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

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A series of iridium(III)–lanthanide(III) bimetallic coordination polymers were successfully obtained by hydrothermal reactions based on the Ir unit $[\text{Ir}(\text{ppy})_2(\text{Hdc bpy})]$, namely, $[\text{Ln}(\text{Ir}(\text{ppy})_2(\text{dc bpy}))_2(\text{NO}_3)(\text{H}_2\text{O})_n]\text{-solvent}$ (**Ir₂Ln**, $n = 5$, Ln = Gd and Dy; and $n = 4$, Ln = Er and Yb) and $[\text{Ln}_2(\text{OH})\{\text{Ir}(\text{ppy})_2(\text{dc bpy})\}_4(\text{NO}_3)(\text{H}_2\text{O})_4]\text{-solvent}$ (**Ir₄Ln₂**, Ln = Gd, Dy, Er, and Yb). Compounds **Ir₂Ln** show chain structures in which the lanthanide ions are bridged by the $\text{Ir}(\text{ppy})_2(\text{dc bpy})^-$ ligands through the carboxylate groups. Compounds **Ir₄Ln₂** have double-chain structures, in which the dimers of $\text{Yb}_2(\text{OH})$ are connected by the $\text{Ir}(\text{ppy})_2(\text{dc bpy})^-$ ligands. Magnetic studies reveal that **Ir₂Dy** and **Ir₄Dy₂** exhibit slow magnetic relaxation behaviour in zero dc field, which is characteristic of single molecule magnets, but **Ir₂Er**, **Ir₄Yb₂**, **Ir₄Er₂** and **Ir₄Yb₂** require a field to induce such characteristics. Moreover, since the iridium(III) moiety can serve as an “antenna” to effectively sensitize the f–f transitions of the lanthanide ions, near-infrared luminescence has been observed for the Yb^{III} and Er^{III} complexes. As far as we know, this is the first observation of SMM behaviour and NIR luminescence in iridium(III)–lanthanide(III) bimetallic coordination polymers.

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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.¹ Magneto-luminescent 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.^{2,3} 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),^{4,5} but also excellent luminescence properties including narrow line-like emission, high quantum yield and long lifetime.^{2,6} Since the direct exci-

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}

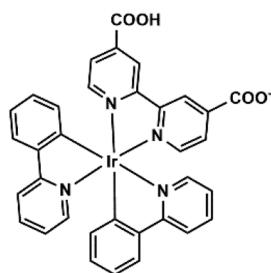
Among the transition metals, the Ir^{III} complexes with energy levels modifiable through the cyclometalated ligands stand out as sensitizers for NIR emission from lanthanide ions.¹¹ The advantage is that the excitation is done in the visible region of the spectrum instead of the destructive UV light normally needed for organics. In 2008, De Cola and co-workers 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

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Scheme 1 The molecular structure of the metalloligand $\text{Ir}(\text{ppy})_2(\text{Hdc bpy})$.

On the contrary, luminescent $\text{Ir}^{\text{III}}\text{-Ln}^{\text{III}}$ single molecule magnets (SMMs) have been scarcely described. The only examples, as far as we are aware, are Ir_6Ln ($\text{Ln} = \text{Dy, Er, and Yb}$) clusters which have been reported by us and exhibit simultaneously slow magnetization relaxation from Ln^{III} and luminescence dominated by Ir^{III} .¹⁵ However, no efficient energy transfer between Ir and Ln was observed.

Owing to our long-term interest in magneto-optical bifunctional materials,^{15,16} herein we report two new series of $\text{Ir}^{\text{III}}\text{-Ln}^{\text{III}}$ coordination polymers based on the metalloligand $\text{Ir}(\text{ppy})_2(\text{Hdc bpy})$ (Scheme 1), namely, $[\text{Ln}\{\text{Ir}(\text{ppy})_2(\text{Hdc bpy})\}_2(\text{NO}_3)(\text{H}_2\text{O})_n]\text{-solvent}$ (Ir_2Ln , $n = 5$, $\text{Ln} = \text{Gd and Dy}$; and $n = 4$, $\text{Ln} = \text{Er and Yb}$) and $[\text{Ln}_2(\text{OH})\{\text{Ir}(\text{ppy})_2(\text{Hdc bpy})\}_4(\text{NO}_3)(\text{H}_2\text{O})_4]\text{-solvent}$ (Ir_4Ln_2 , $\text{Ln} = \text{Gd, Dy, Er, and Yb}$). Ir_2Ln show chain structures, in which the Ln^{III} ions are cross-linked by the $\text{Ir}(\text{ppy})_2(\text{Hdc bpy})^-$ ligands *via* the two carboxylate groups. For Ir_4Ln_2 , dimers of $\text{Ln}_2(\text{OH})$ are observed, which are further connected by the carboxylate groups of the $\text{Ir}(\text{ppy})_2(\text{Hdc bpy})^-$ ligands, forming a ladder-like chain structure. Interestingly, both single molecule magnetism

and $\text{Ir} \rightarrow \text{Ln}$ energy transfer accompanied by near-infrared emission were demonstrated to co-exist in Ir_2Ln and Ir_4Ln_2 ($\text{Ln} = \text{Er and Yb}$).

