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Influence of structure–activity relationships on through-space intervalence charge transfer in metal–organic frameworks with cofacial redox-active units†

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Understanding charge transfer in redox-active metal–organic frameworks (MOFs) is of fundamental importance given the potential of these materials to be used in myriad applications including porous conductors, electrocatalysts and battery materials, amongst others. An important challenge is quantifying the spectroscopic features of these materials in order to elucidate their charge transfer properties. Herein, two topologically related Zn(II) and Cd(II) frameworks, $[\text{Zn}_2(\text{DPPTzTz})_2(\text{SDC})_2]$ (1-Zn) and $[\text{Cd}_2(\text{DPPTzTz})_2(\text{SDC})_2]$ (2-Cd) (where DPPTzTz = 2,5-bis(4-(4-pyridinyl)phenyl)thiazolo[5,4-*d*]thiazole and SDC = selenophene-2,5-dicarboxylate), incorporating cofacially stacked pairs of redox-active DPPTzTz ligands are presented. The differences in the through-space intervalence charge transfer properties of the mixed-valence forms of the two frameworks generated upon solid state spectroelectrochemical reduction are quantified using Marcus–Hush theory. Further, charge transfer theory is applied to calculate electron mobilities in both extended framework systems. A larger electronic coupling constant, H_{ab} , of 118 cm^{-1} corresponding to an electron mobility, k , of $6.02 \times 10^8 \text{ s}^{-1}$ was observed for the Zn(II) analogue compared to the Cd(II) analogue ($H_{\text{ab}} = 61.2 \text{ cm}^{-1}$ and $k = 2.22 \times 10^8 \text{ s}^{-1}$) and was correlated primarily with the larger cofacial stacking distance and increasingly offset stacking geometry between DPPTzTz ligands in the latter. Establishing structure–activity relationships in electroactive MOFs, in addition to methods for quantifying their charge transfer properties, represents an important advance in fine tuning solid state materials for device applications.

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Introduction

A key structural feature in a number of early photosynthetic unicellular organisms is a cofacially arranged photoreaction trap, often described as a ‘special pair’.¹ This cofacial moiety plays a vital role in stabilising the photoexcited mixed-valence radical state using through-space intervalence charge transfer (IVCT) and facilitates the conversion of light to chemical energy. This intriguing phenomenon has been the focus of a number of qualitative biomimicry studies using discrete organic molecules mostly based on porphyrin derivatives.² On the other hand, quantitative experimental and theoretical studies on inorganic systems featuring cofacial arrangements of ligands which display through-space IVCT have been relatively limited, and are exemplified by the work by Dinolfo and Hupp on discrete inorganic molecular rectangles.³

Metal–organic frameworks (MOFs) offer an ideal platform for studying outer sphere electron transfer owing to their highly ordered nature and tunability which opens up opportunities to explore structure–activity relationships. MOFs also enable the effects of long-range order to be probed which are not possible in discrete systems.

Driven by a plethora of technological and industrial applications such as lightweight conductors, electrochromic devices and adaptive gas sorption materials, the study of electroactive MOFs has continued to gain momentum.⁴ By incorporating metal and/or ligand based redox-active components, interesting electronic and charge transfer behaviours can be introduced which can be harnessed for redox catalysis,⁵ energy storage⁶ and to induce conductivity⁷ in these materials. While the introduction of donors and acceptors into MOFs is one means of inducing charge transfer interactions,⁸ the inclusion of mixed-valence components is another key design strategy.⁹ Mixed-valence systems arise when either the metal or ligand based centres exist in different formal oxidation states; this results in a rapid oscillation of charge between the centres, manifesting in an IVCT absorption band.

To date, IVCT as a result of mixed valency in MOFs has only been observed to occur ‘through-bond’, but ‘through-space’

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interactions can also be envisaged to occur.¹⁰ One of the most prominent examples is the framework $[(\text{NBu}_4)_2\text{Fe}_2^{\text{III}}(\text{d}h\text{bq})_3]_n$ (where NBu_4 = tetrabutylammonium and $\text{d}h\text{bq}$ = dihydroxybenzoquinone and represents $\text{d}h\text{bq}^{2-}$ and $\text{d}h\text{bq}^{3-}$ in the mixed-valence state),¹¹ where charge transfer occurs between mixed-valence $\text{d}h\text{bq}$ ligands *via* the Fe^{III} centres. IVCT between mixed-valence $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ centres is also observed in the cyanido framework $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$ known as Prussian blue,¹² which gives rise to its striking colour.

