Facile assembly of hybrid materials containing polyoxometalate cluster anions and organic dye cations: crystal structures and initial spectral characterization†

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Salts of the pararosaniline dye cation and four polyoxometalate cluster anions have been isolated under both ambient and hydrothermal conditions; structural and initial spectroscopic data are consistent with significant perturbation of ion electronic states induced by charge-assisted N–H···O hydrogen bonds.

Polyoxometalate anions[1] and triarylmethane dye cations[2] share well-developed redox and photo-chemical properties but have rarely been combined to form hybrid materials.[3] The anions do not absorb significantly in the visible spectrum and strategies to induce visible photo-sensitisation have normally involved incorporation of noble metal complex cations.[4]

In particular, salts $[Ru^{II}(bpy)_3]_2[\alpha\text{-}S_2M_{18}O_{62}]$ (M = Mo, W) exhibited significant quantum yields for visible photo-reduction of the anion in solution.[4g,i,j] This new property was traced to the presence of an absorption band at around 480 nm arising from ion clusters $\{[Ru^{II}(bpy)_3]^{2+}[S_2M_{18}O_{62}]^{4-}\}^{2-}$ and/or $\{[Ru^{II}(bpy)_3]^{2+}_2[S_2M_{18}O_{62}]^{4-}\}$ present in solution. The new transition was assigned to either a Ru → M charge transfer transition or a metal-oxo → bpy interligand transition.[4j]

However, inexpensive triarylmethane dye cations[2] are appealing as more efficient visible energy transfer agents for polyoxometalate anions: (1) the cations absorb intensely in the visible region and specific wavelengths can be tuned by ring substitution; (2) improved solubility should follow from their single cationic charge and from appropriate ring substitution; (3) charge-assisted hydrogen bonds between the cations and the anion surface oxo ligands will facilitate the formation of crystalline materials and ion clusters in solution. We report that salts of the pararosaniline cation $[C(p\text{-}C_6H_4NH_2)_3]^+$ with polyoxometalate anions can be isolated under both ambient and hydrothermal conditions. The anions include $[\alpha\text{-}S_2Mo_{18}O_{62}]^{4-}$, $[\beta\text{-}Mo_8O_{26}]^{4-}$, $[\alpha\text{-}CoW_{12}O_{40}]^{6-}$ and $[\alpha\text{-}ZnW_{12}O_{40}]^{6-}$.

Cuboid black-purple crystals of $[C_{19}H_{18}N_3]_4[\alpha\text{-}S_2Mo_{18}O_{62}]$ (1) were synthesized from pararosaniline hydrochloride and $[Bu_4N]_4[\alpha\text{-}S_2Mo_{18}O_{62}]$ at room temperature (ESI†). The presence of the $[\alpha\text{-}S_2Mo_{18}O_{62}]^{4-}$ anion was confirmed by X-ray crystallography.‡ Its two halves are related by a two-fold axis (Fig. S1†)

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and its dimensions are similar to those observed in salts containing hydrophobic cations.[5] In the central SO_4 tetrahedra, the S–O distances and O–S–O angles are in the ranges 1.454(7)–1.492(6) Å and 107.7(3)–110.7(4)°. The two triarylcarbenium cations in the asymmetric unit exhibit the characteristic three-bladed propeller conformation.[2] The three-dimensional network structure features an extensive array of charge-assisted N–H···O hydrogen bonding interactions between cation amino functions and the anion oxygen atoms (minimum distance $d_{N–H···O}$, 2.92 Å; ESI†). Each anion accepts nineteen hydrogen bonds (Fig. 1, S1†).

The $[S_2Mo_{18}O_{62}]^{4-}$ anion displays a broad absorption band centred at $\lambda \sim 350$ nm (ε, 3×10^4 M^{-1} cm^{-1}) which tails into the visible region.[6] There is no detectable luminescence.[4f] In dry dimethylformamide (DMF), pararosaniline chloride exhibits intense absorption bands centered at 550 (ε, 5.7×10^4 M^{-1} cm^{-1}) and 290 nm,[2,3] with a prominent emission peak at λ_{em}, 610 nm (fwhm ~ 50 nm) when excited in the visible–UV spectrum down to at least 320 nm. This emission provides a sensitive means of inspecting possible electron or energy transfer interactions between the dye cation and $[S_2Mo_{18}O_{62}]^{4-}$.

