Polynuclear cyanoruthenate chromophores based on hexaaza-triphenylene containing up to twelve cyanides: photophysical and structural properties†

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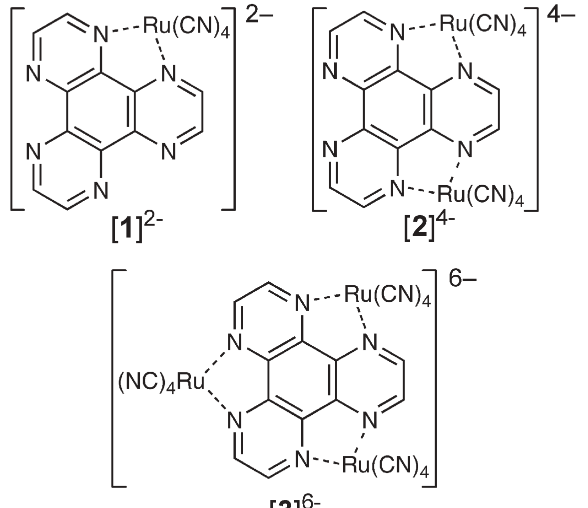
The complexes $[Ru(CN)_4(HAT)]^{2-}$, $[\{Ru(CN)_4\}_2(\mu^2\text{-}HAT)]^{4-}$ and $[\{Ru(CN)_4\}_3(\mu^3\text{-}HAT)]^{6-}$ (HAT = hexaaza-triphenylene) contain four, eight and twelve externally-directed cyanide ligands, respectively; they show strongly solvatochromic and intense MLCT absorptions, and $[3]^{6-}$ forms a high-dimensionality cyanide-bridged coordination network with Nd(III), in which Ru → Nd energy transfer results in sensitised near-IR luminescence.

The complex $[Ru(bipy)(CN)_4]^{2-}$, first reported by Bignozzi and Scandola in 1986, has attracted attention recently because of a unique combination of useful properties.[1,2] Like its better-known cousin $[Ru(bipy)_3]^{2+}$, it has a luminescent Ru → bipy ^{3}MLCT excited state, which is relatively long lived ($\approx$100 ns) in protic solvents. In addition to this, however, it has several other advantages. Firstly, it is strongly solvatochromic, with its ^{1}MLCT and ^{3}MLCT levels, and Ru(II)/Ru(III) redox potential, varying over a wide range in different solvents due to different degrees of hydrogen bonding between the cyanide lone pairs and the solvent. The ^{3}MLCT emission maximum varies from 610 nm in water to $\approx$800 nm in non-hydrogen bonding solvents such as MeCN and DMF, which means that the ability of $[Ru(bipy)(CN)_4]^{2-}$ to act as an energy donor in its excited state can be tuned by varying the solvent composition, which has been exploited as the basis of interesting switching effects.[3] Secondly, the cyanide groups are effective ligands for other metal ions, which means that heteronuclear assemblies based on cyanide-bridged coordination networks can be formed, and we recently demonstrated that energy transfer from $[Ru(bipy)(CN)_4]^{2-}$ to lanthanide(III) ions across a cyanide bridge resulted in sensitised near-IR lanthanide luminescence.[4] Thirdly, the ability of the cyanide groups to act as hydrogen bond acceptors provides the basis for incorporation of $[Ru(bipy)(CN)_4]^{2-}$ into hydrogen-bonded supramolecular assemblies.[5] Finally, the cyanide group provides a convenient spectroscopic handle for monitoring the excited state using transient IR spectroscopy, since the position of the CN vibrations is sensitive to the electron distribution in the complex.[6]