Results and discussion

Crystal structures

Compounds $[\text{Ln}\{\text{Ir}(\text{ppy})_2(\text{Hdc bpy})\}_2(\text{NO}_3)(\text{H}_2\text{O})_n]\text{-solvent}$ (Ir_2Ln , $n = 5$, $\text{Ln} = \text{Gd and Dy}$; and $n = 4$, $\text{Ln} = \text{Er and Yb}$) and $[\text{Ln}_2(\text{OH})\{\text{Ir}(\text{ppy})_2(\text{Hdc bpy})\}_4(\text{NO}_3)(\text{H}_2\text{O})_4]\text{-solvent}$ (Ir_4Ln_2 , $\text{Ln} = \text{Gd, Dy, Er, and Yb}$) were synthesized by solvothermal reactions of $\text{Ir}(\text{ppy})_2(\text{Hdc bpy})$ and $\text{Ln}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ in $\text{H}_2\text{O}/\text{MeOH}$ using different concentrations of NaOH and temperatures. Powder XRD measurements revealed that Ir_2Ln ($\text{Ln} = \text{Gd, Dy, Er, and Yb}$) and Ir_4Ln_2 ($\text{Ln} = \text{Gd, Dy, Er, and Yb}$) are isostructural compounds. However, single crystals of good quality were obtained only for compounds Ir_2Dy , Ir_2Er , Ir_2Yb and Ir_4Yb_2 . The crystallographic data for these four compounds are given in Table 1.

Ir_2Ln are isomorphous compounds that crystallize in the triclinic $\bar{P}\bar{1}$ space group, though the numbers of the coordination water molecules are slightly different ($n = 5$ for $\text{Ln} = \text{Gd and Dy}$; and $n = 4$ for $\text{Ln} = \text{Er and Yb}$). Therefore, Ir_2Yb is selected as a representative for the description of the structures. The asymmetric unit of Ir_2Yb consists of two $\text{Ir}(\text{ppy})_2(\text{Hdc bpy})^-$ ligands, one Yb^{III} , one NO_3^- , 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 Ir_2Dy , Ir_2Er , Ir_2Yb and Ir_4Yb_2

	Ir_2Dy	Ir_2Er	Ir_2Yb	Ir_4Yb_2
Formula	$\text{C}_{68}\text{H}_{54}\text{N}_8\text{O}_{13}\text{DyIr}_2$	$\text{C}_{140}\text{H}_{122}\text{N}_{18}\text{O}_{35}\text{Er}_2\text{Ir}_4$	$\text{C}_{140}\text{H}_{122}\text{N}_{18}\text{O}_{35}\text{Yb}_2\text{Ir}_4$	$\text{C}_{280}\text{H}_{236}\text{N}_{34}\text{O}_{61}\text{Yb}_4\text{Ir}_8$
M	1738.09	3719.87	3731.43	7282.77
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$\bar{P}\bar{1}$	$\bar{P}\bar{1}$	$\bar{P}\bar{1}$	$P2_1/c$
a (Å)	8.5559(13)	8.6129(14)	8.5775(16)	36.569(3)
b (Å)	18.370(3)	18.343(3)	18.360(3)	8.6347(5)
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(5)	90
V (Å ³)	3433.3(9)	3465.9(10)	3449.0(11)	12 850.4(14)
Z	2	1	1	2
ρ_{calcd} (g cm ⁻³)	1.681	1.782	1.797	1.882
μ (mm ⁻¹)	5.009	5.106	5.270	5.653
$F(000)$	1684.0	1812.0	1816.0	7076.0
R_{int}	0.0495	0.0482	0.0432	0.0617
$T_{\text{max}}, T_{\text{min}}$	0.634, 0.350	0.629, 0.350	0.621, 0.350	0.728, 0.360
R_1 ^a , wR_2 ^b [$I > 2\sigma(l)$]	0.1105, 0.2755	0.0795, 0.1847	0.0485, 0.1178	0.0844, 0.1952
R_1 ^a , wR_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
$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}}$ (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 $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