The emission maximum attributed to the pararosaniline cation $[C_{19}H_{18}N_3]^+$ in solutions of 1 in DMF was shifted to 590 nm (from 610 nm) and its intensity was diminished by $\sim 75\%$ (Fig. S2†). Addition of $[Bu_4N]_4[S_2Mo_{18}O_{62}]$ to a solution of $[C_{19}H_{18}N_3]Cl$ (2.0×10^{-4} M) in DMF caused the intensity to decrease progressively (Fig. 2a) until, at a ratio of $[C_{19}H_{18}N_3]^+$: $[S_2Mo_{18}O_{62}]^{4-} = 4 : 1$, the spectrum was similar to that of a *bona fide* solution of 1 at the equivalent absolute concentration (5.0×10^{-5} M). However, no shift in emission intensity was apparent, presumably due to the influence of the additional $[Bu_4N]^+$ and Cl^- ions. The overall results are consistent with static quenching of excited states of $[C_{19}H_{18}N_3]^+$ induced by the presence of ion clusters such as $\{[C_{19}H_{18}N_3]^+_4[\alpha\text{-}S_2Mo_{18}O_{62}]^{4-}\}$, analogous to those such as $\{[Ru^{II}(bpy)_3]^{2+}_2[S_2M_{18}O_{62}]^{4-}\}$ proposed to be present in solutions of $[Ru^{II}(bpy)_3]_2[S_2M_{18}O_{62}]$.[4g,j] However, detailed investigations are needed to determine if there is a contribution from dynamic quenching.

An excitation spectrum records the absorption spectrum for transitions responsible for emission. The excitation spectrum of $[C_{19}H_{18}N_3]Cl$ in DMF exhibited absorbance maxima at 280, 323 and 384 nm for emission at 610 nm (Fig. 2b). The equivalent excitation spectrum of 1 in DMF for emission at 590 nm also showed significant absorbance in the range 250–500 nm (Fig. 2c). However, the absorbance profile showed high relative absorbance below 400 nm, where $[S_2M_{18}O_{62}]^{4-}$ absorbs. These spectra are again consistent with the anion $[S_2M_{18}O_{62}]^{4-}$ perturbing the
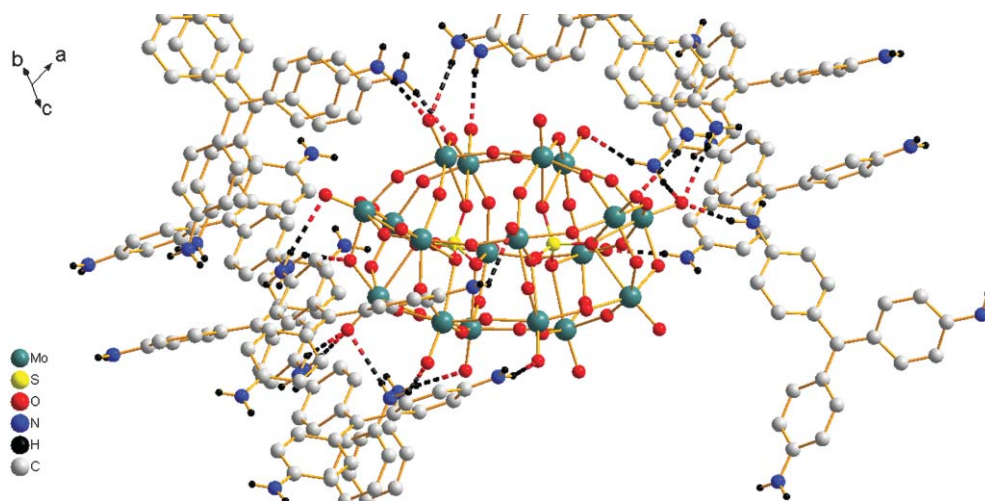
Fig. 1 Three-dimensional network structure of **1** features an extensive array of charge-assisted N–H···O hydrogen bonding interactions.

emission properties of the $[C_{19}H_{18}N_3]^+$ cation. Detailed photophysics investigations are underway (*cf.*, ref. 4*g,i,j*).