Higher nuclearity analogues of $[Ru(bipy)(CN)_4]^{2-}$ are essentially unknown; we have recently prepared dinuclear $[\{Ru(CN)_4\}_2(\mu\text{-}bpym)]^{4-}$ and used it as the basis of coordination networks with lanthanide cations.[7] In this communication we describe the syntheses, spectroscopic and some structural properties of the series of complexes $[Ru(CN)_4(HAT)]^{2-}$ ($[\mathbf{1}]^{2-}$), $[\{Ru(CN)_4\}_2(\mu^2\text{-}HAT)]^{4-}$ ($[\mathbf{2}]^{4-}$) and $[\{Ru(CN)_4\}_3(\mu^3\text{-}HAT)]^{6-}$ ($[\mathbf{3}]^{6-}$) (Scheme 1), in which one, two or three $\{Ru(CN)_4\}^{2-}$ units are connected to the bidentate sites of the tri-topic ligand hexaaza-triphenylene (HAT).[8] The extended aromatic bridging ligand and the presence of up to three chromophoric centres results in a remarkably intense, low energy,[9] highly solvatochromic absorption of light. The connectivity of up to 12, provided by the externally-directed cyanide binding sites of $[\{Ru(CN)_4\}_3(\mu^3\text{-}HAT)]^{6-}$, is unprecedented[10] in cyanide-based coordination networks, for which the highest potential connectivity until now has arisen from octacyanometallates of Mo and W.[11]

Reaction of HAT with 3.6 equivalents of $K_4[Ru(CN)_6]\cdot 3H_2O$ in aqueous acid (pH 1.3) at reflux for 48 h afforded a deep violet solution, from which the complexes $[\mathbf{1}]^{2-}$ (orange-red), $[\mathbf{2}]^{4-}$ (deep red) and $[\mathbf{3}]^{6-}$ (violet) could be isolated as their sodium salts by ion-exchange chromatography on Sephadex QAE-25, eluting with aqueous NaI.‡ In this form, the complexes are water soluble. To render them soluble in organic solvents, the complexes were converted to their PPN$^+$ salts (PPN$^+$ is $Ph_3P{=}N{=}PPh_3{}^+$), which are soluble in polar organic solvents such as MeCN and DMF.[12] The



Scheme 1 Structural formulae of the new cyanoruthenate complexes.

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complexes were satisfactorily characterised on the basis of their elemental analyses and ^{1}H NMR spectra; full details are in Supporting Information.†

The intense colours of the complexes arise from ^{1}MLCT absorptions,[1] which are lower in energy than those of the parent complex $[Ru(bipy)(CN)_4]^{2-}$ because the extended aromatic framework of the HAT ligand means that its π* orbitals are relatively low in energy.[9] For mononuclear $[\mathbf{1}]^{2-}$, the absorption maximum is at 443 nm, *cf.* 400 nm for $[Ru(bipy)(CN)_4]^{2-}$. Coordination of the second and third metal centres to give $[\mathbf{2}]^{4-}$ and $[\mathbf{3}]^{6-}$ results in (i) a red-shift of this absorption maximum to 478 and then 524 nm, respectively, in water, and an approximate trebling of the extinction coefficient to 28 000 M^{-1} cm^{-1} in $[\mathbf{3}]^{6-}$ (Fig. 1). No luminescence could be detected in aqueous solution, but luminescence spectra of the sodium salts show the presence of weak emission in the red/near-IR region which red-shifts and becomes weaker from $[\mathbf{1}]^{2-}$ to $[\mathbf{3}]^{6-}$ (Fig. 1).