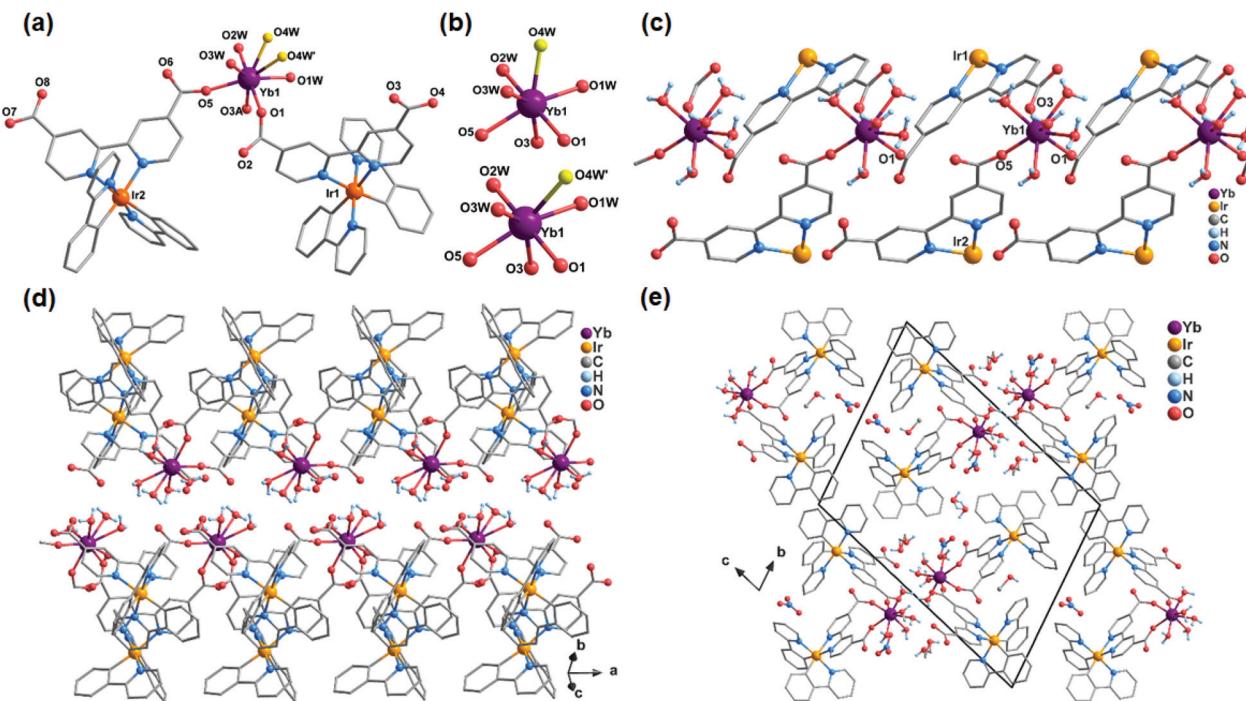


Fig. 1 (a) The building unit of the structure of Ir_2Yb . (b) Coordination environments of the Yb^{3+} ion. (c) The single chain structure of the compound Ir_2Yb . The ppy ligands are omitted for clarity. (d) The double-chain structure of Ir_2Yb . (e) Packing diagram of the structure of Ir_2Yb viewed along the a -axis. All H atoms except those attached to the oxygen atoms are omitted for clarity.

$[\text{YbO}_7]$ polyhedra are slightly deviated from an ideal capped trigonal prism ($\text{CShM} = 1.17$) and pentagonal bipyramidal ($\text{CShM} = 1.25$), respectively. The $\text{Yb}-\text{O}$ bond lengths are in the range of $2.191(7)$ – $2.452(18)$ Å, and the $\text{O}-\text{Yb}-\text{O}$ angles are in the range of $67.4(5)$ – $149.8(3)$ °.

Two $\text{Ir}(\text{ppy})_2(\text{dcbpy})^-$ 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 $\text{Yb}\cdots\text{Yb}$ distance within the chain is 8.58 Å. The chain is polar with the $\text{Ir}(\text{ppy})_2(\text{dcbpy})^-$ 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 non-polar (Fig. 1d). The shortest interchain $\text{Yb}\cdots\text{Yb}$ 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 Ir_2Dy and Ir_2Er 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 Ir_2Dy . (b) The coordination environment of the Dy^{3+} ion.

ment of Dy^{3+} in Ir_2Dy . Unlike the seven-coordinated lanthanide ion in Ir_2Yb and Ir_2Er (Fig. S4†), the Dy atom is eight-coordinated by three carboxylate oxygen atoms from three ligands (O1, O3A, and O5) [$\text{Dy}-\text{O}$: 2.270(16)–2.376(16) Å] and five coordinated water molecules (O1W, O2W, O3W, O4W, and O5W) [$\text{Dy}-\text{O}$: 2.332(19)–2.48(3) Å] (Fig. 2). This can be related to the lanthanide contract effect, the Dy^{3+} ion with larger ionic radius shows higher coordination number. The geometry of Dy^{3+} is best described as a slightly distorted triangular dodecahedron (D_{2d}) with a CShM value of 0.94.

The compound Ir_2Yb_2 crystallizes in the monoclinic space group $P2_1/c$. Its asymmetric unit contains four $\text{Ir}(\text{ppy})_2(\text{dcbpy})^-$ ligands, two Yb^{3+} , one OH^- , one NO_3^- , 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-

