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ARTICLE TYPE

A Mn(II) coordination framework incorporating the redox-active tris(4-(pyridin-4-yl)phenyl)amine ligand (NPy₃): Electrochemical and Spectral Properties

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A new multifunctional coordination framework, [Mn(NPy₃)Cl·3MeOH·DMF]_n, containing the redox-active tris(4-(pyridine-4-yl)phenyl)amine ligand (NPy₃) has been synthesised and characterised. The redox properties of the framework have been investigated and the oxidised state of the framework generated chemically and spectroelectrochemically. This material exhibits multifunctionality by virtue of the ability to switch the fluorescence 'on' and 'off' with redox state.

The development of porous materials that exhibit multifunctional behaviour are attracting considerable attention due to their potential for a plethora of practical applications. Coordination frameworks that are capable of reversibly transforming between different redox states are particularly advantageous, as surfaces with different electrostatic properties are able to be accessed within a given framework structure. By exploiting the differential electrostatic interactions of analytes and guest molecules with the surface of the material, host-guest interactions can be utilised for the selective adsorption and desorption of gases.^{[1],[2],[3],[4]} Frameworks with reversible redox state changes also have potential as electronic switches, where the difference in conductivity with between redox states would allow the material to be selectively turned 'on' and 'off'.^[5]

Coordination frameworks and metal-organic frameworks (MOFs) are ideal candidates for the exploration of the fundamental aspects of multifunctionality in 3-dimensional coordination space.^{[6],[7]} The advantageous structural properties of these materials including their porosities, in addition to their thermal and chemical robustness in many cases, endows them with the potential for use in a variety of applications.

The incorporation of a redox-active ligand into coordination frameworks offers one elegant strategy towards the synthesis of multifunctional materials. The triarylamine functionality has been widely explored, particularly in organic mixed-valence chemistry,^{[8],[9]} and can be reversibly oxidised to its radical cation and dication states by electrochemical or chemical methods.^{[8],[10]} The redox and spectral properties of the triarylamine core are well known, and the functionality is an attractive moiety for incorporation into a coordination framework. A number of frameworks containing the triarylamine functionality have previously been reported, however, the core has predominantly

been employed as a an *N*-centred tridentate structural motif,^{[11],[12]} while the redox activity has in the majority of cases, not been explored.^{[1],[13],[14]}

Herein, we report the synthesis of a Mn²⁺ framework containing the redox-active tris(4-(pyridine-4-yl)phenyl)amine ligand (NPy₃) and its electrochemical and spectral properties. The synthesis of an electroactive framework through incorporation of a redox-active ligand, where the oxidised state of framework can be generated, demonstrates the synthetic accessibility of materials that may exhibit multifunctional properties.

[Mn(NPy₃)Cl·3MeOH·DMF]_n was synthesised by heating MnCl₂·4H₂O and NPy₃ in a mixture of DMF and methanol at 45 °C for 30 minutes to obtain the framework as prismatic yellow crystals. The synthesis was readily scaled to produce 0.5 g of the material upon increasing the reaction time from 30 minutes (on a 20 mg scale) to 24 hours.

The structure was refined in the orthorhombic space group *Pbcn*. The Mn²⁺ centre exhibits an octahedral coordination sphere, with four nitrogen donors in the equatorial plane from four separate NPy₃ ligands and two chloride ligands located on the axial positions of the metal centre (Figure 1a). The phenyl rings on the NPy₃ ligand exhibit the typical propeller-like orientation which is common for triphenylamine systems.^[15]

Elemental analysis suggests that there are 3 methanol molecules and one DMF molecule present in the asymmetric unit. In the region below 180 °C in the thermal gravimetric analysis, an 82% weight loss was observed (ESI), which corresponds approximately to the loss of 3 methanol molecules and 1 DMF molecule (calculated 83%). Two methanol molecules are lost from the framework below the inflection point observed at 55 °C. The loss of the third methanol molecule (along with the DMF molecule) occurs between 55 °C and 180 °C, where the higher temperature required for removal of the methanol molecules from the pores of the framework is indicative of the highly interpenetrated nature of the structure. Using the SQUEEZE function in PLATON,^[16] a void accessible volume of 31% was calculated.

