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Luminescent Ir(III)—Ln(III) coordination polymers showing slow magnetization relaxation†

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A series of iridium(|||)-lanthanide(|||) bimetallic coordination polymers were successfully obtained by hydrothermal reactions based on the Ir unit $[Ir(ppy)_2(Hdcbpy)]$, namely, $[Ln\{Ir(ppy)_2(dcbpy)\}_2(NO_3)]$ ($H_2O)_n$]-solvent (Ir_2Ln , n=5, Ln=Gd and Dy; and n=4, Ln=Er and Yb) and $[Ln_2(OH)\{Ir(ppy)_2(dcbpy)\}_4(NO_3)(H_2O)_4]$ -solvent (Ir_4Ln_2 , Ln=Gd, Dy, Er, and Er). Compounds Er_2Ln show chain structures in which the lanthanide ions are bridged by the $Er(ppy)_2(dcbpy)$ - ligands through the carboxy-late groups. Compounds Er_4Ln_2 have double-chain structures, in which the dimers of Er0(Er0) are connected by the Er1(Er1)-Er2 (Er2)-Er3 (Er3)-Er4)-Er5 (Er4)-Er5 (Er4)-Er6 (Er4)-Er7 (Er6)-Er8)-Er9 (Er8)-Er9)-Er9 (Er9)-Er9)-Er9 (Er9)-

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Introduction

The exponential growth of studies related to multifunctional coordination polymers integrating several physical and chemical properties into one single crystalline structure has become a hot topic of research over the last two decades. Magnetoluminescent molecular materials belong to one family of those multifunctional materials which are gaining increasing attention due to their potential applications in several areas such as quantum computing, medical imaging and sensors. One of the most effective strategies to combine magnetism with luminescence is the synthesis of lanthanide complexes which exhibit not only large unquenched orbital angular momentum and strong spin-orbit coupling that are ideal for the construction of single-molecule magnets (SMMs), to but also excellent luminescence properties including narrow line-like emission, high quantum yield and long lifetime.

Among the transition metals, the Ir^{III} complexes with energy levels modifiable through the cyclometalated ligands stand out as sensitizers for NIR emission from lanthanide ions.¹¹ The advantage is that the excitation is done in the visible region of the spectrum instead of the destructive UV light normally needed for organics. In 2008, De Cola and coworkers first reported a tetrametallic iridium-ytterbium complex showing NIR emission from Yb sensitized by the Ir complex.¹² Since then, several Ir^{III}-Ln^{III} bimetallic complexes showing NIR emission have been reported.¹³ Furthermore, only three Ir^{III}-Ln^{III} (Ln = Yb, Er, and Nd) coordination polymers exhibiting NIR luminescence were reported by Luo *et al.* in 2014, which successfully extended the dimension of luminescent Ir^{III}-Ln^{III} system.¹⁴

tation of a lanthanide ion requires a Laporte forbidden f-f transition, indirect excitation *via* light-harvesting antennas or sensitizing chromophores is generally employed.⁷ In comparison with the traditional organic chromophores being used as sensitizing groups,⁸ using transition metal complexes allows more design flexibility, offering longer emission lifetime and extends the optical excitation window to lower energy region.⁹ Their promising characteristics have therefore attracted substantial attention in recent years. Lanthanide ions that are near-infrared (NIR) emitters (Nd^{III}, Yb^{III}, Er^{III}, and Pr^{III}) have been involved in most of the work in this area and are useful in optical communication, medical imaging and biological labelling.^{9,10}

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Scheme 1 The molecular structure metalloligand (ppy)2(Hdcbpy).

On the contrary, luminescent IrIII-LnIII single molecule magnets (SMMs) have been scarcely described. The only examples, as far as we are aware, are Ir₆Ln (Ln = Dy, Er, and Yb) clusters which have been reported by us and exhibit simultaneously slow magnetization relaxation from LnIII and luminescence dominated by Ir^{III}. However, no efficient energy transfer between Ir and Ln was observed.

Owing to our long-term interest in magnetooptical bifunctional materials, 15,16 herein we report two new series of Ir^{III}-Ln^{III} coordination polymers based on the metalloligand Ir(ppy)2(Hdcbpy) (Scheme 1), namely, $[Ln{Ir(ppy)_2(dcbpy)}_2(NO_3)(H_2O)_n]$ ·solvent $(Ir_2Ln, n = 5,$ Ln = Gd and Dy; and n = 4, Ln = Er and Yb) and $[Ln_2(OH)\{Ir(ppy)_2(dcbpy)\}_4(NO_3)(H_2O)_4]\cdot solvent (Ir_4Ln_2, Ln =$ Gd, Dy, Er, and Yb). Ir₂Ln show chain structures, in which the Ln^{III} ions are cross-linked by the Ir(ppy)₂(dcbpy)⁻ ligands via the two carboxylate groups. For Ir₄Ln₂, dimers of Ln₂(OH) are observed, which are further connected by the carboxylate groups of the Ir(ppy)₂(dcbpy)⁻ ligands, forming a ladder-like chain structure. Interestingly, both single molecule magnetism

and Ir -> Ln energy transfer accompanied by near-infrared emission were demonstrated to co-exist in Ir₂Ln and Ir₄Ln₂ (Ln = Er and Yb).

Results and discussion

Crystal structures

Compounds $[Ln{Ir(ppy)_2(dcbpy)}_2(NO_3)(H_2O)_n]$ -solvent $(Ir_2Ln,$ n = 5, Ln = Gd and Dy; and n = 4, Ln = Er and Yb) and $[Ln_2(OH) \{Ir(ppy)_2(dcbpy)\}_4(NO_3)(H_2O)_4]$ ·solvent $(Ir_4Ln_2, Ln =$ Gd, Dy, Er, and Yb) were synthesized by solvothermal reactions of Ir(ppy)₂(Hdcbpy) and Ln(NO₃)₃·6H₂O in H₂O/MeOH using different concentrations of NaOH and temperatures. Powder XRD measurements revealed that Ir_2Ln (Ln = Gd, Dy, Er, and Yb) and Ir_4Ln_2 (Ln = Gd, Dy, Er, and Yb) are isostructural compounds. However, single crystals of good quality were obtained only for compounds Ir₂Dy, Ir₂Er, Ir₂Yb and Ir₄Yb₂. The crystallographic data for these four compounds are given in Table 1.