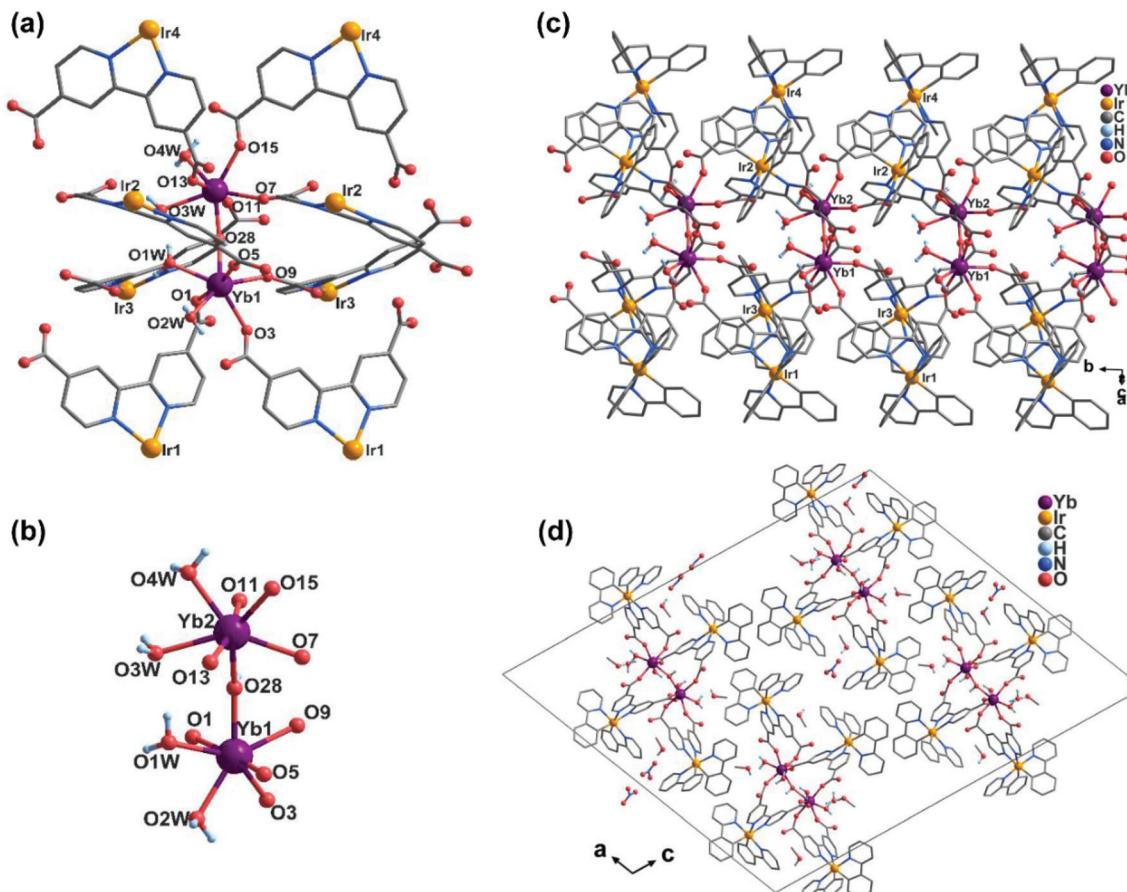


Fig. 3 (a) The building unit of the structure of Ir_4Yb_2 . The ppy ligands are omitted for clarity. (b) Coordination environments of the Yb^{III} ions. (c) The double-chain structure of the compound Ir_4Yb_2 . (d) Packing diagram of the structure of Ir_4Yb_2 viewed along the b -axis. All H atoms except 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 $S(D_{5\text{h}}) = 1.80$ (Yb1) and $S(D_{5\text{h}}) = 0.96$ (Yb2). The neighbouring $[\text{Yb}_2\text{O}_7]$ polyhedra are linked *via* the OH^- group, forming a dimer of $\{\text{Yb}_2(\text{OH})(\text{COO})_8(\text{H}_2\text{O})_4\}$ ($\text{Yb}-\text{O}-\text{Yb} = 159.6(1)^\circ$ and $\text{Yb} \cdots \text{Yb} = 4.3962(11) \text{ \AA}$). All of the Ir (ppy)₂(dc bpy)⁻ ligands adopt a bi-dentate coordination mode, unlike those in Ir_2Ln , and connect the $\{\text{Yb}_2(\text{OH})(\text{COO})_8(\text{H}_2\text{O})_4\}$ dimers into a one-dimensional double-chain structure (Fig. 3c). The intrachain $\text{Yb} \cdots \text{Yb}$ distance between the dimers is 8.63 \AA . 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 Ir_2Gd , Ir_4Gd_2 , Ir_4Dy_2 and Ir_4Er_2 , 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 Ir_4Yb_2 is significantly different from that of Ir_2Yb . A careful analysis reveals, however, that the double chain in Ir_4Yb_2 can be viewed as two single chains in

Ir_2Yb connected by the hydroxyl groups. The involvement of an OH^- group in Ir_4Yb_2 can be explained by the more basic reaction condition used for the synthesis of Ir_4Yb_2 .

Notably, $\text{Ir}^{\text{III}}\text{-Ln}^{\text{III}}$ coordination polymers containing the same ligand $\text{Ir}(\text{ppy})_2(\text{Hdc bpy})$ are still rare. The only examples, as far as we are aware, are $\text{Ln}[\text{Ir}(\text{ppy})_2(\text{dc bpy})]_2(\text{OH})\cdot\text{H}_2\text{O}$ ($\text{Ln} = \text{Gd, Yb, Er, and Nd}$)¹⁴ and $\text{Y}[\text{Ir}(\text{ppy})_2(\text{dc bpy})]_2(\text{OH})$.¹⁸ These compounds possess identical chain structures that are remarkably different from those of Ir_2Yb and Ir_4Yb_2 , in which the dimers of edge-sharing $\{\text{LnO}_7\}$ or $\{\text{YO}_7\}$ pentagonal bipyramidal *via* two OH^- groups are further connected by the carboxylate groups in the metalloligand. Therefore compounds Ir_2Ln and Ir_4Ln_2 provide new structural types of the $\text{Ir}^{\text{III}}\text{-Ln}^{\text{III}}$ coordination polymers based on $\text{Ir}(\text{ppy})_2(\text{Hdc bpy})$.