The solvatochromism of complexes of this type is well known and is related to the number of cyanide ligands available for interaction with the solvent.[2] Thus, for example, $[Ru(bipy)(CN)_4]^{2-}$, with four cyanides, shows a greater variation in its absorption and emission energies than $[Ru(bipy)_2(CN)_2]$, which has only two cyanides.[2] Complexes $[\mathbf{2}]^{4-}$ and $[\mathbf{3}]^{6-}$ have eight and twelve cyanide groups, respectively, to interact with the solvent, and their solvatochromic behaviour is accordingly enhanced; Fig. 1 showing their absorption spectra in DMF compared to those in water. The effect for $[\mathbf{3}]^{6-}$, in particular, is quite dramatic, with its absorption maximum in DMF being red-shifted to 692 nm and the absorption manifold being broadened to such an extent that the complex becomes a panchromatic absorber throughout the 450–1000 nm region, with at least four components being apparent in the MLCT absorption manifold. Complex $[\mathbf{2}]^{4-}$ in DMF, likewise, absorbs across the range *ca.* 450–950 nm. In solvents of intermediate hydrogen bonding ability, intermediate absorption spectra can be obtained, with Fig. 1 showing the extremes. For example, the absorption maximum of $[\mathbf{3}]^{6-}$ occurs at 524, 575, 632, 666 and 692 nm in water, MeOH, CH_2Cl_2, MeCN and DMF, respectively. These complexes, particularly $[\mathbf{2}]^{4-}$ and $[\mathbf{3}]^{6-}$, are therefore strong light absorbers, whose ability to, for example, act as energy donors in polynuclear assemblies or harvest light in solar cells is tunable across a wide range of wavelengths.

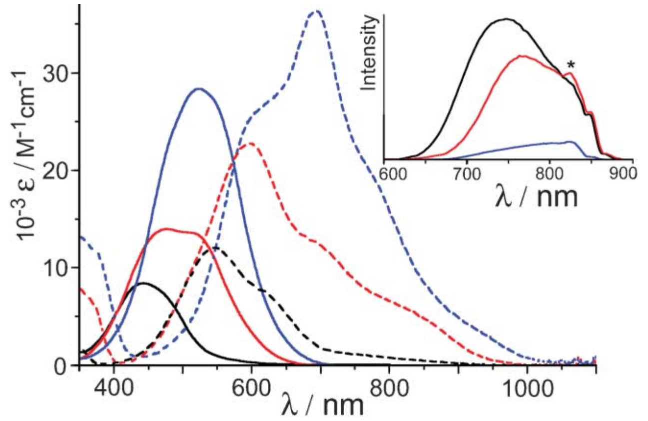

Fig. 1 Main picture: Absorption spectra of $[\mathbf{1}]^{2-}$ (black lines), $[\mathbf{2}]^{4-}$ (red lines) and $[\mathbf{3}]^{6-}$ (blue lines) as their sodium salts in water (solid lines) and their PPN salts in DMF (dashed lines). The inset shows the luminescence spectra of the sodium salts as powders using the same colour scheme (the features denoted * are artefacts arising from the correction algorithm applied by the luminescence spectrometer).

The crystal structure of the Nd(III) salt of $[\mathbf{3}]^{6-}$, $Nd_2[\{Ru(CN)_4\}_3(\mu^3\text{-HAT})]\cdot 23H_2O$, illustrates the potential of these high connectivity complex anions as components of coordination networks (Fig. 2).§ The structure consists of two-dimensional sheets, in which the six cyanides of each $[\{Ru(CN)_4\}_3(\mu^3\text{-HAT})]^{6-}$ unit that are in the same plane as the HAT ligand all coordinate to Nd(III) centres. Each Nd(III) is 9-coordinate, from five water and four cyanide ligands, with three of the cyanide ligands coming from ‘in-plane’ $[\mathbf{3}]^{6-}$ units. These sheets are held together by two additional bridging cyanide interactions from two of the six axial cyanides, which connect to