Ir₂Ln are isomorphous compounds that crystallize in the triclinic P1 space group, though the numbers of the coordination water molecules are slightly different (n = 5 for Ln = Gd and Dy; and n = 4 for Ln = Er and Yb). Therefore, Ir_2Yb is selected as a representative for the description of the structures. The asymmetric unit of Ir2Yb consists of two Ir (ppy)2(dcbpy) ligands, one YbIII, one NO3-, four coordinated water molecules, two MeOH and 0.5 lattice water molecule. As shown in Fig. 1a and b, the Yb atom is seven-coordinated by three carboxylate oxygen atoms from three ligands (O1, O3A, and O5) and four coordination water molecules. One of the coordination water molecules is disordered over two sites (O4W and O4W') (Fig. 1b). Continuous Shape Measure (CShM) analysis¹⁷ suggests that the geometries of the two possible

Table 1 Crystallographic data for compounds Ir₂Dy, Ir₂Er, Ir₂Yb and Ir₄Yb₂

-	Ir ₂ Dy	Ir ₂ Er	Ir ₂ Yb	Ir ₄ Yb ₂
Formula	C ₆₈ H ₅₄ N ₈ O ₁₃ DyIr ₂	C ₁₄₀ H ₁₂₂ N ₁₈ O ₃₅ Er ₂ Ir ₄	$C_{140}H_{122}N_{18}O_{35}Yb_2Ir_4$	C ₂₈₀ H ₂₃₆ N ₃₄ O ₆₁ Yb ₄ Ir ₈
M	1738.09	3719.87	3731.43	7282.77
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$Par{1}$	$Par{1}$	$Par{1}$	$P2_1/c$
a (Å)	8.5559(13)	8.6129(14)	8.5775(16)	36.569(3)
$b(\mathring{A})$	18.370(3)	18.343(3)	18.360(3)	8.6347(5)
b (Å) c (Å)	23.830(4)	23.903(4)	23.823(4)	43.991(3)
α (°)	70.638(3)	70.841(4)	70.887(̇̀5)	90
β (°)	80.107(3)	80.828(4)	81.179(6)	112.317(2)
γ (°)	77.866(3)	77.440(3)	77.676(S)	90
$V(\mathring{A}^3)$	3433.3(9)	3465.9(10)	3449.0(11)	12 850.4(14)
Z	2	1	1	2
$\rho_{\rm calcd} ({\rm g cm}^{-3})$	1.681	1.782	1.797	1.882
$\mu (\text{mm}^{-1})$	5.009	5.106	5.270	5.653
F(000)	1684.0	1812.0	1816.0	7076.0
$R_{ m int}$	0.0495	0.0482	0.0432	0.0617
$T_{ m max}$, $T_{ m min}$	0.634, 0.350	0.629, 0.350	0.621, 0.350	0.728, 0.360
$R_1^a, wR_2^b [I > 2\sigma(I)]$	0.1105, 0.2755	0.0795, 0.1847	0.0485, 0.1178	0.0844, 0.1952
R_1^a , w R_2^b (all data)	0.1273, 0.2852	0.1093, 0.2019	0.0621, 0.1244	0.1012, 0.2036
GoF on F^2	1.110	1.031	0.998	1.022
$(\Delta \rho)_{\rm max}$, $(\Delta \rho)_{\rm min}$ (e Å ⁻³)	5.05, -8.18	4.86, -6.94	2.22, -1.97	5.32, -3.22
CCDC	1956646	1956647	1956648	1956649

 $^{{}^{}a}R_{1} = \sum ||F_{0}| - |F_{c}||/\sum |F_{0}|$. ${}^{b}WR_{2} = [\sum W(F_{0}^{2} - F_{c}^{2})^{2}/\sum W(F_{0}^{2})^{2}]^{1/2}$.

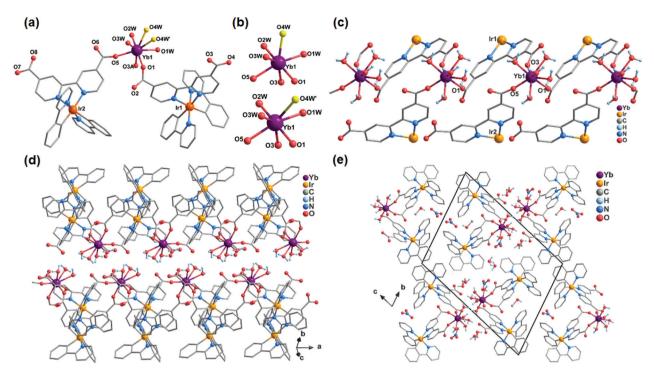


Fig. 1 (a) The building unit of the structure of Ir_2Yb . (b) Coordination environments of the Yb^{III} ion. (c) The single chain structure of the compound Ir₂Yb. The ppy ligands are omitted for clarity. (d) The double-chain structure of Ir₂Yb. (e) Packing diagram of the structure of Ir₂Yb viewed along the a-axis. All H atoms except those attached to the oxygen atoms are omitted for clarity.

[YbO₇] polyhedra are slightly deviated from an ideal capped trigonal prism (CShM = 1.17) and pentagonal bipyramid (CShM = 1.25), respectively. The Yb-O bond lengths are in the range of 2.191(7)-2.452(18) Å, and the O-Yb-O angles are in the range of 67.4(5)-149.8(3)°.

Two Ir(ppy)₂(dcbpy)⁻ ligands are crystallographically distinguished. One ligand (Ir1) adopts a bi-dentate coordination mode by using two of its four carboxylate oxygen atoms (O1 and O3), and connects the neighbouring Yb centres into an infinite chain running along the a-axis. The other ligand (Ir2) adopts a mono-dentate coordination mode and binds the Yb atom through its carboxylate oxygen atom O5 (Fig. 1c). The Yb...Yb distance within the chain is 8.58 Å. The chain is polar with the Ir(ppy)₂(dcbpy)⁻ ligands sitting on one side and the coordination water molecules on the other side. Two equivalent chains are connected through extensive hydrogen bonding interactions between the coordination water molecules, forming a supramolecular double chain which is nonpolar (Fig. 1d). The shortest interchain Yb...Yb separation is 6.20 Å. The double chains are stacked along the a-axis with the space between the double-chains filled with lattice water and methanol molecules and nitrate anions (Fig. 1e). Extensive H-bonds are observed among the aromatic groups, the non-coordinated carboxylate oxygen atoms, the coordination and lattice water molecules and the nitrate anions. A three-dimensional supramolecular network is thus constructed.

Compounds Ir₂Dy and Ir₂Er show similar 3D supramolecular structures made up of 1D chain (Fig. S3 and S4†). However, a significant difference is found in the coordination environ-

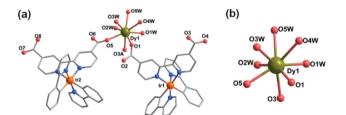


Fig. 2 (a) The building unit of the structure of Ir2Dy. (b) The coordination environment of the Dy^{III} ion.

ment of DyIII in Ir2Dy. Unlike the seven-coordinated lanthanide ion in Ir₂Yb and Ir₂Er (Fig. S4†), the Dy atom is eight-coordinated by three carboxylate oxygen atoms from three ligands (O1, O3A, and O5) [Dy-O: 2.270(16)-2.376(16) Å] and five coordinated water molecules (O1W, O2W, O3W, O4W, and O5W) [Dy-O: 2.332(19)-2.48(3) Å] (Fig. 2). This can be related to the lanthanide contract effect, the DyIII ion with larger ionic radius shows higher coordination number. The geometry of DyIII is best described as a slightly distorted triangular dodecahedron (D_{2d}) with a CShM value of 0.94.