An important set of tools to study charge transfer in MOFs are *in situ* solid state spectroelectrochemical (SEC) techniques,¹³ where electrochemistry is coupled with spectroscopic methods. The two key SEC techniques for study of charge transfer in frameworks are electron paramagnetic resonance (EPR) SEC,^{8,14} which allows the formation and progression of radicals in a system to be monitored, and Vis-NIR SEC, which enables insights into the evolution of charge transfer bands. Although Vis-NIR SEC permits identification of new charge transfer bands, observations remain qualitative, as the development of reliable means for quantifying solid state reflectance spectroscopic data (*i.e.*, obtaining extinction coefficients for charge transfer bands) is challenging. Quantifying spectroscopic data is crucial for application of Marcus–Hush theory which provides insight into the nature of charge transfer.¹⁵ The Robin and Day classification scheme can subsequently be applied,¹⁶ and materials can be considered in one of three classes: Class I represents redox-active materials where the centres do not interact electronically; Class II represents weakly coupled interacting centres with charge mainly localised on the sites; and Class III represents systems in which there is full delocalisation. From application of Marcus–Hush theory, increasingly detailed analyses can be obtained, including, for example, mobility calculations to connect with quantum analysis.¹⁷

Herein we describe two topologically related MOFs with $\text{Zn}(\text{II})$ and $\text{Cd}(\text{II})$ metal centres featuring cofacially stacked redox-active 2,5-bis(4-(4-pyridinyl)phenyl)thiazolo[5,4-*d*]thiazole (DPPTzTz) ligands and selenophene-2,5-dicarboxylate (SDC) co-ligands, namely $[\text{Zn}_2(\text{DPPTzTz})_2(\text{SDC})_2]$ (**1-Zn**) and $[\text{Cd}_2(\text{DPPTzTz})_2(\text{SDC})_2]$ (**2-Cd**). The through-space IVCT interaction originating from the cofacial arrangement of the ligand pairs is investigated using *in situ* SEC experiments and is quantified using Marcus–Hush theory, from which electron mobilities within cofacial units are calculated. This work represents one of the first studies to examine structure–activity relationships and their effect on IVCT in the solid state, thus providing important insights into through-space electronic communication in MOFs. Furthermore, the development of a protocol for quantifying solid state SEC spectra will be presented as a basis for applying Marcus–Hush theory to elucidate the nature of electron transfer within solid state materials.

Results and discussion

Synthesis and structural comparison

The solvothermal syntheses of **1-Zn** and **2-Cd** were achieved in DMF at 120 °C. The structure of **1-Zn** was solved and refined in the monoclinic space group $P2_1/c$ with unit cell parameters of $a = 25.811(5)$, $b = 18.453(4)$, $c = 15.943(3)$ Å and $\beta = 90.91(3)^\circ$,

while **2-Cd** was solved in the triclinic space group $P\bar{1}$ with unit cell parameters of $a = 15.868(3)$, $b = 19.123(4)$, $c = 26.124(5)$ Å and $\alpha = 82.02(3)$, $\beta = 87.25(3)$, $\gamma = 89.73(3)^\circ$.

The frameworks are isotopological (Fig. 1) and consist of two interpenetrating 3D networks (Fig. 1b) with α -Po primitive cubic topology (**pcu**), where 2D layers of the SDC ligand and metal atoms are linked together by bridging DPPTzTz ligands. The metal centres for both **2-Cd** and **1-Zn** exhibit a distorted octahedral coordination sphere each consisting of four bound O-donors in the equatorial positions from the carboxylate



Fig. 1 Representation of the crystal structures of **1-Zn** and **2-Cd** showing (a) overall structure of **1-Zn**, (b) two fold interpenetration of **1-Zn**, (c) 2D coordination geometry of selenophene dicarboxylate and $\text{Zn}(\text{II})$ nodes in **1-Zn** resulting in dimeric metal–oxygen clusters, (d) cofacial dimer pairs of the DPPTzTz ligand in **1-Zn**, (e) cofacial DPPTzTz dimers of **1-Zn** viewed normal to the plane of the TzTz cores revealing the offset nature of cofacial stacking, (f) overall structure of **2-Cd**, and (g) comparison between the metal–oxygen clusters of both frameworks exhibiting the structural differences induced by inclusion of different metal centres with atom names and distances in angstrom as given. Atom colours are grey (C), blue (N), red (O), yellow (S), green (Se), orange (Zn) and light green (Cd).