The framework consists of a series of nets containing four NPy₃ ligands coordinated to four different Mn²⁺ centres forming a distorted diamondoid shape, which extends in 2 dimensions to form a sheet-like structure (Figure 1b). The interwoven nature of the 2D sheets leads to the 3D structure (Figure 1c).

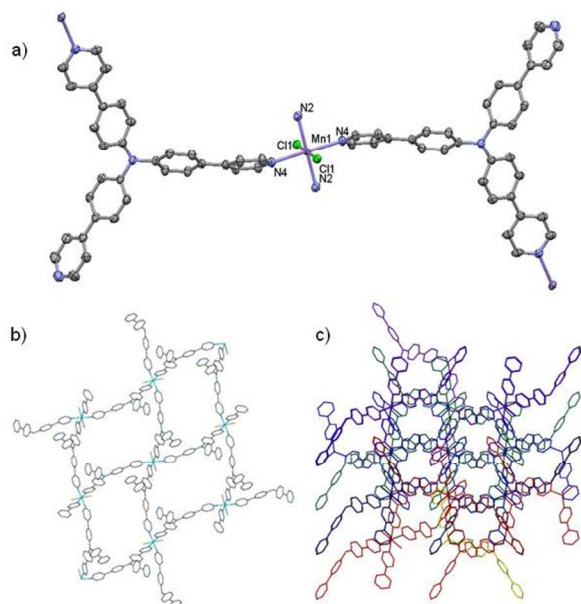


Fig. 1 Crystal structure of the $[\text{Mn}(\text{NPy}_3)\text{Cl}\cdot 3\text{MeOH}\cdot \text{DMF}]_n$ framework showing a) coordination sphere around the Mn^{2+} centre; b) one network containing four NPy_3 ligands and four Mn^{2+} metal centres along the b axis; and c) interwoven 2D networks forming a 3D network along the a axis.

The electrochemical properties of $[\text{Mn}(\text{NPy}_3)\text{Cl}\cdot 3\text{MeOH}\cdot \text{DMF}]_n$ were investigated by performing solid state cyclic voltammetry in 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{PF}_6/\text{CH}_3\text{CN}$ electrolyte at scan rates over the range 100–1000 mV/s. The anodic region displays one quasi-reversible peak at ~ 1.0 V vs Fc/Fc^+ which can be assigned to oxidation of the triarylamine core of the NPy_3 ligand (Figure 2a). The overlapping redox wave at ~ 0.75 V vs Fc/Fc^+ may be indicative of the one electron oxidation of the triarylamine core to the radical cation state, such that the second oxidative peak at ~ 1.0 V vs Fc/Fc^+ is indicative of oxidation from the radical cation to the dication state.^{[8],[10],[13]} The peak at ~ 1.0 V vs Fc/Fc^+ becomes increasingly reversible at faster scan rates, indicating the improved chemical stability of the radical cation state of the framework at faster scan rates which inhibit chemical degradation.

The redox process corresponding to oxidation of the Mn^{2+} centre to Mn^{3+} is likely to be overlapped by the peak due to oxidation of the triarylamine core. One irreversible redox process is observed in the cathodic region, which may correspond to reduction of the Mn^{3+} centre to Mn^{2+} (Figure 2b).

The UV/Vis/NIR spectrum of $[\text{Mn}(\text{NPy}_3)\text{Cl}\cdot 3\text{MeOH}\cdot \text{DMF}]_n$ is characterised by electronic transitions due to the Mn^{2+} centre and the triarylamine core of the NPy_3 ligand (Figure 3). The broad band above 30000 cm^{-1} is attributed to the π to π^* transition of the triarylamine ligand.^[10] No bands were observed in the NIR region. The absence of $d-d$ bands is consistent with the high spin d^5 Mn^{2+} octahedral centre. Despite the presence of this centre, which is both spin- and Laporte-forbidden, three distinct peaks are observed due to charge transfer transitions from the ${}^6\text{A}_1$ ground state to the ${}^4\text{G}$, ${}^4\text{D}$, ${}^4\text{P}$ and ${}^4\text{F}$ excited states of the Mn^{2+} ion.^{[17],[18]}