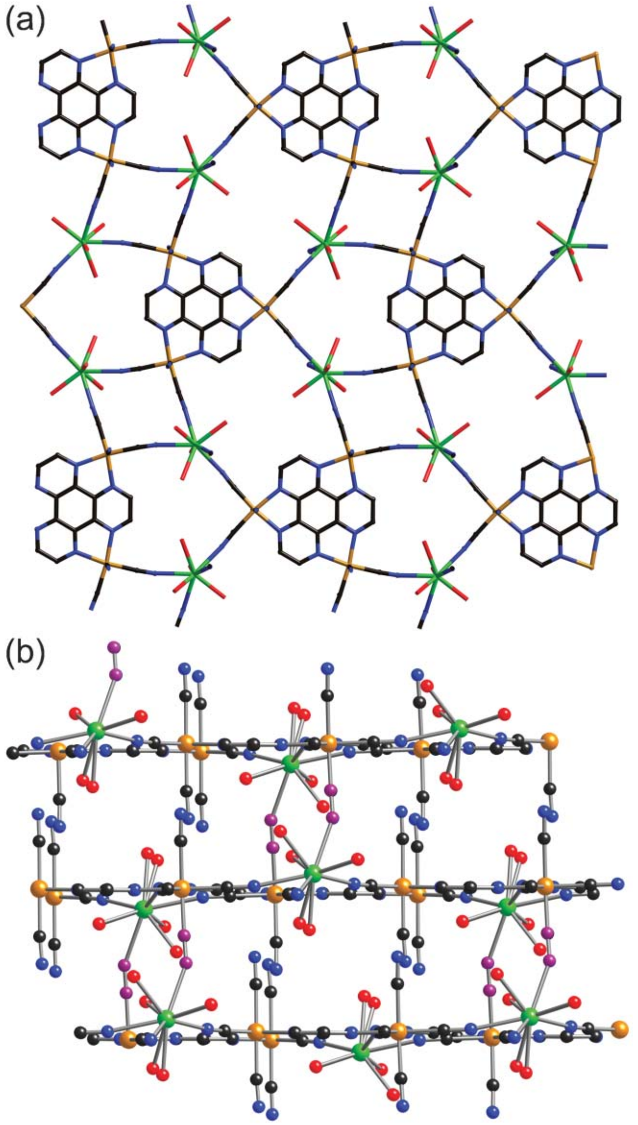

Fig. 2 Two views of the structure of $Nd_2[\{Ru(CN)_4\}_3(\mu^3\text{-HAT})]\cdot 23H_2O$: (a) a view showing one of the two-dimensional layers containing the $[\mathbf{3}]^{6-}$ units and the Nd(III) centres (C = black, N = blue, O = red, Nd = green, Ru = orange); (b) a view perpendicular to the first one showing the layers edge-on with the cyanide ligands, which act as ‘pillars’ linking the layers, coloured in purple. For selected bond lengths and angles, see the ESI.†

Nd(III) centres in the layers above and below. Accordingly, each $[\{Ru(CN)_4\}_3(\mu^3\text{-HAT})]^{6-}$ unit uses eight of its twelve cyanide ligands in bridging interactions to propagate the network (six in the plane; two axial on the same face of the $[\mathbf{3}]^{6-}$ unit, connected to the same adjacent layer), with the rest being involved in hydrogen bonding interactions with some of the lattice water molecules or the Nd-bonded water ligands in adjacent layers.

The ability of the $[\mathbf{3}]^{6-}$ chromophore to act as a sensitiser for lanthanide luminescence in these networks was shown by excitation of a solid sample of $Nd_2[\{Ru(CN)_4\}_3(\mu^3\text{-HAT})]\cdot23H_2O$ at 337 nm. This resulted in the appearance of sensitised luminescence from Nd(III) in the near-IR region, with characteristic emission maxima at 1060 and 1340 nm from the $^4F_{3/2} \rightarrow {}^4F_{11/2}$ and $^4F_{3/2} \rightarrow {}^4F_{13/2}$ transitions, respectively, and a lifetime of $\approx$100 ns was obtained at each wavelength.¶

In conclusion, these new polynuclear cyanoruthenate chromophores are of interest for both their structural properties (in cyanide-bridged coordination networks with high connectivities), and for their photophysical properties (with the ability to act as panchromatic light absorbers and energy donors whose properties can be tuned by the nature of the solvent).