Magnetic properties

Variable temperature dc magnetic susceptibilities of Ir_2Ln and Ir_4Ln_2 ($\text{Ln} = \text{Gd, Dy, Er, and Yb}$) were measured in the temperature range of 2–300 K in an applied field of 1 kOe. Plots of $\chi_M T$ versus T (χ_M is the molar magnetic susceptibility per Ln^{III} ion) for these compounds are shown in Fig. 4. At 300 K, the $\chi_M T$ values are 7.73 and 7.84 $\text{cm}^3 \text{ K mol}^{-1}$ for Ir_2Gd and Ir_4Gd_2 ,

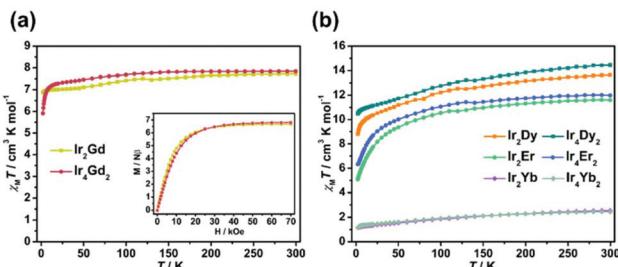


Fig. 4 (a) Temperature dependence of $\chi_M T$ per Gd on cooling in a field of 1 kOe for Ir_2Gd and Ir_4Gd_2 . Inset: M vs. H plots of the two compounds at 2 K. (b) Temperature dependence of $\chi_M T$ per Ln on cooling in a field of 1 kOe for Ir_2Ln and Ir_4Ln_2 (Ln = Dy, Er, and Yb).

respectively, which are close to the expected value of $7.88 \text{ cm}^3 \text{K mol}^{-1}$ for an isolated Gd^{III} ion ($S = 7/2, L = 0, {}^8\text{S}_{7/2}, J = 7/2, g = 2$). Upon cooling, the $\chi_M T$ value of Ir_2Gd decreases continuously in the range of 300–50 K and then decreases smoothly to the minimum value of $6.88 \text{ cm}^3 \text{K mol}^{-1}$ 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 $5.91 \text{ cm}^3 \text{K mol}^{-1}$ at 2 K. The low temperature feature could be attributed to the occurrence of the $\text{Gd}^{\text{III}}\cdots\text{Gd}^{\text{III}}$ antiferromagnetic exchange interactions, and is given by the negative values of the Weiss constants (θ) as -0.04 K for Ir_2Gd and -0.54 K for Ir_4Gd_2 (Fig. S11†). The stronger antiferromagnetic interactions in Ir_4Gd_2 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 $7N\beta$ for an isolated Gd^{III} ion.

The dc magnetic susceptibilities of compounds Ir_2Ln and Ir_4Ln_2 (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 (Ir_2Dy), 14.44 (Ir_4Dy_2), 11.60 (Ir_2Er), 11.98 (Ir_4Er_2), 2.53 (Ir_2Yb) and 2.45 (Ir_4Yb_2) $\text{cm}^3 \text{K mol}^{-1}$, which are consistent with the theoretical values of 14.17 ($\text{Dy}^{\text{III}}, {}^6\text{H}_{15/2}$), 11.48 ($\text{Er}^{\text{III}}, {}^4\text{I}_{15/2}$) and 2.57 ($\text{Yb}^{\text{III}}, {}^2\text{F}_{7/2}$) $\text{cm}^3 \text{K mol}^{-1}$. The decrease in the $\chi_M T$ value on lowering the temperature is attributed to the thermal depopulation of the excited M_J sublevels and/or the weak antiferromagnetic exchange interactions between the metal centres.¹⁹ The magnetization values of compounds Ir_2Ln and Ir_4Ln_2 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

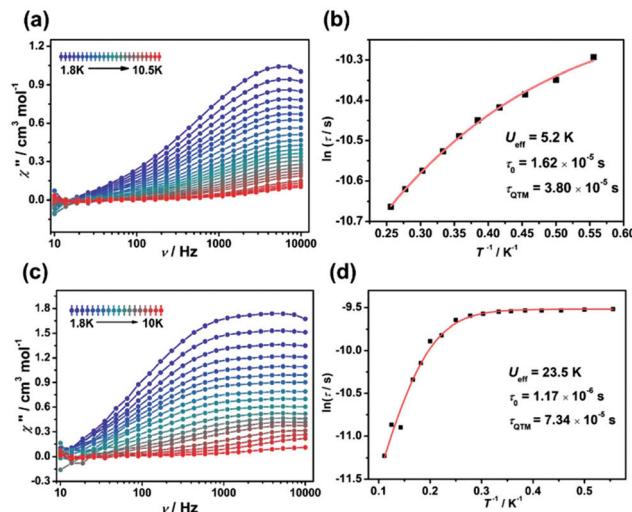


Fig. 5 Out-of-phase (χ'') ac susceptibilities of Ir_2Dy (a) and Ir_4Dy_2 (c) under zero dc field. Plots of $\ln(\tau)$ vs. $1/T$ for Ir_2Dy (b) and Ir_4Dy_2 (d).