The compound Ir₄Yb₂ crystallizes in the monoclinic space group $P2_1/c$. Its asymmetric unit contains four $Ir(ppy)_2(dcbpy)^$ ligands, two Yb^{III}, one OH⁻, one NO₃⁻, four coordinated water molecules, four free MeOH molecules and two and a half lattice water molecules. As shown in Fig. 3, both the crystallographically distinct Yb atoms have seven coordinated environments, viz. four carboxylate oxygen atoms, one bridging co-

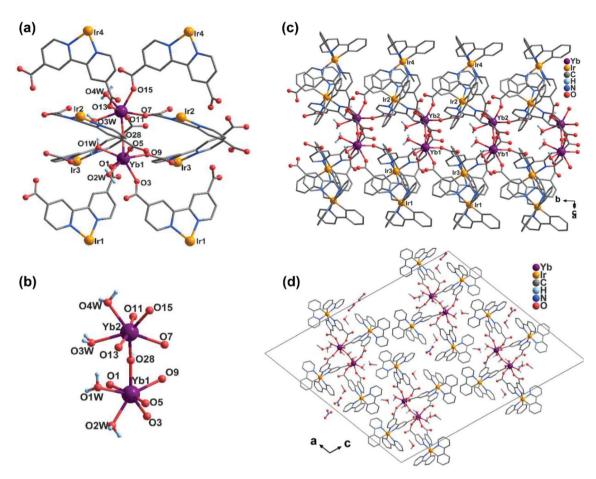


Fig. 3 (a) The building unit of the structure of Ir₄Yb₂. The ppy ligands are omitted for clarity. (b) Coordination environments of the Yb^{III} ions. (c) The double-chain structure of the compound Ir_4Yb_2 . (d) Packing diagram of the structure of Ir_4Yb_2 viewed along the b-axis. All H atoms except those attached to the oxygen atoms are omitted for clarity.

ordinated OH⁻ and two oxygen atoms from water (Fig. 3b). Both Yb^{III} ions adopt pentagonal bipyramidal geometry, as suggested by the CShM values $S(D_{5h}) = 1.80$ (Yb1) and $S(D_{5h}) =$ 0.96 (Yb2). The neighbouring [YbO₇] polyhedra are linked via the OH group, forming a dimer of $\{Yb_2(OH)(COO)_8(H_2O)_4\}$ $(Yb-O-Yb = 159.6(1)^{\circ} \text{ and } Yb\cdots Yb = 4.3962(11) \text{ Å})$. All of the Ir (ppy)₂(dcbpy)⁻ ligands adopt a bi-dentate coordination mode, unlike those in Ir_2Ln , and connect the $\{Yb_2(OH)(COO)_8(H_2O)_4\}$ dimers into a one-dimensional double-chain structure (Fig. 3c). The intrachain Yb...Yb distance between the dimers is 8.63 Å. The double chains are stacked in the lattice. The lattice solvent molecules and the nitrate anions occupy the inter-chain spaces, and are involved in the extensive H-bond network.

Although single crystals of good quality were not obtained for compounds Ir₂Gd, Ir₄Gd₂, Ir₄Dy₂ and Ir₄Er₂, the unit cell parameters were confirmed by Pawley fitting of their powder diffraction patterns using TOPAS 5.0 program (Table S8, Fig. S5-S10†).

Obviously, the structure of Ir₄Yb₂ is significantly different from that of Ir₂Yb. A careful analysis reveals, however, that the double chain in Ir₄Yb₂ can be viewed as two single chains in

Ir₂Yb connected by the hydroxyl groups. The involvement of an OH group in Ir₄Yb₂ can be explained by the more basic reaction condition used for the synthesis of Ir₄Yb₂.

Notably, IrIII-LnIII coordination polymers containing the same ligand Ir(ppy)2(Hdcbpy) are still rare. The only examples, as far as we are aware, are Ln[Ir(ppy)₂(dcbpy)]₂(OH)·H₂O (Ln = Gd, Yb, Er, and Nd)¹⁴ and $Y[Ir(ppy)_2(dcbpy)]_2(OH)$.¹⁸ These compounds possess identical chain structures that are remarkably different from those of Ir2Yb and Ir4Yb2, in which the dimers of edge-sharing {LnO₇} or {YO₇} pentagonal bipyramid via two OH groups are further connected by the carboxylate groups in the metalloligand. Therefore compounds Ir2Ln and Ir₄Ln₂ provide new structural types of the Ir^{III}-Ln^{III} coordination polymers based on Ir(ppy)2(Hdcbpy).

Magnetic properties

Variable temperature dc magnetic susceptibilities of Ir₂Ln and Ir_4Ln_2 (Ln = Gd, Dy, Er, and Yb) were measured in the temperature range of 2–300 K in an applied field of 1 kOe. Plots of $\chi_{\rm M}T$ versus $T(\chi_{M})$ is the molar magnetic susceptibility per Ln^{III} ion) for these compounds are shown in Fig. 4. At 300 K, the $\chi_{\rm M}T$ values are 7.73 and 7.84 cm³ K mol⁻¹ for Ir₂Gd and Ir₄Gd₂,

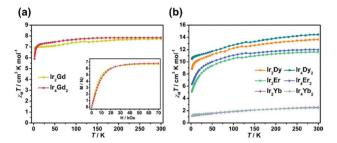


Fig. 4 (a) Temperature dependence of $\chi_M T$ per Gd on cooling in a field of 1 kOe for Ir₂Gd and Ir₄Gd₂. Inset: M vs. H plots of the two compounds at 2 K. (b) Temperature dependence of $\chi_{\rm M}T$ per Ln on cooling in a field of 1 kOe for Ir_2Ln and Ir_4Ln_2 (Ln = Dy, Er, and Yb).

respectively, which are close to the expected value of 7.88 cm³ K mol⁻¹ for an isolated Gd^{III} ion $(S = 7/2, L = 0, {}^{8}S_{7/2}, J = 7/2, g$ = 2). Upon cooling, the $\chi_{\rm M}T$ value of ${\rm Ir}_2{\rm Gd}$ decreases continuously in the range of 300-50 K and then decreases smoothly to the minimum value of 6.88 cm³ K mol⁻¹ at 2 K. In contrast, for compound Ir_4Gd_2 , the $\chi_M T$ value decreases to 20 K followed by a rapid drop to the minimum value of 5.91 cm³ K mol⁻¹ at 2 K. The low temperature feature could be attributed to the occurrence of the GdIII...GdIII antiferromagnetic exchange interactions, and is given by the negative values of the Weiss constants (θ) as -0.04 K for Ir₂Gd and -0.54 K for Ir₄Gd₂ (Fig. S11†). The stronger antiferromagnetic interactions in Ir₄Gd₂ may be due to short distances of the Gd^{III} ions in the dimer connected via the OH group. The field dependence of the magnetization at 2 K shows a rapid increase at low field and then slowly reaches the corresponding maximum values of $6.67N\beta$ per Gd for Ir_2Gd and $6.80N\beta$ per Gd for Ir_4Gd_2 at 70 kOe, which are close to the theoretical saturation value of 7NB for an isolated GdIII ion.