Exploratory synthesis employing both ambient and hydrothermal conditions suggests that an extended range of salts of dye cations and polyoxometalate anions are accessible from a variety of sources. For example, while reaction of the labile hexametalate $[Mo_6O_{19}]^{2-}$ anion with $[C_{19}H_{18}N_3]^+Cl^-$ at room temperature provided $[C_{19}H_{18}N_3]_2[Mo_6O_{19}]$, reflux of the CH_3CN–H_2O reaction solution led to $[C_{19}H_{18}N_3]_4[Mo_8O_{26}]\cdot8.5DMF$ (**2**) after recrystallisation. This salt features the $[\beta\text{-}Mo_8O_{26}]^{4-}$ anion (C_{2h} point symmetry) comprising eight edge-sharing octahedra (Fig. S3†).[7] As for salt **1**, both Λ and Δ enantiomers of the $[C_{19}H_{18}N_3]^+$ cation are present resulting in an achiral crystal which is stabilised by multiple charge-assisted N–H···O hydrogen bonds (Table S1†).‡

Under hydrothermal conditions in the presence of $[C_{19}H_{18}N_3]^+Cl^-$, the Tourné sandwich anions $[WM_3(H_2O)_2(MW_9O_{34})_2]^{12-}$ (M = Co or Zn) were transformed to $[C_{19}H_{18}N_3]_6[MW_{12}O_{40}]\cdot H_2O$ (M = Co (**3**); Zn (**4**)) (ESI†).‡ These salts feature the Keggin anions $[MW_{12}O_{40}]^{6-}$,[8] presumably the most thermodynamically stable clusters under the conditions. It should be noted that each of the two anions exhibits disorder around a site of -3 symmetry which corresponds to the position of the metal ion at the centre of the Keggin anion. A consequence of this disorder is that the divalent metal appears to be 8-coordinate (Fig. 3). Similar
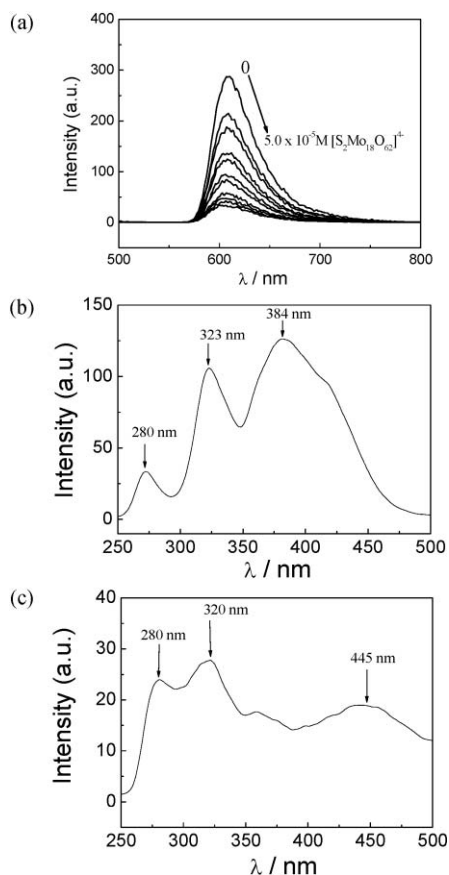
Fig. 2 (a) Emission spectrum of $[C_{19}H_{18}N_3]^+Cl^-$ in dry DMF (2.0 × 10^{-4} M) upon addition of $[Bu_4N]_4[\alpha\text{-}S_2Mo_{18}O_{62}]$ (excitation wavelength 385 nm). Excitation spectra of (b) $[C_{19}H_{18}N_3]^+Cl^-$ in DMF (6.0 × 10^{-4} M) for emission at 610 nm, and (c) $[C_{19}H_{18}N_3]_4[\alpha\text{-}S_2Mo_{18}O_{62}]$ (**1**) in DMF (2.5 × 10^{-5} M) for emission at 590 nm.
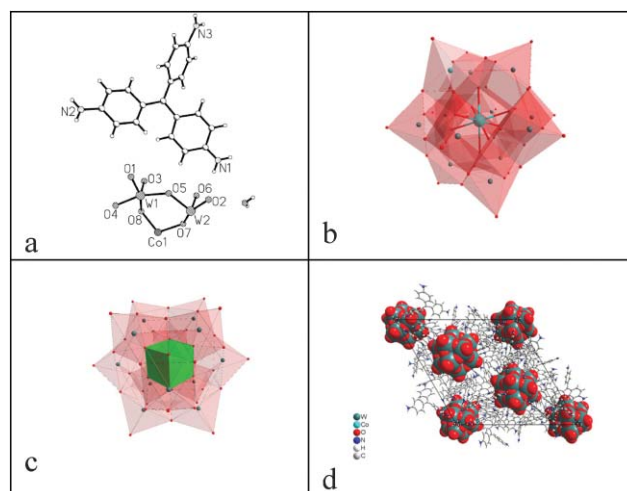
Fig. 3 Molecular structure of $[(C_{19}H_{18}N_3)_6][\alpha\text{-}CoW_{12}O_{40}]\cdot H_2O$ (**3**). (a) Asymmetric unit. Polyhedral structure of the Keggin ion $[CoW_{12}O_{40}]^{6-}$ with disorder in the tetrahedral CoO_4 unit shown, (b) as a ball and stick representation (blue: Co; red: O; grey: W) and (c) as a pseudo-cubic polyhedron. (d) Packing diagram when viewed along *c*-axis.

disorder of Keggin ions has been observed previously.[9] ESI-MS in the negative ion mode provides supporting characterisation: experimental m/z 969.5; theory for $[H_3CoW_{12}O_{40}]^{3-}$: 969.4 (2908.12/3).