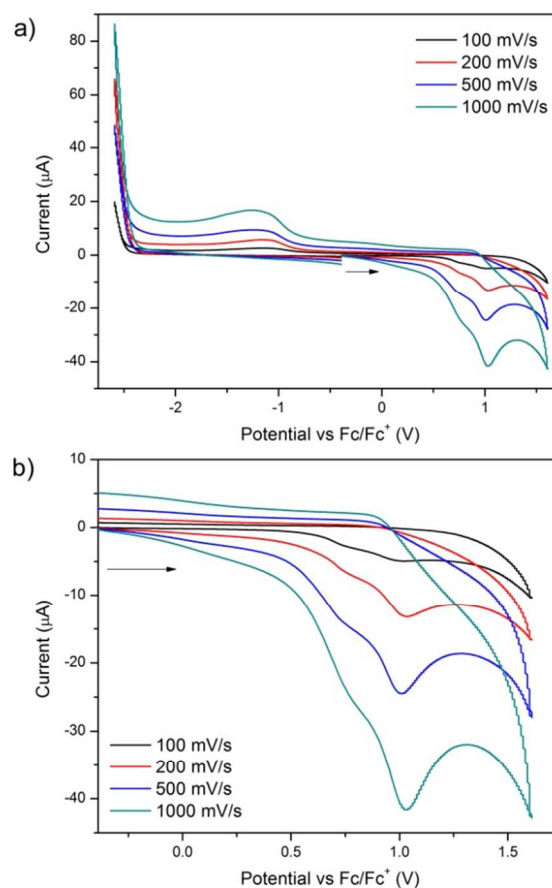


Fig. 2 Solid state cyclic voltammograms of $[\text{Mn}(\text{NPy}_3)\text{Cl}\cdot 3\text{MeOH}\cdot \text{DMF}]_n$ in 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{PF}_6/\text{CH}_3\text{CN}$ electrolyte at scan rates in the range 100–1000 mV/s. Potentials are reported vs Fc/Fc^+ and the arrow indicates the direction of the forward scan.

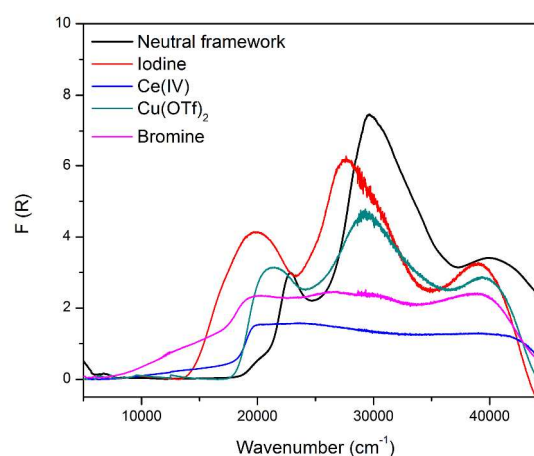


Fig. 3 Overlay of the UV/Vis/NIR diffuse reflectance spectra of $[\text{Mn}(\text{NPy}_3)\text{Cl}\cdot 3\text{MeOH}\cdot \text{DMF}]_n$ and its various oxidised analogues over the range $5000\text{--}45000\text{ cm}^{-1}$.

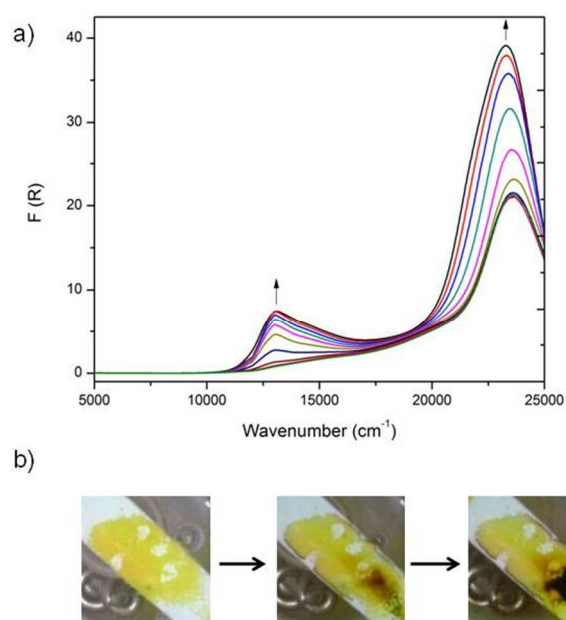


Fig. 4 *In situ* solid state spectroelectrochemistry on $[\text{Mn}(\text{NPY}_3)\text{Cl}\cdot 3\text{MeOH}\cdot \text{DMF}]_n$ in 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{PF}_6/\text{CH}_3\text{CN}$ electrolyte showing a) oxidation to the radical cation state and b) photographs through the transparent working electrode during the spectroelectrochemical experiment with an increasing anodic potential.

