excitation properties<sup>†</sup>

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Near-infrared emitting ytterbium metal-organic frameworks with tunable

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The design of metal-organic frameworks (MOFs) incorporating near-infrared emitting ytterbium cations and organic sensitizers allows for the preparation of new materials with tunable and enhanced photophysical properties.

Near-infrared (NIR) luminescent lanthanides exhibit useful photophysical properties that make them crucial components for applications such as photonic materials and optical telecommunication devices, as well as bioanalytical and biological imaging probes and sensors.<sup>1</sup> To take advantage of lanthanide luminescence, several requirements must be fulfilled to obtain a sufficient number of photons for an adequate detection sensitivity. Lanthanides need to be sensitized by a suitable chromophoric moiety since the weak absorbtivity of free lanthanide cations limits their luminescence intensity.<sup>1</sup> The sensitization (called "antenna effect")<sup>2,3</sup> involves placing lanthanide cations in proximity to chromophoric molecules having high absorptivity ("the antenna") that efficiently transfer energy to lanthanide accepting levels to trigger their emission. Secondly, the photophysical properties of lanthanide cations can be affected by their environment; for example, -OH, -NH, and -CH vibrational overtones quench luminescence intensity.<sup>1</sup> Thus it is crucial to control the environment around these cations; however, lanthanides have low stereochemical requirements. Their coordination must be tridimensionally manipulated by the design of the overall molecular complex in which the antennae are arranged to provide control of the photophysical properties and protection of the metal cations. In addition, for practical applications, it is advantageous to have control over the excitation wavelength.

In this communication, we address these antenna requirements by using a novel metal–organic framework (MOF) approach<sup>4</sup> to achieve control of lanthanide luminescence properties. Our results demonstrate for the first time that (i) within a MOF, efficient sensitization is achieved of a NIR emitting lanthanide,  $Yb^{3+}$ , and (ii) modification of our MOF structure, without changing the chromophore linker, allows for tuning of the luminescence properties of the resulting

ical NIR emitting lanthanides such as  $Yb^{3+}$ , which offer a new variety of applications for Ln-MOF materials. It has also not been shown that one can modify the structural parameters of MOFs to tune the photophysical properties of NIR emitting lanthanide–MOF compounds. The strategies presented herein will be useful for creating, optimizing, and tailoring lanthanide-based materials for specific NIR applications. We identified a ligand that could both sensitize NIR-emitting Yb<sup>3+</sup> and direct its assembly into an extended porous network. 4,4'-[(2,5-Dimethoxy-1,4-phenylene)di-2,1-ethenediyl]bis-benzoic acid (H<sub>2</sub>-PVDC) was chosen because it absorbs strongly in the visible range, it could promote the formation of extended MOF structures, and our preliminary studies (*vide infra*)

MOF structures, and our preliminary studies (vide infra) demonstrated that it was capable of sensitizing NIR-emitting Yb<sup>3+</sup>. Reacting Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O with H<sub>2</sub>-PVDC yielded yellow needles of **Yb-PVDC-1**,  $[Yb_2(C_{26}H_{20}O_6)_3(H_2O)_2]$ . (DMF)<sub>6</sub>(H<sub>2</sub>O)<sub>8.5</sub>.<sup>‡</sup> The material maintains its crystallinity in a variety of solvents, as confirmed by powder X-ray diffraction studies of solvent exchanged samples. Single crystal X-ray diffraction analysis revealed that Yb-PVDC-1 crystallizes in the high symmetry *Fddd* space group and is composed of infinite Yb-carboxylate chains aligned along the a crystallographic direction (Fig. 1a-c).<sup>6</sup> The chains consist of alternating octa- and hexa-coordinated Yb<sup>3+</sup>, bridged in a di-monodentate fashion via the carboxylates of three different PVDC linkers (Fig. 1a and b). Two water molecules terminally coordinate to the octa-coordinate Yb<sup>3+</sup>. The chains are connected along [110] via the phenylene vinylene portion of the ligand resulting in the formation of large  $24 \times 40$  Å channels (Fig. 1c).

Ho  $H_2$ -PVDC The UV-Vis absorption, emission, and excitation spectra were measured for **Yb-PVDC-1** and compared to corresponding

spectra recorded for the ligand H2-PVDC and a 1:1 Yb-PVDC

molecular complex (see ESI<sup>†</sup>) to determine how the MOF

Yb<sup>3+</sup> MOFs. MOFs are extensively studied for their gas

storage, catalytic, and molecular sieving properties; however,

their regular and tailorable structures render them potentially useful materials for numerous other applications. Several

lanthanide-containing MOFs emitting in the visible have been prepared and characterized spectroscopically<sup>5</sup> but, to the best

of our knowledge, no MOF has been demonstrated to sensitize



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**Fig. 1** Structure and spectral data for **Yb-PVDC-1**. (a) Ball and stick depiction of infinite SBU and (b) SBU with Yb<sup>3+</sup> represented as polyhedra (C, grey; O, red; Yb<sup>3+</sup>, dark green); (c) projection view of the framework viewed along the *a* crystallographic direction; (d) ligand stacking motif along [110], and (e) luminescence data comparing the excitation profiles of the Yb–PVDC molecular complex (red;  $\lambda_{em} = 980$  nm) to **Yb-PVDC-1** (blue;  $\lambda_{em} = 980$  nm) and displaying the Yb<sup>III</sup> emission (green;  $\lambda_{ex} = 470$  nm) upon excitation of **Yb-PVDC-1**.