Fig. 3 Solid state EPR SEC of **1-Zn** in 0.1 M $[n\text{-Bu}_4\text{N}]\text{PF}_6/\text{MeCN}$, showing the appearance of the TzTz organic radical signal at $g = 2.0043$ upon initial reduction.

moieties. Further increasing the applied cathodic potential resulted in a reduction in the intensity of the radical bands for both materials. However, the intensity of this signal began to increase upon continued application of even higher cathodic potentials, which would not have been observed if there was straightforward reduction to the spin paired TzTz dianion state as seen in the solid state EPR SEC of DPPTzTz (ESI Fig. S6[†]). Thus the EPR SEC behaviour again suggests the occurrence of electronic communication in both **1-Zn** and **2-Cd**, resulting in a mixing of radical states. From structural data, this can be postulated to occur within the cofacial TzTz units. Upon returning the applied potential to 0 V, the EPR silent neutral states of both frameworks were reproduced, demonstrating redox reversibility.

Ex situ chemical reduction on both **1-Zn** and **2-Cd** was performed using lithium naphthalenide (LiNP) applied in stoichiometric ratios of 0.5, 1.0, 2.0 and 3.0 equivalents per TzTz core, to provide a comparison with trends observed in the *in situ* SEC data. As chemical reduction results in the intercalation of Li^+ ions for charge balance with the reduced frameworks, the extent of reduction was determined by measuring the Li content against that of Zn or Cd respectively using ICP-AES (ESI Table S3[†]). An actual reduction extent of around 70% that of the theoretical value was observed for the **1-Zn** samples, and of around 50% for the **2-Cd** samples. These results, in conjunction with PXRD data demonstrating retention of crystallinity (ESI Fig. S12 and S14;[†] Pawley extraction of unit cell parameters provided in Tables S5 and S6[†]) upon reduction, show that the frameworks respond well to chemical reduction by LiNP and the resulting intercalation of Li^+ ions.

EPR experiments were performed on chemically reduced samples to confirm the formation of the monoanion radical state. The radical signals for both **1-Zn** and **2-Cd** reduced samples occurred at comparable g -values ($g = 2.0051$ and 2.0024 , respectively) to those generated electrochemically (ESI Fig. S15 and S16[†]).

Solid state Vis-NIR SEC experiments were conducted on both **1-Zn** (Fig. 4, ESI Fig. S7[†]) and **2-Cd** (Fig. 5, ESI Fig. S9[†]), which revealed differing behaviour upon reduction which was correlated to subtle structural differences. The starting spectrum for



Fig. 4 Solid state Vis-NIR SEC of **1-Zn** in 0.1 M $[n\text{-Bu}_4\text{N}]\text{PF}_6/\text{MeCN}$ with arrows indicating progression of spectral bands at an applied potential of (a) -2.1 V; (b) -2.4 V, with insets showing the NIR region as well as photos displaying the colour of the frameworks at respective potentials.

the neutral state in the Vis-NIR SEC of **1-Zn** was dominated by the edge of the UV-Vis $\pi \rightarrow \pi^*$ transition for the DPPTzTz ligand at $27\,000\text{ cm}^{-1}$ (peak position obtained from the UV-Vis-NIR spectrum of as-synthesised **1-Zn**, ESI Fig. S17[†]). As an initial cathodic potential of -2.1 V vs. Ag/Ag^+ was applied to **1-Zn**, a set of bands in the visible region from $13\,000$ to $25\,000\text{ cm}^{-1}$ appeared. These bands were assigned to intra-ligand radical processes for the monoanion radical of DPPTzTz, in accordance with the reductive Vis-NIR SEC behaviour of the DPPTzTz ligand itself (ESI Fig. S5a[†]). Two distinct bands also appeared in the NIR region (deconvoluted spectrum shown in ESI Fig. S23a[†]), which were not observed in the Vis-NIR SEC of the DPPTzTz ligand (ESI Fig. S5a[†]). The NIR bands were assigned to a through-space IVCT transition between cofacial DPPTzTz ligands, which exist in a mixed-valence state that involves the monoanion radical state of one DPPTzTz ligand in each cofacial pair. Increasing the applied reductive potential to -2.4 V in **1-Zn** resulted in the equilibration of all visible region radical bands to their maximum intensities, suggesting that the radical mixed-valence state was being accessed fully throughout the **1-Zn** sample. This corresponded to a colour change from yellow in the neutral state, to deep green in the mixed-valence state. In





Fig. 5 Solid state Vis-NIR SEC of **2-Cd** in 0.1 M $[n\text{-Bu}_4\text{N}]\text{PF}_6/\text{MeCN}$ with arrows indicating progression of spectral bands at an applied potential of (a) -2.4 V with image of the green reduced frameworks provided; (b) -2.4 V after this potential was held for 40 min. Insets show the NIR regions for each plot.