Chemical oxidation of the $[\text{Mn}(\text{NPY}_3)\text{Cl}\cdot 3\text{MeOH}\cdot \text{DMF}]_n$ framework was achieved *ex situ* using bromine vapour, and formation of the radical cation was evidenced by the presence of a band at 11860 cm^{-1} (Figure 3). Attempts to use several different chemical oxidants including NOBF_4 , copper triflate and $\text{Ce}(\text{IV})$ led to decomposition of the material.^[19] A small degree of oxidation was observed using iodine as the oxidant, as was evident from the red shift of the band at $\sim 22720\text{ cm}^{-1}$ to 19790 cm^{-1} , however no bands corresponding to formation of the radical cation state of the triarylamine centre were observed. The red shift and broadening of this band to 19790 cm^{-1} may be indicative of oxidation of the Mn^{2+} centre to Mn^{3+} where this peak would correspond to the spin allowed electronic transition from the 5E_g to ${}^5T_{2g}$ state.^[17] The use of bromine as the chemical oxidant was shown to be more appropriate for the oxidation of the triarylamine unit in the $[\text{Mn}(\text{NPY}_3)\text{Cl}\cdot 3\text{MeOH}\cdot \text{DMF}]_n$ framework to the corresponding radical cation, as bromine has a higher oxidation potential (0.07 V vs Fc/Fc^+ in acetonitrile) when compared to that of iodine ($-0.14\text{ V vs Fc/Fc}^+$ in acetonitrile).^[19]

In situ solid state spectroelectrochemistry^[20] on the $[\text{Mn}(\text{NPY}_3)\text{Cl}\cdot 3\text{MeOH}\cdot \text{DMF}]_n$ framework was conducted in 0.1 M $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{PF}_6/\text{CH}_3\text{CN}$ electrolyte over the potential range of 0–2.75 V in an attempt to elucidate the spectral properties of the radical cation form of the framework (Figure 4). Potentials more anodic than those required in the electrochemical measurements were employed during spectroelectrochemistry due to the higher cell resistance.

The framework exhibited a colour change from bright yellow to brown upon application of an anodic potential of 2.0 V (Figure 4b). This colour change was accompanied by the appearance of a band at 12730 cm^{-1} , which is in the range for the localised D_0 to D_1 electronic transition of the radical cation state of the triarylamine core (Figure 4a).^[10] A slight red shift of the π to π^*

transition of the triarylamine centre from 23250 to 23450 cm^{-1} was also observed upon oxidation of the framework, and can be attributed to formation of the radical cation state of the triarylamine core.

Following application of a higher anodic potential of 2.5 V, the framework was observed to degrade with an overall decrease in intensity across the entire spectral region. It is likely that oxidation of the Mn^{2+} centre to Mn^{3+} drives ligand dissociation and degradation of the framework. No bands were observed in the NIR region of the spectrum, indicating the absence of any intervalence charge transfer transitions in this high spin d^5 Mn^{2+} framework. This is not surprising given the 21.5 \AA distance between adjoining triarylamine cores, which are bridged via a Mn^{2+} centre.

The NPY_3 ligand has previously been demonstrated to exhibit fluorescence upon excitation at 380 nm into the π to π^* transition of the triphenylamine core.^[13] It was of particular interest to ascertain whether fluorescence was retained in the $[\text{Mn}(\text{NPY}_3)\text{Cl}\cdot 3\text{MeOH}\cdot \text{DMF}]_n$ framework, as the triarylamine chromophore has previously been used in photoluminescent and LED devices owing to its fluorescent properties.^[21] A fluorescence peak at 446 nm was observed for $[\text{Mn}(\text{NPY}_3)\text{Cl}\cdot 3\text{MeOH}\cdot \text{DMF}]_n$ upon excitation at 400 nm (ESI). A small Stokes shift of 7 nm was observed upon comparison with the absorption spectrum. The framework which had been oxidised with bromine vapour, however, was not fluorescent, demonstrating that the fluorescence can be turned 'on' and 'off' by changing the redox state.