Ir_2Dy and Ir_4Dy_2 showed clear frequency dependence of in-phase (χ') and out-of-phase (χ'') 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_2Dy and in the range of 0.25–0.45 for Ir_4Dy_2 , 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 $U_{\text{eff}} = 5.2 \text{ K}$, $\tau_0 = 1.6 \times 10^{-5} \text{ s}$, and $\tau_{\text{QTM}} = 3.8 \times 10^{-5} \text{ s}$ for Ir_2Dy (Fig. 5b), and $U_{\text{eff}} = 23.5 \text{ K}$, $\tau_0 = 1.17 \times 10^{-6} \text{ s}$, and $\tau_{\text{QTM}} = 7.34 \times 10^{-4} \text{ s}$ for Ir_4Dy_2 (Fig. 5d), respectively.

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

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

In order to suppress the QTM and get further insight into the magnetic relaxation dynamics of complexes Ir_2Dy and Ir_4Dy_2 , we obtained the ac magnetic susceptibilities under an applied dc bias field of 2 kOe. Variable-frequency ac magnetic susceptibilities of Ir_2Dy 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 $U_{\text{eff}} = 38.1$ K and $\tau_0 = 2.93 \times 10^{-6}$ 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 Ir_4Dy_2 , 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: $U_{\text{eff}} = 21.4$ K, $\tau_0 = 2.89 \times 10^{-6}$ s, $\tau_{\text{QTM}} = 7.98 \times 10^{-4}$ s 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 Ir_2Er and Ir_4Er_2 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 Ir_2Yb and Ir_4Yb_2 were also investigated under an external dc field (Fig. 6, S24–S27, Tables S15 and S16†). For Ir_2Yb , 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 $U_{\text{eff}} = 24.4$ K, $\tau_0 = 2.88 \times 10^{-7}$ s, and $A = 687.9$ K⁻¹ s⁻¹. However, two distinct peaks at low temperatures were observed in the temperature-dependent magnetic dynamics of Ir_4Yb_2 , 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 $U_{\text{eff}} = 22.2$ K, $\tau_0 = 2.03 \times 10^{-7}$ s and $A = 8678$ K⁻¹ s⁻¹ for the FR process, while $U_{\text{eff}} = 28.3$ K, $\tau_0 = 2.5 \times 10^{-8}$ s and $A = 682$ K⁻¹ s⁻¹ for the SR process. The observation of dual magnetization relaxation processes in Ir_4Yb_2 could result from the presence of two crystallographic sites with two different environments in the structure.

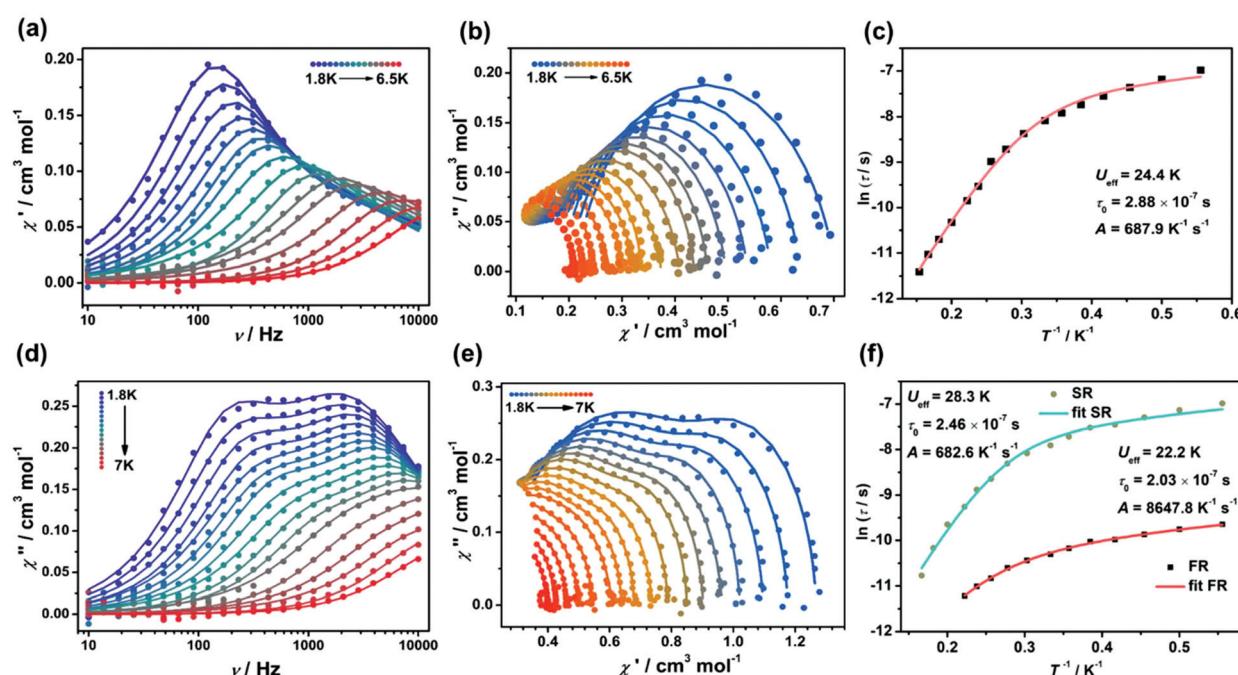


Fig. 6 Frequency dependence of out-of-phase (χ'') ac susceptibilities at different temperatures for Ir_2Yb (a) and Ir_4Yb_2 (d) under an external dc field. The Cole–Cole plots of the ac susceptibilities for Ir_2Yb (b) and Ir_4Yb_2 (e). Plots of $\ln(\tau)$ vs. $1/T$ for Ir_2Yb (c) and Ir_4Yb_2 (f).

