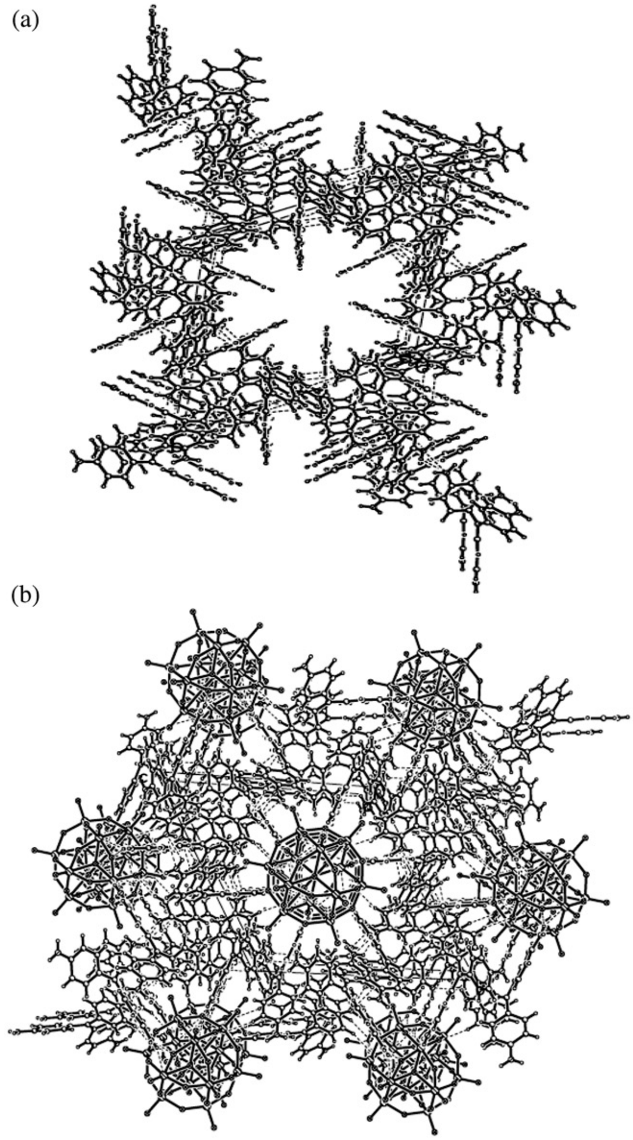

Figure 4. (a) Three-dimensional network structure formed by $C_{19}H_{18}N_3^+$ in **2**. (b) Molecule packing of **2**.

Similarly, in figure 5(b), **2** has strong absorbance around 553 nm in the visible range, ascribed to $C_{19}H_{18}N_3^+$. The bands at 290 nm and 260 nm are assigned to the Pararosaniline cation and $BW_{12}O_{40}^{6-}$, respectively.

3.3. *Investigation of fluorescence properties*

New Fuchsin has one prominent emission peak at 614 nm (fwhm $\approx$ 50 nm) when excited by a wide spectral range down to at least 320 nm. The absorption band centered at 262 nm observed for $[SiW_{12}O_{40}]^{4-}$, attributed to the oxygen-to-metal charge transfer

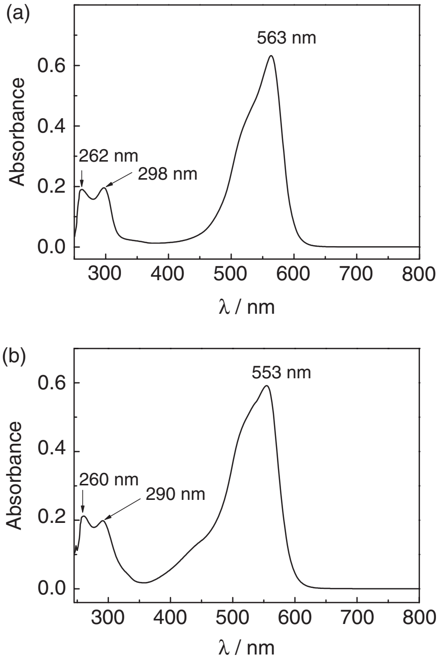

Figure 5. (a) UV-Vis spectrum of **1** (1.0×10^{-5} M in spectrophotometric grade DMF). (b) UV-Vis spectrum of **2** (1.0×10^{-5} M in spectrophotometric grade DMF).