In summary, a new framework, $[\text{Mn}(\text{NPY}_3)\text{Cl}\cdot 3\text{MeOH}\cdot \text{DMF}]_n$ containing the redox-active tris(4-(pyridine-4-yl)phenyl)amine ligand (NPY_3) has been synthesised and crystallographically characterised. The electrochemical and spectral properties of the framework have been investigated and the radical cation state of the framework has been successfully generated. Importantly, the fluorescence response is dependent on the redox state of the framework, demonstrating the potential future application of these materials in host-guest sensing. The use of ligands containing redox-active entities, such as the tris(4-(pyridine-4-yl)phenyl)amine ligand represents an elegant strategy towards the development of multifunctional materials.

Notes and references

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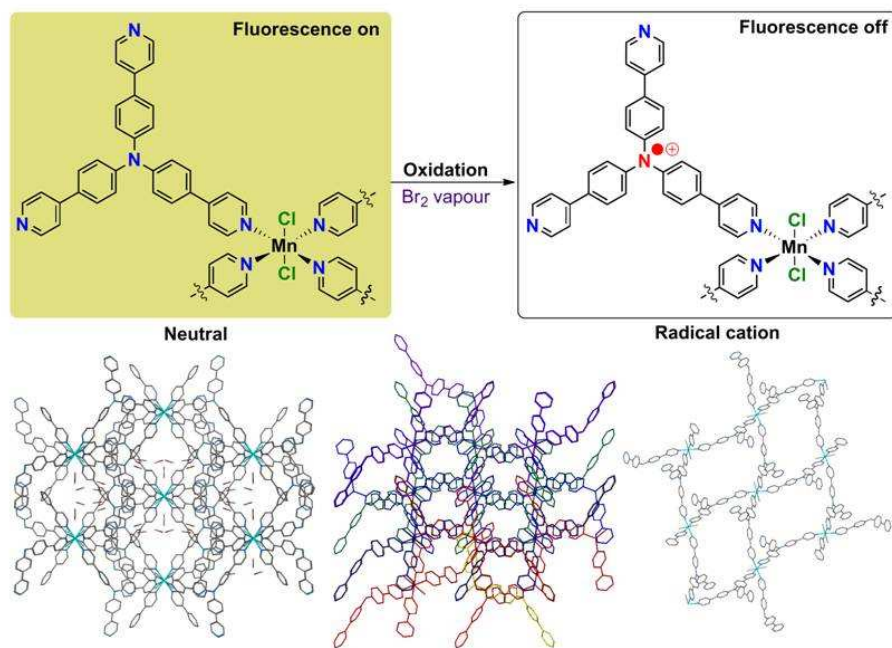
[†] Electronic Supplementary Information (ESI) available: An X-ray crystallographic file in CIF format, table of crystallographic information, full experimental details, powder X-ray diffraction, TGA, infrared and fluorescence spectra for the neutral and oxidised frameworks. See DOI: 10.1039/b000000x/

[‡] Crystallographic data for $\text{C}_{33}\text{H}_{24}\text{ClMnO}_{.5}\text{N}_4$ ($M = 539.48$): orthorhombic, space group $Pbcn$, $a = 28.7320(1)\text{ \AA}$, $b = 13.5996(1)\text{ \AA}$, $c = 17.5750(1)\text{ \AA}$, $V = 6867.32(7)\text{ \AA}^3$, $Z = 8$, $T = 150(2)\text{ K}$, $\mu(\text{CuK}\alpha) = 1.478\text{ mm}^{-1}$, $D_{\text{calc}} = 1.044\text{ g/mm}^3$, 170412 reflections measured ($6.2 \leq 2\theta \leq 154$), 7215 unique ($R_{\text{int}} = 0.034$) which were used in all calculations. The final R_1 was 0.0342 ($>2\sigma(I)$) and wR_2 was 0.0941 (all data). CCDC 975492 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via

www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Investigation of the electronic and spectral properties of a redox-active Mn²⁺ coordination framework demonstrates the accessibility of the oxidised state of the framework upon oxidation.