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 Dy^{III} and Er^{III} 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

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 $\pi - \pi^*$ 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 $^1\text{LLCT}$ (ligand-to-ligand charge-

transfer) and $^1\text{MLCT}$ (metal-to-ligand charge-transfer). The lower energy absorptions (*ca.* 450–550 nm) originate from the spin forbidden $^3\text{MLCT}$ 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 ($13\,245\text{ cm}^{-1}$) and 654 nm ($15\,290\text{ cm}^{-1}$) were observed for Ir_2Dy and Ir_2Er , respectively, corresponding to the f–f transitions of the Dy^{III} ions ($^5\text{H}_{15/2}$ to $^6\text{F}_{3/2}$) and Er^{III} ions ($^4\text{I}_{15/2}$ to $^4\text{F}_{9/2}$).³⁵ Although the structures are different, a similar phenomenon was also observed for Ir_4Dy_2 and Ir_4Er_2 .

Upon excitation in the visible region at 375 nm, Ir(ppy)₂(Hdcbpy) exhibits a strong emission band at 605 nm, corresponding to the $^3\text{MLCT}$ transition as a consequence of the heavy-atom effect. As is to be expected, the solid-state luminescence spectra of compounds Ir_2Ln and Ir_4Ln_2 (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

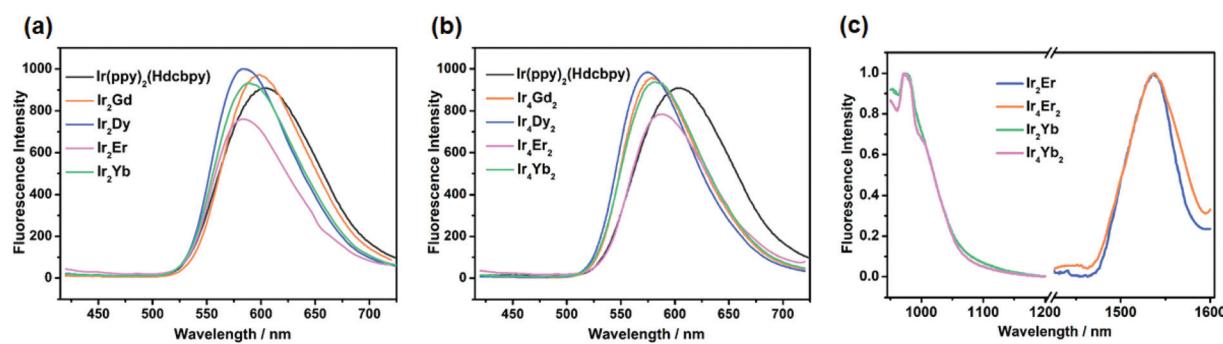


Fig. 7 (a) The emission spectra of $\text{Ir}(\text{ppy})_2(\text{Hdcbpy})$ and Ir_2Ln in the solid-state ($\lambda_{\text{ex}} = 375\text{ nm}$). (b) The emission spectra of $\text{Ir}(\text{ppy})_2(\text{Hdcbpy})$ and Ir_4Ln_2 (Ln = Gd, Dy, Er, Yb) in the solid-state ($\lambda_{\text{ex}} = 375\text{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

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	$\lambda_{\text{em}}/\text{nm}$	$\tau/\mu\text{s}$	QY/%
Ir(ppy) ₂ (Hdcbpy)	—	—	—	605	6.60	4.22
Ir_2Gd	—	—	—	598	8.69	5.83
Ir_4Gd_2	—	—	—	578	7.74	8.08
Ir_2Dy	0 kOe	Orbach, QTM	$U_{\text{eff}} = 5.2\text{ K}$, $\tau_0 = 1.62 \times 10^{-5}\text{ s}$, $\tau_{\text{QTM}} = 3.80 \times 10^{-5}\text{ s}$	583	4.79	6.00
	2.0 kOe	QTM (FR)	$\tau_{\text{QTM}} = 2.25 \times 10^{-5}$			
		Orbach(SR)	$U_{\text{eff}} = 38.1\text{ K}$, $\tau_0 = 2.93 \times 10^{-6}\text{ s}$			
Ir_4Dy_2	0 kOe	Orbach, QTM	$U_{\text{eff}} = 23.5\text{ K}$, $\tau_0 = 1.17 \times 10^{-6}\text{ s}$	575	0.66	11.94
	2.0 kOe	Orbach, QTM; direct	$\tau_{\text{QTM}} = 7.34 \times 10^{-4}\text{ s}$ $U_{\text{eff}} = 21.4\text{ K}$, $\tau_0 = 2.89 \times 10^{-6}\text{ s}$			
			$\tau_{\text{QTM}} = 7.98 \times 10^{-4}\text{ s}$, $A = 193.9\text{ K}^{-1}\text{ s}^{-1}$			
Ir_2Er	1.0 kOe	Orbach	$U_{\text{eff}} = 13.6\text{ K}$, $\tau_0 = 2.72 \times 10^{-8}\text{ s}$	584	6.37	0.68
	1.5 kOe	Orbach	$U_{\text{eff}} = 11.8\text{ K}$, $\tau_0 = 6.68 \times 10^{-8}\text{ s}$	1538	1.40	—
Ir_4Er_2	1.0 kOe	Orbach, direct	$U_{\text{eff}} = 24.4\text{ K}$, $\tau_0 = 2.88 \times 10^{-7}\text{ s}$, $A = 687.9\text{ K}^{-1}\text{ s}^{-1}$	588	5.47	1.08
	1.5 kOe	Orbach	$U_{\text{eff}} = 22.2\text{ K}$, $\tau_0 = 2.03 \times 10^{-7}\text{ s}$	1538	1.37	—
Ir_2Yb	1.0 kOe	Orbach, direct	$U_{\text{eff}} = 8647.8\text{ K}^{-1}\text{ s}^{-1}$	590	2.23	5.60
Ir_4Yb_2	1.5 kOe	Orbach, direct (FR)	$U_{\text{eff}} = 28.3\text{ K}$, $\tau_0 = 2.46 \times 10^{-8}\text{ s}$, $A = 682.6\text{ K}^{-1}\text{ s}^{-1}$	975	0.92	—
		Orbach, direct (SR)	$U_{\text{eff}} = 28.3\text{ K}$, $\tau_0 = 2.46 \times 10^{-8}\text{ s}$, $A = 682.6\text{ K}^{-1}\text{ s}^{-1}$	975	0.86	—