The dc magnetic susceptibilities of compounds Ir₂Ln and Ir₄Ln₂ (Ln = Dy, Er, and Yb) were measured under the same conditions. As shown in Fig. 4b, all the compounds show a similar behaviour. The room temperature $\chi_{M}T$ values per Ln are 13.65 (Ir₂Dy), 14.44 (Ir₄Dy₂), 11.60 (Ir₂Er), 11.98 (Ir₄Er₂), 2.53 (Ir_2Yb) and 2.45 (Ir_4Yb_2) cm³ K mol⁻¹, which are consistent with the theoretical values of 14.17 (Dy $^{\rm III}$, $^6{\rm H}_{15/2}$), 11.48 (Er $^{III},\ ^4I_{15/2})$ and 2.57 (Yb $^{III},\ ^2F_{7/2})\ cm^3\ K\ mol^{-1}.$ The decrease in the $\chi_{\rm M}T$ value on lowering the temperature is attributed to the thermal depopulation of the excited M_I sublevels and/or the weak antiferromagnetic exchange interactions between the metal centres. 19 The magnetization values of compounds Ir₂Ln and Ir₄Ln₂ at 2 K and 70 kOe are significantly smaller than the expected saturation values for the corresponding lanthanide ions, revealing the existence of a significant magnetic anisotropy²⁰ which is further confirmed by the non-superimposed M vs. H/T plots at different temperatures (Fig. S12 and S13†).

In order to assess the effect of coordination configuration on the dynamic magnetic properties, the alternative-current (ac) magnetic susceptibilities of Ir_2Ln and Ir_4Ln_2 (Ln = Dy, Er, and Yb) were measured using a Quantum Design PPMS in the frequency range of 10-10 000 Hz. Under the zero dc field, only

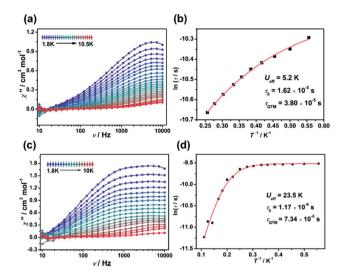


Fig. 5 Out-of-phase (χ'') ac susceptibilities of Ir_2Dy (a) and Ir_4Dy_2 (c) under zero dc field. Plots of $ln(\tau)$ vs. 1/T for lr_2Dy (b) and lr_4Dy_2 (d).

Ir2Dy and Ir4Dy2 showed clear frequency dependence of inphase (γ') and out-of-phase (γ'') susceptibilities below ca. 11 K, indicating a zero-field SMM with slow magnetization relaxation (Fig. 5a and c). However, the peak value of χ'' did not change significantly with increasing temperature, indicating that the magnetic relaxation mainly originated from the quantum tunnelling process.²¹ The Cole-Cole plots can be well fit by the generalized Debye model to extract the relaxation time (τ) (Tables S9 and S14†).²² The distribution parameters (α) are in the range of 0.34-0.37 for Ir_2Dv and in the range of 0.25-0.45 for Ir₄Dy₂, suggesting multiple relaxation processes with broad distribution of the relaxation times. Moreover, the $\ln \tau \ vs. \ T^{-1}$ curve can be fit by considering the Orbach and quantum tunnelling process using eqn (1), and determining the parameters $U_{\rm eff}$ = 5.2 K, τ_0 = 1.6 × 10⁻⁵ s, and $au_{\mathrm{OTM}} = 3.8 \times 10^{-5} \mathrm{s}$ for $\mathbf{Ir_2Dy}$ (Fig. 5b), and $U_{\mathrm{eff}} = 23.5 \mathrm{K}$, $au_0 =$ 1.17×10^{-6} s, and $\tau_{QTM} = 7.34 \times 10^{-4}$ s for Ir_4Dy_2 (Fig. 5d), respectively.

$$\tau^{-1} = \tau_{\rm QTM}^{-1} + \tau_0^{-1} \, \exp(-U_{\rm eff}/kT) \tag{1}$$

$$\tau^{-1} = \tau_{\text{QTM}}^{-1} + AT + \tau_0^{-1} \exp(-U_{\text{eff}}/kT)$$
 (2)

In order to suppress the QTM and get further insight into the magnetic relaxation dynamics of complexes Ir₂Dy and Ir₄Dy₂, we obtained the ac magnetic susceptibilities under an applied dc bias field of 2 kOe. Variable-frequency ac magnetic susceptibilities of Ir₂Dy are shown in Fig. S15 and S16.† With increasing temperature, the position of χ'' peak did not change below 5.4 K, indicating a complicated relaxation process. The Cole-Cole plots were generated using the frequency dependent ac susceptibilities in the temperature region of 5.4-7.5 K, and can be well fit by employing the sum of two modified Debye functions. For the fast relaxation (FR) process, the low value of the relaxation width ($\alpha_1 \approx 0$, Table S10†) suggests a narrow distribution of relaxation times, and the temperature

independence of $\ln \tau$ also indicates that only the quantum tunnelling mechanism is involved.²⁴ However, the slow relaxation (SR) processes show a linear temperature dependence of $\ln \tau$ corresponding to an Orbach relaxation mechanism, 25 leading to the parameters $U_{\rm eff}$ = 38.1 K and τ_0 = 2.93 × 10⁻⁶ s according to the Arrhenius law (Fig. S16d†).

For compounds Ir_4Dy_2 , the frequency-dependent χ'' exhibits more clear peaks than in zero-dc field and the positions of maxima change from high to low frequency as the temperature is decreased. Although there are two crystallographic sites differing in environments in Ir₄Dy₂, no dual magnetization relaxation processes were distinguished. It is possible to fit the Cole-Cole plots with only one relaxation process (Fig. S18 and 19, Table S12†).²⁶ Furthermore, the temperature dependent relaxation time profiles can be fit as a sum of the contributions of the Orbach, quantum tunnelling, and direct mechanisms (eqn (2)).²⁷ The best fit led to the following parameters: $U_{\rm eff} = 21.4 \text{ K}, \ \tau_0 = 2.89 \times 10^{-6} \text{ s}, \ \tau_{\rm OTM} = 7.98 \times 10^{-4} \text{ s} \ \text{and} \ A =$ 193.9 K⁻¹ s⁻¹. Obviously, the parameters of Orbach and quantum tunnelling processes do not change significantly under an applied field, but the direct process induced by the applied field results in the decrease of the magnetic relaxation rate.