structure impacts the luminescence properties of the system. The absorption spectrum of H<sub>2</sub>-PVDC displays two bands with apparent maxima centered at 340 and 415 nm. Excitation through either of these bands produces a fluorescence band centered at 485 nm. The excitation spectrum recorded upon this fluorescence band shows a profile similar to the absorption spectrum (Fig. S2, ESI<sup>†</sup>). The Yb-PVDC molecular complex displays the typical Yb<sup>3+</sup> emission band in the NIR range with an apparent maximum at 980 nm (Fig. S3, ESI<sup>†</sup>). The excitation spectrum for this complex collected upon monitoring Yb<sup>3+</sup> emission (Fig. 1e and Fig. S3 (ESI<sup>+</sup>)) also contains two bands centered at 340 and 415 nm that adopt the same profile as the absorption of H<sub>2</sub>-PVDC, indicating that PVDC sensitizes Yb<sup>3+</sup> via the antenna effect. Luminescence analysis of Yb-PVDC-1 (chloroform-exchanged material) displays  $Yb^{3+}$  luminescence in the NIR (Fig. 1e). The MOF excitation spectrum is notably red-shifted, displaying bands with maxima at 370 and 470 nm (Fig. 1e). The apparent maximum of the excitation band shifts significantly from 415 nm for the Yb-PVDC complex to 470 nm for Yb-PVDC-1. Although the Yb-PVDC complex experiments were performed in DMSO due to solubility constraints, this observed shift of over 50 nm cannot solely be attributed to a solvatochromic effect. We tentatively attribute a significant component of this shift to organizational constraints that the MOF architecture imparts on the phenylene vinylene linkers. In Yb-PVDC-1, the ligands are arranged in parallel along [110], which may allow for weak interactions between neighboring chromophoric ligands (Fig. 1d). These interactions are hypothesized to affect the electronic structure of the chromophore, resulting in decreased excitation energy.

To evaluate the extent to which ligand–ligand interactions impact the excitation and emission properties of Yb-PVDC systems, we prepared a second MOF, Yb-PVDC-2,  $[Yb_2(C_{26}H_{20}O_6)_3] \cdot (DMF)_{12}(H_2O)_{10}$ .‡ Yb-PVDC-2 crystallizes in the orthorhombic *Pnna* space group and also exhibits



**Fig. 2** Structure and spectral data for **Yb-PVDC-2**. Ball and stick depiction of infinite SBU (a) and SBU with Yb<sup>3+</sup> represented as polyhedra (b); projection view of the framework viewed along the *a* crystallographic direction (c); ligand stacking motifs (d) (C, grey; O, red; Yb<sup>3+</sup>, dark green), and (e) luminescence data comparing the excitation profiles of **Yb-PVDC-1** (red;  $\lambda_{em} = 980$  nm) to **Yb-PVDC-2** (blue;  $\lambda_{em} = 980$  nm) and displaying the Yb<sup>3+</sup> emission (green;  $\lambda_{ex} = 500$  nm) upon excitation of **Yb-PVDC-2**.

infinite Yb-carboxylate SBUs. However, the connectivity within the SBU differs from that of Yb-PVDC-1. The SBU is composed of alternating octa- and hexa-coordinated Yb<sup>3+</sup>. The  $Yb^{3+}$  are bridged by two carboxylates in a di-monodentate fashion and by a third carboxylate that chelates the octacoordinate Yb<sup>3+</sup> and coordinates in a monodentate fashion to the hexa-coordinate  $Yb^{3+}$  (Fig. 2a and b). These coordination modes result in a chain of corner-sharing polyhedral  $Yb^{3+}$ . Each chain is linked to six other chains via the phenylene vinylene portion of the PVDC linkers (Fig. 2c). The linkers connecting the chains along the [001] stack in parallel, while those that connect the chains in the [011] form criss-crossing pairs with close  $\pi - \pi$  interactions<sup>7</sup> (perpendicular distance between planes: 3.6 Å) between the central phenyl rings of the PVDC linkers (Fig. 2d). Because each infinite SBU is connected to six other SBUs, the resulting triangular channels are smaller than those observed for Yb-PVDC-1, measuring ~13–14 Å from corner to edge (Fig. 2c).

The luminescent properties of **Yb-PVDC-2** (chloroformexchanged material) were examined to determine the impact the structural changes have on the photophysical properties of this system. The excitation spectrum collected upon monitoring the emission intensity of Yb<sup>3+</sup> luminescence at 980 nm displayed apparent band maxima at 370 and 500 nm (Fig. 2e). The emission spectra collected in the NIR range upon excitation at these wavelengths produce characteristic Yb<sup>3+</sup> emission. Interestingly, the lowest energy excitation band of **Yb-PVDC-2** is further red-shifted to 500 nm from 470 nm in **Yb-PVDC-1**. We tentatively propose that the close  $\pi$ - $\pi$  interactions between the PVDC linkers decrease the energy of the  $\pi \rightarrow \pi^*$  transition, resulting in a lowered excitation energy.