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Notes and references

‡ **Syntheses**: A solution of 1,4,5,8,9,12-hexaazatriphenylene (0.12 g, 0.5 mmol) and $K_4[Ru(CN)_6]\cdot3H_2O$ (0.84 g, 1.8 mmol) in aqueous HCl at pH 1.3 was heated under reflux with stirring for 48 h and then cooled down to room temperature. The resulting dark violet solution was filtered over Celite to remove unreacted HAT and then evaporated to dryness. The solid residue was dissolved in the minimum quantity of water and MeOH added to precipitate unreacted $K_4[Ru(CN)_6]\cdot3H_2O$, which was filtered off. The product was purified by column chromatography on a SEPHADEX QAE-25, eluting with aqueous NaI. The use of 0.1 M NaI resulted in the elution of orange-red $Na_2[Ru(C_{12}N_6H_6)(CN)_4]$ ($Na_2[\mathbf{1}]$). Increasing the concentration to 0.2 M then resulted in the elution of deep red $Na_4[Ru_2(C_{12}N_6H_6)(CN)_8]$ ($Na_4[\mathbf{2}]$) which was the major product. Finally, the use of 0.3 M NaI resulted in the elution of violet $Na_6[Ru_3(C_{12}N_6H_6)(CN)_{12}]$ ($Na_6[\mathbf{3}]$). Solutions of the three complexes so-obtained were reduced in volume to 5 cm^3. The products were precipitated by the addition of acetone, further recrystallized from H_2O/acetone and dried *in vacuo* to give the pure products as a orange-red (mononuclear), deep red (dinuclear) and violet (trinuclear) products. Yields: $Na_2[\mathbf{1}]$, 25%; $Na_4[\mathbf{2}]$, 39%; $Na_6[\mathbf{3}]$, 18%. Conversion to the PPN^+ salts was accomplished using the method in ref. 12.

$Nd_2[\{Ru(CN)_4\}_3(\mu^3\text{-HAT})]\cdot23H_2O$ was prepared as follows. Solutions of $Na_6[\mathbf{3}]$ (40 μmol) in water (1 ml) and $Nd(NO_3)_3\cdot6H_2O$ (0.2 mmol) in water (1 ml) were mixed to give a deep violet solution that was stirred for 10 min. Slow evaporation of the resulting solution over a period of 2 weeks resulted in a crop of crystals that were filtered off, washed with methanol and dried *in vacuo* (yield: 68%). IR: v_{max}/cm^{-1}: 3399(vs), 2120(m), 2084(s), 1618(m), 1455(m), 1384(s) and 1330(m).

§ **Crystallography**: A small crystal of $Nd_2[\{Ru(CN)_4\}_3(\mu^3\text{-HAT})]\cdot23H_2O$ (0.20 × 0.15 × 0.07 mm) was mounted on a Bruker APEX-2 diffractometer at 150K. Formula: $C_{24}H_{52}N_{18}Nd_2O_{23}Ru_3$, F_w = 1552.53, monoclinic, $P2_1/m$, a = 8.7731(7), b = 25.689(2), c = 11.0330(9) Å, β = 101.834(4)°, V = 2433.7(3) Å^3, Z = 2, ρ_{calc} = 2.119 g cm^{-3}, μ(Mo-K$_\alpha$) = 3.101 mm^{-1}, λ = 0.71073 Å. 51709 reflections were measured which afforded 5651 reflections (R_{int} = 0.128) after merging. Refinement of 350 parameters converged at $R1$ = 0.0668 (selected data with $I > 2\sigma(I)$), w$R2$ = 0.1239 (all data). The $[\{Ru(CN)_4\}_3(\mu^3\text{-HAT})]^{6-}$ unit lies astride a mirror plane which includes Ru(2) and which bisects the HAT ligand. CCDC 297959. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601876a

¶ This lifetime for Nd(III)-based emission was the best fit of the observed emission to a single exponential decay. A better fit could be obtained using a biexponential decay, with lifetime components of 44 and 150 ns in a 3 : 1 ratio (based on the pre-exponential values). In the crystal structure, all Nd(III) centres are crystallographically-equivalent so should have the same emission lifetime. However, we have found that in crystalline solids, the luminescence behaviour is considerably more complex than in solution, possibly due to crystal defects and/or surface effects resulting in inhomogeneities (ref. 4).

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