The magnetization dynamics of compounds Ir₂Er and Ir₄Er₂ were also explored. Unfortunately, under zero external field, neither peaks nor frequency dependence of χ' and χ'' was found at 2 K, indicating the presence of significant QTM effect. When an external dc field was applied, both χ' and χ'' were found and they showed frequency-dependence, which are typical of a field-induced SMM behaviour (Fig. S20-S23, Tables S13 and S14†). As shown in Fig. S21 and S23,† the maximum of χ'' gradually shifted to high frequencies with increasing temperature, while no maximum was observed above 2.2 K. The relaxation time τ can be extracted by fitting the Cole–Cole plots using the generalized Debye model assuming a single relaxation process. The $\ln \tau$ values increase linearly with temperature in the range of 1.8-2.6 K, and an Arrhenius law fitting results in the energy barriers of 13.6 K ($\tau_0 = 2.72 \times 10^{-8}$ s) for Ir_2Er and 11.8 K ($\tau_0 = 6.68 \times 10^{-8}$ s) for Ir_4Er_2 .

The temperature-dependent magnetic dynamics of Ir₂Yb and Ir₄Yb₂ were also investigated under an external dc field (Fig. 6, S24–S27, Tables S15 and S16†). For Ir₂Yb, the frequency scan of χ'' exhibited single peaks below 6 K and the maxima gradually shifted to high frequencies upon heating. By assuming a single relaxation process, the relaxation time τ can again be extracted by fitting the Cole-Cole plots using the generalized Debye model. The $\ln \tau$ vs. T^{-1} curve can be reasonably fit by using eqn (2), leading to the parameters $U_{\rm eff}$ = 24.4 K, τ_0 = 2.88×10^{-7} s, and $A = 687.9 \text{ K}^{-1} \text{ s}^{-1}$. However, two distinct peaks at low temperatures were observed in the temperaturedependent magnetic dynamics of Ir₄Yb₂, indicating dual relaxation processes by accounting for the different combinations of contributions from the direct and Orbach relaxation processes. The $\ln \tau$ vs. T^{-1} profile can be fit in the whole temperature range, ²⁸ and the resulting parameters are $U_{\rm eff}$ = 22.2 K, τ_0 = 2.03×10^{-7} s and $A = 8678 \text{ K}^{-1} \text{ s}^{-1}$ for the FR process, while $U_{\text{eff}} = 28.3 \text{ K}, \tau_0 = 2.5 \times 10^{-8} \text{ s} \text{ and } A = 682 \text{ K}^{-1} \text{ s}^{-1} \text{ for the SR}$ process. The observation of dual magnetization relaxation processes in Ir₄Yb₂ could result from the presence of two crystallographic sites with two different environments in the structure.

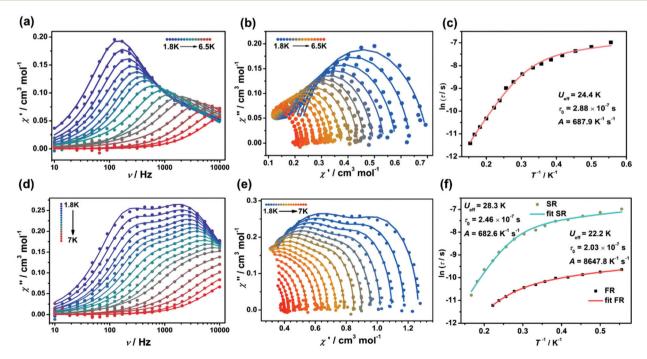


Fig. 6 Frequency dependence of out-of-phase (y'') ac susceptibilities at different temperatures for Ir_2Yb (a) and Ir_4Yb_2 (d) under an external dc field. The Cole-Cole plots of the ac susceptibilities for Ir_2Yb (b) and Ir_4Yb_2 (e). Plots of $Ir(\tau)$ vs. 1/T for Ir_2Yb (c) and Ir_4Yb_2 (f).

A similar phenomenon was also observed in a few other Yb dimer complexes.²⁹

To the benefit of the D_{5h} symmetry, especially the Kramers DyIII and ErIII ions, the observation of high energy barrier to moment reversal in Ln-SMMs was reported by several groups. 30-32 Therefore, a small anisotropy barrier in Ir-Ln bimetallic complexes is not expected. This may be explained by the orientation of the easy-axis anisotropy deviating significantly from an idealized C_5 axis, which has been observed in other lanthanide complexes.33

Optical properties

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The UV-vis spectra of the free metalloligand and Ir-Ln coordination polymers in the solid state were transformed from the diffuse reflectance spectra using the Kubelka-Munk equation: $F(R) = (1 - R)^2/2R$. As shown in Fig. S28,† the absorptions in the high energy region (250-330 nm) are associated with the π - π * transition of the aromatic ligands (Hdcbpy and ppy) and the intense absorption bands at 330-450 nm can be explained by the mixed spin-allowed ¹LLCT (ligand-to-ligand chargetransfer) and ¹MLCT (metal-to-ligand charge-transfer). The lower energy absorptions (ca. 450-550 nm) originate from the spin forbidden ³MLCT and are common in cyclometalated iridium derivatives.³⁴ The absorption profiles of all Ir-Ln complexes show a similar electronic transition to the Ir^{III} unit. However, the most significant difference is that weak absorption peaks located at 755 nm (13 245 cm⁻¹) and 654 nm (15 290 cm⁻¹) were observed for Ir₂Dy and Ir₂Er, respectively, corresponding to the f-f transitions of the DyIII ions (5H15/2 to $^6\mathrm{F}_{3/2}$) and $\mathrm{Er^{III}}$ ions ($^4\mathrm{I}_{15/2}$ to $^4\mathrm{F}_{9/2}$). Although the structures are different, a similar phenomenon was also observed for Ir₄Dv₂ and Ir₄Er₂.