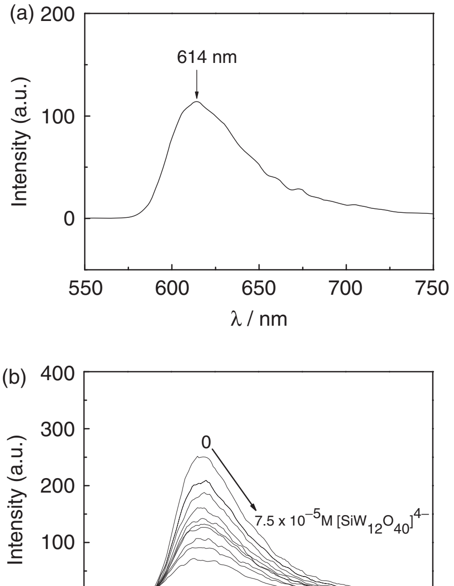

Figure 6. (a) Fluorescence emission spectra of **1** (3.0×10^{-5} M in DMF). (b) Emission spectrum of New Fuchsin in 95/5 DMF/H_2O (3.0×10^{-4} M) on addition of $[SiW_{12}O_{40}]^{4-}$ (excitation wavelength 320 nm).

transition, has no visible absorbance and no detectable luminescence [22, 40]. Studies of the photoluminescence properties of **1** revealed a luminescence peak with a maximum at 614 nm, as shown in figure 6(a), which was attributed to the existence of New Fuchsin. Monitoring the dye emission (λ_{em}) provided a feasible way of observing the energy transfer interactions between the dye molecule and the POM anions. Figure 6(b) demonstrates the impact of addition of $[SiW_{12}O_{40}]^{4-}$ (up to 7.5×10^{-5} M) on the emission spectrum of New Fuchsin (3.0×10^{-4} M) in 95/5 DMF/H_2O solution by displaying the quenching effect of POM anions with increasing concentration. The dye molecule emission undertakes no detectable wavelength shift when varying excitation wavelength, *i.e.* 320 nm or 370 nm. Contrary to **1**, investigations of **2** showed an emission peak at 610 nm, which was assigned to the dye cation $C_{19}H_{18}N_3^+$. It should be noted that compared with the slight blue shift from 610 nm (original dye: Basic Fuchsin) to 590 nm observed in $[C_{19}H_{18}N_3]_4[\alpha\text{-}S_2Mo_{18}O_{62}]$ [16], the extent of perturbation between ion electronic states of **1** and **2** in solution phase is weak, indicating a careful choice of both organic dyes and POMs anions is still a challenge.

4. Conclusions

Two new ionic-pair salts containing organic dyes and POMs were prepared and characterized. This work is in the initial stages of general design principals for combination of inorganic anions and organic cations and we believe it will shed light on designated strategy for tailoring more systems consisting of triarylmethane dye cations and different polyoxometalate anions such as $[AlW_{12}O_{40}]^{5-}$ and $[PW_{12}O_{40}]^{3-}$. Much effort should therefore be directed toward understanding hydrothermal synthetic methods and the influence of reaction temperature and pressure, pH values, the nature of the solvent, stoichiometries and reaction concentrations and kinetic and thermodynamic factors controlling the sequence of reaction steps [41]. More detailed investigations into the photoelectrochemical properties of these two compounds are being pursued.

Supplementary data

Crystallographic data for the structure have been deposited with Cambridge Crystallographic Data Centre. CCDC-664493(**1**), 664492(**2**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif

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