This work demonstrates that crystalline salts of the dye cation pararosaniline $[C_{19}H_{18}N_3]^+$ with a variety of polyoxometalate anions are readily formed under a range of synthetic conditions. Salt **1** shows interesting optical energy interactions between the cations and anions. The approach is readily extendable to interaction of the full range of triarylmethane dye cations with the numerous photoactive polyoxometalate anions and will provide an interesting set of photoactive hybrid materials.

Notes and references

1 (*a*) Special issue in *Chem. Rev.*, 1998, **98**(1), and references therein; (*b*) D. L. Long, E. Burkholder and L. Cronin, *Chem. Soc. Rev.*, 2007, **36**, 105.
2 D. F. Duxbury, *Chem. Rev.*, 1993, **93**, 381.
3 G. Liu, Q. Li and S. W. Zhang, *Z. Anorg. Allg. Chem.*, 2002, **628**, 1895.
4 (*a*) C. L. Hill and I. A. Weinstock, *Nature*, 1997, **388**, 332; (*b*) R. Neumann and M. Dahan, *Nature*, 1997, **388**, 353; (*c*) W. B. Kim, T. Voitl, G. J. Rodriguez-Rivera and J. A. Dumesic, *Science*, 2004, **305**, 1280; (*d*) K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi and N. Mizuno, *Science*, 2003, **300**, 964; (*e*) C.-X. Yin and R. G. Finke, *Inorg. Chem.*, 2005, **44**, 4175; (*f*) T. E. Keyes, E. Gicquel, L. Guerin, R. J. Forster, V. Hultgren, A. M. Bond and A. G. Wedd, *Inorg. Chem.*, 2003, **42**, 7897; (*g*) M. K. Seery, L. Guerin, R. J. Forster, E. Gicquel, V. Hultgren, A. G. Wedd and T. E. Keyes, *J. Phys. Chem. A*, 2004, **108**, 7399; (*h*) P. Mialane, A. Dolbecq and F. Sécheresse, *Chem. Commun.*, 2006, 3477; (*i*) T. Rüther, V. M. Hultgren, B. P. Timko, A. M. Bond, W. R. Jackson and A. G. Wedd, *J. Am. Chem. Soc.*, 2003, **125**, 10133; (*j*) N. Fay, V. M. Hultgren, A. G. Wedd, T. E. Keyes, R. J. Forster, D. Leane and A. M. Bond, *Dalton Trans.*, 2006, 4218.
5 T. Hori, O. Tamada and S. Himeno, *J. Chem. Soc., Dalton Trans.*, 1989, 1491.
6 A. M. Bond, D. M. Way, A. G. Wedd, R. G. Compton, J. Booth and J. C. Eklund, *Inorg. Chem.*, 1995, **34**, 3378.
7 (*a*) A. F. Masters, S. F. Gheller, R. T. C. Brownlee, M. J. O'Connor and A. G. Wedd, *Inorg. Chem.*, 1980, **19**, 3866; (*b*) J. Q. Xu, R. Z. Wang, G. Y. Yang, Y. H. Xing, D. M. Li, W. M. Bu, L. Ye, Y. G. Fan, G. D. Yang, Y. Xing, Y. H. Lin and H. Q. Jia, *Chem. Commun.*, 1999, 983; (*c*) R. S. Rarig and J. Zubieta, *Inorg. Chim. Acta*, 2001, **312**, 188.
8 (*a*) N. Casaň-Pastor, P. Gomez-Romero, G. B. Jameson and L. C. W. Baker, *J. Am. Chem. Soc.*, 1991, **113**, 5658; (*b*) A. L. Nolan, C. C. Allen, R. C. Burns, D. C. Craig and G. A. Lawrance, *Aust. J. Chem.*, 2000, **53**, 59.
9 (*a*) R. Neier, C. Trojanowski and R. Mattes, *J. Chem. Soc., Dalton Trans.*, 1995, 2521; (*b*) H. T. Evans, Jr. and M. T. Pope, *Inorg. Chem.*, 1984, **23**, 501.