Upon excitation in the visible region at 375 nm, Ir (ppy)₂(Hdcbpy) exhibits a strong emission band at 605 nm, corresponding to the 3MLCT transition as a consequence of the heavy-atom effect. As is to be expected, the solid-state luminescence spectra of compounds Ir₂Ln and Ir₄Ln₂ (Ln = Gd, Dy, Er, and Yb) are similar to that of the free metalloligand, indicating that the phosphorescence of polymers arises from the Ir(III) unit (Fig. 7 and Table 2). However, the emission

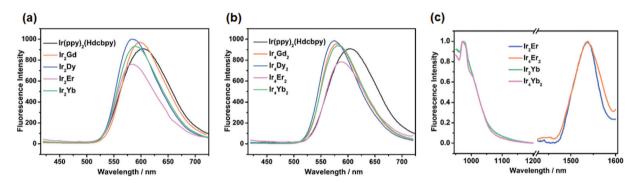


Fig. 7 (a) The emission spectra of $Ir(ppy)_2(Hdcbpy)$ and Ir_2Ln in the solid-state ($\lambda_{ex} = 375$ nm). (b) The emission spectra of $Ir(ppy)_2(Hdcbpy)$ and Ir_4Ln_2 (Ln = Gd, Dy, Er, Yb) in the solid-state (λ_{ex} = 375 nm). (c) The solid-state NIR emission spectra of the Ir-Yb (left) and Ir-Er (right) complexes $(\lambda_{ex} = 500 \text{ nm}).$

Table 2 Magnetic and photophysical parameters of Ir_2Ln and Ir_4Ln_2 (Ln = Gd, Dy, Er, and Yb)

	dc field	Relaxation processes	Fitting parameters	$\lambda_{\rm em}/nm$	$\tau/\mu s$	QY/%
Ir(ppy) ₂ (Hdcbpy)	_	_	_	605	6.60	4.22
Ir ₂ Gd	_	_	_	598	8.69	5.83
Ir ₄ Gd ₂	_	_	_	578	7.74	8.08
Ir ₂ Dy	0 kOe 2.0 kOe	Orbach, QTM QTM (FR) Orbach(SR)	$U_{\rm eff} = 5.2 \text{ K}, au_0 = 1.62 \times 10^{-5} \text{ s}, au_{\rm QTM} = 3.80 \times 10^{-5} \text{ s} $ $ au_{\rm QTM} = 2.25 \times 10^{-5}$ $U_{\rm eff} = 38.1 \text{ K}, au_0 = 2.93 \times 10^{-6} \text{ s}$	583	4.79	6.00
Ir_4Dy_2	0 kOe	Orbach, QTM	$U_{\text{eff}} = 33.1 \text{ K}, t_0 = 2.93 \times 10^{-8} \text{ S}$ $U_{\text{eff}} = 23.5 \text{ K}, \tau_0 = 1.17 \times 10^{-6} \text{ S}$ $\tau_{\text{OTM}} = 7.34 \times 10^{-4} \text{ S}$	575	0.66	11.94
	2.0 kOe	Orbach, QTM; direct	$U_{\text{eff}} = 21.4 \text{ K}, \tau_0 = 2.89 \times 10^{-6} \text{ s}$ $\tau_{\text{OTM}} = 7.98 \times 10^{-4} \text{ s}, A = 193.9 \text{ K}^{-1} \text{ s}^{-1}$			
Ir ₂ Er	1.0 kOe	Orbach	$U_{\rm eff} = 13.6 \text{ K}, \tau_0 = 2.72 \times 10^{-8} \text{ s}$	584	6.37	0.68
2				1538	1.40	_
Ir ₄ Er ₂	1.5 kOe	Orbach	$U_{\rm eff} = 11.8 \text{ K}, \tau_0 = 6.68 \times 10^{-8} \text{ s}$	588	5.47	1.08
				1538	1.37	_
Ir ₂ Yb	1.0 kOe	Orbach, direct	$U_{\rm eff} = 24.4 \text{ k}, \tau_0 = 2.88 \times 10^{-7} \text{ s}, A = 687.9 \text{ K}^{-1} \text{ s}^{-1}$	590	2.23	5.60
_		·		975	0.92	_
Ir ₄ Yb ₂	1.5 kOe	Orbach, direct (FR)	$U_{\rm eff} = 22.2 \text{ K}, \tau_0 = 2.03 \times 10^{-7} \text{ s}$	582	1.24	7.91
		, ,	$A = 8647.8 \text{ K}^{-1} \text{ s}^{-1}$	975	0.86	_
		Orbach, direct (SR)	$U_{\rm eff} = 28.3 \text{ K}, \tau_0 = 2.46 \times 10^{-8} \text{ s}, A = 682.6 \text{ K}^{-1} \text{ s}^{-1}$			

maxima of Ir-Ln compounds were blue-shifted with respect to the parent metalloligand, which may be attributed to the deprotonation of the carboxylate groups upon coordination, leading to a decrease in the intermolecular H-bond interactions in the polymers.36

Further research on the photoluminescence efficiencies and time-resolved luminescence decay of the IrIII unit and Ir-Ln compounds was carried out, and the data are summarized in Table 2. Owing to the mismatch in the energy levels, the GdIII ions cannot accept energy from the triplet state of the Ir (III) unit, 37 so the photoluminescence efficiencies of Ir₂Gd and Ir₄Gd₂ can be used as the reference for the other Ir-Ln (Ln = Dy, Yb, and Er) complexes. The quantum yield increases slightly from 4.22% to 5.83% (Ir_2Gd) and 8.08% (Ir_4Gd_2), which is attributed to the rigidity of the coordination framework that reduces self-quenching and the possibility of nonradiative transitions.³⁸ In addition, the long lifetime compared to the parent linker (6.60 µs) also implies that no d-f energy transfer occurs in Ir₂Gd and Ir₄Gd₂ (Fig. S29†), while for the other luminescent Ir-Ln (Ln = Dy, Er, and Yb) coordination polymers, the lifetimes were shortened to varying degrees, which indicates that the energy effectively transfers from the light-harvesting Ir unit to the lanthanide centres. Moreover, according to the emission spectrum, the triplet energy level of Ir(ppy)₂(Hdcbpy) is 16 600 cm⁻¹, which is suitable for sensitizing the NIR lanthanide ions YbIII and ErIII, but is too low to sensitize the low-lying excited state (${}^{4}F_{9/2}$, 21 000 cm $^{-1}$) of Dy^{III} ions. 35,39

In order to detect whether a lanthanide ion can be sensitized by the metalloligand Ir(ppy)₂(Hdcbpy), upon irradiation at 500 nm, the near-infrared emission spectra of Ir-Ln (Ln = Er and Yb) compounds were examined in the solid-state. For the Yb^{III} complexes, the emission bands occurring at 978 nm can be assigned to the ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition, while in Ir_4Yb_2 , the emission peak shows a shoulder at 1005 nm, indicating that the local symmetry environment around the metal centre is affected by crystal-field splitting, 40 which is in agreement with the two independent Yb^{III} ions in the single crystal structure. The emission spectra of the ErIII complexes show an emission peak at around 1530 nm, which is attributed to the ${}^4I_{13/2} \rightarrow$ ⁴I_{15/2} transition. ⁴¹ Moreover, the luminescence decay is well fit to a bi-exponential curve, affording lifetimes of 0.92 µs for Ir_2Yb , 0.86 µs for Ir_4Yb_2 , 1.40 µs for Ir_2Er and 1.37 µs for Ir_4Er_2 (Fig. S30 and S31†). Noting that the quantum yields of Ir_2Er (ϕ = 0.68%) and Ir_4Er_2 (ϕ = 1.08%) in the solid state are markedly lower than those of the other Ir-Ln (Ln = Gd, Dy, and Yb) complexes, the energy transfer between the metalloligand and erbium could be more efficient. This can be explained by the effective energy overlap between the 3MLCT state of Ir (ppy)₂(Hdcbpy) and the f-f excited states of erbium.