the NIR region, the IVCT band also intensified to its maximal value at -2.4 V. Further holding the potential at -2.4 V resulted in a moderate reduction in the intensities of the radical transitions in the visible region (ESI Fig. S7d†). This was correlated with the gradual reduction to the fully reduced double dianion state within a portion of DPPTzTz cofacial dimer units, in accord with trends observed in the Vis-NIR SEC of the DPPTzTz ligand itself (ESI Fig. S5b†). Reduction to the double dianion configuration also breaks the mixed-valence interaction within cofacial DPPTzTz dimers, consistent with the observed decrease in intensity of the mixed-valence IVCT transition in the NIR region.

The Vis-NIR SEC behaviour of **2-Cd** is similar to that of **1-Zn**, aside from two key points of difference. Firstly, as the mono-anion radical state was being accessed in **2-Cd**, a further distinctive visible band at $19\,000\text{ cm}^{-1}$ appeared at -2.1 V vs. Ag/Ag^+ (ESI Fig. S9a†), which was not observed for **1-Zn**. This was assigned to a ligand to metal charge transfer (LMCT) process in **2-Cd**,²¹ facilitated by the more diffuse d-orbitals on $\text{Cd}(\text{II})$ compared to $\text{Zn}(\text{II})$. The LMCT transition at $19\,000\text{ cm}^{-1}$ subsequently decreased as the applied potential was increased to -2.3 V (ESI Fig. S9b†).

The most significant difference between the Vis-NIR SEC behaviour of **2-Cd** and **1-Zn** was apparent when the applied potential was held at -2.4 V. For **1-Zn**, this resulted in the accessing of the fully reduced double dianion configuration within only a portion of DPPTzTz dimer units. On the other hand, for **2-Cd** a reduction in intensities for all bands except for the UV $\pi \rightarrow \pi^*$ band was observed, resulting in the disappearance of all transitions associated with the radical in the visible and NIR regions (Fig. 5b). In the latter case, the behaviour suggests that the double dianion state for DPPTzTz cofacial dimers in **2-Cd** is more readily accessed compared with **1-Zn**.

The differences in the spectroelectrochemical behaviour at the potential at -2.4 V can be rationalised by considering the structural differences between **2-Cd** and **1-Zn**. From the crystallographic studies of both frameworks, it was observed that the DPPTzTz ligands in **2-Cd** adopt a spatial configuration that is less favourable for cofacial interactions than in **1-Zn**, with a larger cofacial distance and degree of slippage in the offset stacking. The variation in cofacial stacking results in weaker IVCT interactions in **2-Cd** compared to **1-Zn**, decreasing the favourability of the mixed-valence IVCT state (and increasing the favourability of the double dianion state) in **2-Cd**. This observation is closely related to that made by Hupp *et al.* for through-space IVCT in discrete molecular rectangle systems,^{3b} where an alignment of chromophores in the mixed-valence state increased the cofacial interactions, compared with the slipped conformation in the neutral state. Such structural influences on cofacial IVCT interactions are also alluded to by the unit cell parameters obtained from Pawley extractions of the PXRD patterns for **1-Zn** and **2-Cd**, where noticeably larger changes were observed for **2-Cd** (particularly in the α -angle) compared to **1-Zn** upon chemical reduction to the mixed-valence IVCT state.

Finally, to demonstrate redox reversibility for both frameworks, the applied potential was returned from -2.4 to 0 V, regenerating the starting spectrum in 1 h. The appearance of radical and NIR IVCT transitions were reproduced by UV-Vis-NIR experiments on chemically reduced samples of both **1-Zn** and **2-Cd** (ESI Fig. S17 and S18†).

Quantification of solid state SEC data and IVCT analysis

In order to apply Marcus-Hush theory to the IVCT bands, quantification of the molar extinction coefficient of the NIR band was performed. This was not achievable by direct solid state spectroscopic measurements of chemically reduced samples due to difficulties in ensuring that the samples would not auto-oxidise in air during the measurements. Thus, an alternate methodology was developed.

Quantification of NIR bands was achieved by first determining the molar extinction coefficient of the $\pi \rightarrow \pi^*$ band at $22\,680\text{ cm}^{-1}$ in the neutral frameworks using transmission measurements on KBr pellets containing the framework at various dilutions (see ESI†). From the extinction coefficient of the $\pi \rightarrow \pi^*$ band in the neutral **1-Zn** and **2-Cd** systems, the molar extinction coefficient of the NIR bands in the mixed-valence frameworks were calculated using Vis-NIR SEC data



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