To determine whether the MOF architecture provides efficient protection for the lanthanide cations from solvent quenching and to quantify the intramolecular energy transfer

**Table 1** Absolute emission quantum yields  $(\Phi)^a$  and luminescent lifetimes  $(\tau_x, \mu s)^b$  of Yb<sup>3+</sup> centered emission at 980 nm for the MOFs<sup>c</sup>

	${\Phi_{\mathrm{Yb}}}^d$	$\tau_1^{\ d}$	$\tau_2$	τ <sub>3</sub>	$ au_4$
Yb-PVDC-1 Yb-PVDC-2	$\begin{array}{c} 3.3 \; (\pm 0.5) \times 10^{-3} \\ 1.8 \; (\pm 0.2) \times 10^{-2} \end{array}$	29 (±2) 22 (±4)	10 (±1) 5.6 (±1.5)	$\begin{array}{c} 1.5 \ (\pm 0.5) \\ 1.7 \ (\pm 0.3) \end{array}$	0.34 (±0.06) 0.61 (±0.17)
$^{a} \lambda_{\text{ex}} = 490 \text{ nm.} ^{b} \lambda_{\text{e}}$	$e_x = 354$ nm. <sup>c</sup> MOFs as crystal	lline solids under chlor	oform. <sup>d</sup> Error included	in parentheses.	

of the systems, we measured quantum yield values using an integration sphere (Table 1). The quantum yield of **Yb-PVDC-2** is five times higher than **Yb-PVDC-1** when excited through the lower energy band (490 nm). The quantum yield of **Yb-PVDC-2** is among the highest values reported for ytterbium systems under solvent.<sup>8</sup> These quantum yields are global: the excitation is performed through the sensitizer and the emission is observed through the Yb<sup>3+</sup> cations that have different coordination environments and levels of protection in both MOFs. In **Yb-PVDC-1**, the octa-coordinate Yb<sup>3+</sup> coordinate two water molecules which quench ytterbium emission and lower the global quantum yield.

We monitored ytterbium centered luminescence lifetimes in order to further determine the effectiveness of the MOFs in protecting the lanthanide cations from non-radiative deactivation. Both MOFs displayed multi-exponential decay patterns and were best fit with four components (Table 1), which are attributed to four different lanthanide environments: the hexacoordinate and octa-coordinate Yb<sup>3+</sup> sites within the core of the MOF structures and those along the terminating edges of the crystals, where the lanthanide cations are more exposed to sources of non-radiative deactivation. The long component values are up to two times longer than the longest lifetimes reported for Yb<sup>3+</sup> molecular species in solution.<sup>2,9</sup> These luminescence lifetimes demonstrate that MOFs can provide coordination environments with improved protection from quenching than molecular complexes.

We have illustrated the validity of a MOF-based approach to sensitize NIR emitting Yb<sup>3+</sup>, which results in materials with enhanced and controlled luminescence properties. Specifically, we have shown that a chromophoric antenna molecule and NIR emitting Yb<sup>3+</sup> can be assembled into rigid MOF structures that effectively control the coordination environments around the lanthanide cations and the arrangement of chromophoric antennae. Using this strategy, we obtained a lower energy excitation wavelength by modifying the three-dimensional MOF structure to allow for close  $\pi - \pi$ interactions between the chromophores. The possibility to have different excitation ranges without altering the structure of the sensitizer provides a new route for controlling the photophysical properties of lanthanide complexes, in contrast to more traditional approaches which involve changing the antenna's structure. The structures of the MOFs also provide protection of the lanthanide cations from solvent vibrations. The ability to design MOFs and control their structural features makes them ideal materials for carefully controlling and optimizing the photophysical properties of lanthanide cations.

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## Notes and references

‡ Crystal data. **Yb-PVDC-1**.  $C_{39}H_{30}O_{10}$ Yb,  $M_w = 831.67$ , orthorhombic, a = 16.247(6), b = 48.939(19), c = 80.84(3) Å, V = 64280(43) Å<sup>3</sup>, T = 253 K, space group *Fddd*, Z = 32, 95070 reflections collected, 11506 unique ( $R_{int} = 0.1522$ ) which were used in all calculations. The final  $wR(F_2)$  was 0.1484 (all data). **Yb-PVDC-2**.  $C_{78}H_{60}O_{18}$ Yb<sub>2</sub>,  $M_w = 1631.34$ , orthorhombic, a = 16.0798(14), b = 22.7096(19), c = 38.484(3) Å, V = 14053(2) Å<sup>3</sup>, T = 298 K, space group *Pnna*, Z = 4, 123 644 reflections collected, 17 435 unique ( $R_{int} = 0.0580$ ) which were used in all calculations. The final  $wR(F_2)$  was 0.2528 (all data).

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