Conclusion

In this work, we report a series of iridium(III)-lanthanide(III) bimetallic coordination polymers with single-chain (for Ir₂Ln)

and double-chain (for Ir₄Ln₂) structures. Magnetic studies demonstrate that complexes Ir2Dy and Ir4Dy2 exhibit SMM behaviour in zero dc field, while complexes Ir₂Er, Ir₂Yb, Ir₄Er₂ and Ir₄Yb₂ show field-induced slow magnetic relaxation. The complex Ir4Yb2 is of particular interest because of the fieldinduced dual relaxation processes, which may originate from the two different coordinated geometries of lanthanide ions. Moreover, in the complexes Ir₂Er, Ir₂Yb, Ir₄Er₂ and Ir₄Yb₂, the Ir unit can act as a good light-harvesting antenna to effectively sensitize Ln-based near-infrared (NIR) luminescence by energy transfer from the Ir unit to the Ln³⁺ ions. As far as we know, this is the first observation of SMM behaviour and NIR luminescence coexisting in iridium(III)-lanthanide(III) bimetallic CPs.

Experimental section

Materials and physical measurements

All the starting materials were of reagent grade and were obtained from the commercial sources and used without further purification. Powder X-ray diffraction (PXRD) data were obtained using a Bruker D8 ADVANCE X-ray powder diffractometer (Cu- K_{α}) at room temperature. Infrared spectra were recorded on a Bruker Tensor 27 spectrometer using KBr pellets in the range of 400-4000 cm⁻¹. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere in the temperature range of 25-600 °C at a heating rate of 5 °C min⁻¹ using a METTLER TOLEDO TGA/DSC 1 instrument. Elemental analyses for C, H and N were performed with a PerkinElmer 240C elemental analyzer. The UV-vis spectra were recorded on a PerkinElmer Lambda 950 UV/Vis/NIR spectrometer using powder samples. The steady fluorescence spectra in the visible region were obtained using a PerkinElmer LS55 fluorescence spectrometer and a Xenon lamp as the excitation source. The emission lifetime and the absolute luminescent quantum yields in the solid state at room temperature were determined using a HORIBA FM-4P-TCSPC spectrometer. The steady state near infrared (NIR) emission spectra were recorded on an Edinburgh FLS980 fluorescence spectrometer equipped with a Hamamatsu R5509-72 photomultiplier. The magnetic susceptibility data were obtained using Quantum Design SQUID MPMS-XL7, VSM and PPMS magnetometer for freshly prepared samples. The diamagnetic contributions of the samples were estimated from Pascal's constants.

Synthesis of $[Ln{Ir(ppy)_2(dcbpy)}_2(NO_3)(H_2O)_n]$ -solvent $(Ir_2Ln,$ n = 5, Ln = Gd and Dy; n = 4, Ln = Er and Yb)

Compounds Ir_2Ln (Ln = Gd, Dy, Er, and Yb) were synthesized under similar optimized experimental conditions. A typical procedure for the preparation of [Yb{Ir(ppy)₂(dcbpy)}₂(NO₃) $(H_2O)_4$]·2CH₃OH·0.5H₂O (Ir₂Yb) is described below. Ir (ppy)₂(Hdcbpy) (7.4 mg, 0.01 mmol) was suspended in 2 mL of distilled water and dissolved in 5 µL of aqueous NaOH (1 M). Then $Yb(NO_3)_3 \cdot 6H_2O$ (9.34 mg, 0.02 mmol) in 7 mL of MeOH was added. After keeping the vial at 60 °C for 2 days, orange rod crystals were obtained. The crystalline product of Ir₂Yb was

separated by filtration and washed with distilled water and a minimum amount of methanol. Yield: 29%. Elemental analyses (%) calcd for $C_{70}H_{61}YbIr_2N_9O_{17.5}$, C, 45.06; H, 3.29; N, 6.76; found: C, 45.09; H, 3.12; N, 6.74. IR (KBr, cm⁻¹): 3384 (m), 3105 (m), 3062 (m), 3043 (m), 1606 (s), 1585 (s), 1546 (m), 1477 (s), 1423 (s), 1380 (s), 1317 (w), 1288 (m), 1269 (m), 1234 (m), 1031 (w), 783 (m), 759 (s), 738 (w), 730 (w), 696 (w).

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For $[Gd{Ir(ppy)_2(dcbpy)}_2(NO_3)(H_2O)_5]\cdot 2CH_3OH\cdot 0.5H_2O$ (Ir_2Gd): yield: 18%. Elemental analyses (%) calcd for $C_{70}H_{61}GdIr_2N_9O_{17.5}$, C, 45.45; H, 3.32; N, 6.81; found: C, 44.89; H, 3.27; N, 6.81. IR (KBr, cm⁻¹): 3355 (m), 3107 (w), 3059 (m), 2925 (m), 1631 (s), 1585 (s), 1544 (s), 1476 (s), 1421 (s), 1367 (s), 1270 (m), 1233 (m), 1160 (w), 864 (m), 781 (m), 758 (m), 694 (m), 670(w).

For $[Dy{Ir(ppy)_2(dcbpy)}_2(NO_3)(H_2O)_5]$ -2CH₃OH-0.5H₂O (Ir_2Dy) : yield: 41%. Elemental analyses (%) calcd for $C_{70}H_{61}DyIr_2N_9O_{17.5}$, C, 45.32; H, 3.31; N, 6.79; found: C, 43.93; H, 3.26; N, 6.63. IR (KBr, cm⁻¹): 3423 (s), 3107 (w), 3049 (w), 1610 (s), 1546 (m), 1477 (s), 1427 (s), 1379 (s), 1313 (m), 1274 (m), 1234 (m), 1161 (w), 1062 (w), 1031 (w), 761 (m), 734 (w), 698 (w), 628 (w), 603 (w), 567 (w).

For $[Er{Ir(ppy)_2(dcbpy)}_2(NO_3)(H_2O)_4]\cdot 2CH_3OH\cdot 0.5H_2O$ (Ir_2Er) : yield: 37%. Elemental analyses (%) calcd for $C_{70}H_{61}ErIr_2N_9O_{17.5}$, C, 45.20; H, 3.30; N, 6.77; found: C, 44.76; H, 3.24; N, 6.83. IR (KBr, cm⁻¹): 3375 (m), 3103 (m), 3043 (m), 1606 (s), 1585 (s), 1546 (m), 1514 (w), 1477 (s), 1421 (s), 1377 (s), 1286 (m), 1269 (m), 1232 (m), 1161 (w), 1031 (w), 781 (m), 759 (s), 738 (w), 729 (w), 696 (w).

Thermal analyses reveal that the weight losses at 90 °C are 4.2% (for Ir_2Dy), 4.4% (for Ir_2Er) and 3.9% (for Ir_2Yb) (Fig. S32†), which is in agreement with the release of lattice solvents (calcd 3.9% for $2CH_3OH + 0.5H_2O$). The weight loss for Ir_2Gd (5.6%) is higher than those for others, suggesting that one coordination water molecule could also be released below this temperature (calcd 4.9%). Between 90 and 300 °C slow weight losses occur corresponding to the partial removal of the coordination water molecule. Above 300 °C, the organic ligands start to decompose and the framework structures collapse.

Synthesis of $[Ln_2\{Ir(ppy)_2(dcbpy)\}_4(NO_3)_2(H_2O)_4]$ -solvent $(Ir_4Ln_2; Ln = Gd, Dy, Er, and Yb)$

Compounds Ir_4Ln_2 (Ln = Gd, Dy, Er, and Yb) were synthesized under similar optimized experimental conditions. A typical preparation procedure for [Yb₂(OH){Ir(ppy)₂(dcbpy)}₄(NO₃) $(H_2O)_4$]-2CH₃OH-2.5H₂O (Ir_4Yb_2) is as follows. (ppy)₂(Hdcbpy) (7.4 mg, 0.01 mmol) was suspended in 2 mL of distilled water and dissolved in 10 µL of aqueous NaOH (1 M). Then Yb(NO₃)₃·6H₂O (9.34 mg, 0.02 mmol) in 7 mL of MeOH was added. An immediate precipitate of a green powder was obtained. After keeping the vial at 80 °C for 2 days, orange rod crystals were obtained. The crystalline product of Ir₄Yb₂ was separated by filtration and washed with distilled water and a minimum amount of methanol. Yield: 23%. Elemental analyses (%) calcd for $C_{138}H_{110}N_{17}Yb_2Ir_4O_{28.5}$, C, 46.33; H, 3.10; N, 6.66; found: C, 45.82; H, 3.16; N, 6.83. IR (KBr, cm⁻¹): 3400 (s),

3103 (m), 3043 (m), 1608 (s), 1546 (m), 1477 (s), 1427 (s), 1379 (s), 1272 (w), 1232 (m), 1161 (w), 1031 (w), 866 (w), 784 (m), 761 (m), 734 (w), 698 (w), 630 (w).

For $[Gd_2(OH)\{Ir(ppy)_2(debpy)\}_4(NO_3)(H_2O)_4]\cdot 2CH_3OH\cdot 2.5H_2O$ (Ir_4Gd_2) : yield: 15%. Elemental analyses (%) calcd for $C_{138}H_{110}N_{17}Gd_2Ir_4O_{28.5}$, C, 46.74; H, 3.13; N, 6.71; found: C, 45.97; H, 3.48; N, 6.99. IR (KBr, cm⁻¹): 3357 (s), 3105 (m), 3042 (m), 1604 (s), 1583 (s), 1562 (m), 1544 (s), 1476 (s), 1420 (s), 1365 (s), 1317 (m), 1269 (w), 1235 (m), 782 (m), 729 (w), 694 (w), 629 (w).

For $[Dy_2(OH)\{Ir(ppy)_2(debpy)\}_4(NO_3)(H_2O)_4]\cdot 2CH_3OH\cdot 2.5$ H_2O (Ir_4Dy_2) : yield: 26%. Elemental analyses (%) calcd for $C_{138}H_{110}N_{17}Dy_2Ir_4O_{28.5}$, C, 46.61; H, 3.12; N, 6.70; found: C, 45.74; H, 3.21; N, 6.68. IR (KBr, cm⁻¹): 3429 (m), 3107 (m), 3053 (m), 1610 (s), 1548 (m), 1477 (s), 1425 (s), 1379 (s), 1271 (w), 1234 (w), 1162 (w), 1033 (w), 761 (s), 734 (w), 698 (w), 669 (w), 628 (w), 559 (w), 426 (w).

For $[Er_2(OH)\{Ir(ppy)_2(dcbpy)\}_4(NO_3)$ $(H_2O)_4]$ ·3CH₃OH·2.5H₂O (Ir_4Er_2) : yield: 28%. Elemental analyses (%) calcd For C₁₃₉H₁₁₄N₁₇Er₂Ir₄O_{29.5}, C, 46.40; H, 3.19; N, 6.62; found: C, 45.50; H, 3.57; N, 6.48. IR (KBr, cm⁻¹): 3402 (m), 3107 (m), 3045 (m), 1608 (s), 1546 (m), 1477 (s), 1427 (s), 1380 (s), 1271 (w), 1234 (w), 1161 (w), 1031 (w), 784 (m), 761 (m), 734 (w), 698 (w), 630 (w).

Thermal analyses reveal that the weight losses at 100 °C are 2.8% for Ir_4Gd_2 , Ir_4Dy_2 and Ir_4Yb_2 (Fig. S33†), which is in agreement with the release of two CH_3OH and 2.5 H_2O molecules (calcd 3.0–3.1%). The weight loss for Ir_4Er_2 is 4.1%, corresponding to the release of three CH_3OH and 2.5 H_2O molecules (calcd 3.9%). The number of solvent molecules for Ir_4Yb_2 is less than that obtained from the single crystal structural determination, suggesting that the lattice solvents are partially released at room temperature. The weight losses between 100 and 300 °C are attributed to the partial release of the coordination water molecules, and above 300 °C the structure begins to collapse.

X-ray crystallographic analyses

Suitable single crystals were selected for indexing and obtaining intensity data using a Bruker SMART APEX D8 diffractometer equipped with a graphite-monochromated Mo K α radiation source (λ = 0.71073 Å) at 150 K. ⁴² Adsorption corrections were carefully performed for all data. The structures were solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL. ⁴³ All non-hydrogen atoms were located in the Fourier maps and were refined with anisotropic thermal parameters. All H atoms were either placed in the calculated positions or found in the F-maps and refined isotropically.

In the case of Ir₂Dy, the residual electron densities in the solvent-accessible void due to heavily disordered solvent molecules and nitrate anions were determined using the PLATON/SQUEEZE program.⁴⁴ In cases of Ir₂Er, Ir₂Yb and Ir₄Yb₂, the lattice solvent molecules and nitrate anions were found in the Fourier map. The hydrogen atoms of disordered water molecules were not placed. Quite large (2.2–5.3 e A³) residual elec-

tron density peaks were located near the Ln or Ir atoms in the corresponding structures, and could not be reasonably modelled with the disordered atoms. The crystallographic data and refinement details are listed in Table 1. The selected bond lengths and angles for Ir2Dy, Ir2Er, Ir2Yb and Ir4Yb2 are given in Tables S1-S7.†

Conflicts of interest

There are no conflicts to declare.

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