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 Ir^{III} 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 Gd^{III} 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% (**Ir₂Gd**) and 8.08% (**Ir₄Gd₂**), which is attributed to the rigidity of the coordination framework that reduces self-quenching and the possibility of non-radiative 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(Hdc bpy) is 16 600 cm^{−1}, which is suitable for sensitizing the NIR lanthanide ions Yb^{III} and Er^{III}, but is too low to sensitize the low-lying excited state (⁴F_{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(Hdc bpy), 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} → ²F_{7/2} transition, while in **Ir₄Yb₂**, 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 Er^{III} complexes show an emission peak at around 1530 nm, which is attributed to the ⁴I_{13/2} → ⁴I_{15/2} transition.⁴¹ Moreover, the luminescence decay is well fit to a bi-exponential curve, affording lifetimes of 0.92 μs for **Ir₂Yb**, 0.86 μs for **Ir₄Yb₂**, 1.40 μs for **Ir₂Er** and 1.37 μs for **Ir₄Er₂** (Fig. S30 and S31†). Noting that the quantum yields of **Ir₂Er** (ϕ = 0.68%) and **Ir₄Er₂** (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(Hdc bpy) 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 field-induced 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(dc bpy)}₂(NO₃)(H₂O)_n]_·solvent (**Ir₂Ln**, $n = 5$, Ln = Gd and Dy; $n = 4$, Ln = Er and Yb)

Compounds **Ir₂Ln** (Ln = Gd, Dy, Er, and Yb) were synthesized under similar optimized experimental conditions. A typical procedure for the preparation of [Yb{Ir(ppy)₂(dc bpy)}₂(NO₃)(H₂O)₄]_·2CH₃OH_·0.5H₂O (**Ir₂Yb**) is described below. Ir(ppy)₂(Hdc bpy) (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(NO₃)₃_·6H₂O (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).

For $[\text{Gd}\{\text{Ir}(\text{ppy})_2(\text{dcbpy})\}_2(\text{NO}_3)(\text{H}_2\text{O})_5]\cdot2\text{CH}_3\text{OH}\cdot0.5\text{H}_2\text{O}$ (**Ir₂Gd**): yield: 18%. Elemental analyses (%) calcd for $C_{70}H_{61}\text{GdIr}_2N_9O_{17.5}$, 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 $[\text{Dy}\{\text{Ir}(\text{ppy})_2(\text{dcbpy})\}_2(\text{NO}_3)(\text{H}_2\text{O})_5]\cdot2\text{CH}_3\text{OH}\cdot0.5\text{H}_2\text{O}$ (**Ir₂Dy**): yield: 41%. Elemental analyses (%) calcd for $C_{70}H_{61}\text{DyIr}_2N_9O_{17.5}$, 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 $[\text{Er}\{\text{Ir}(\text{ppy})_2(\text{dcbpy})\}_2(\text{NO}_3)(\text{H}_2\text{O})_4]\cdot2\text{CH}_3\text{OH}\cdot0.5\text{H}_2\text{O}$ (**Ir₂Er**): yield: 37%. Elemental analyses (%) calcd for $C_{70}H_{61}\text{ErIr}_2N_9O_{17.5}$, 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 **Ir₂Dy**), 4.4% (for **Ir₂Er**) and 3.9% (for **Ir₂Yb**) (Fig. S32†), which is in agreement with the release of lattice solvents (calcd 3.9% for $2\text{CH}_3\text{OH} + 0.5\text{H}_2\text{O}$). The weight loss for **Ir₂Gd** (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 $[\text{Ln}_2\{\text{Ir}(\text{ppy})_2(\text{dcbpy})\}_4(\text{NO}_3)_2(\text{H}_2\text{O})_4]\cdot\text{solvent}$ (**Ir₄Ln₂**; Ln = Gd, Dy, Er, and Yb)

Compounds **Ir₄Ln₂** (Ln = Gd, Dy, Er, and Yb) were synthesized under similar optimized experimental conditions. A typical preparation procedure for $[\text{Yb}_2(\text{OH})\{\text{Ir}(\text{ppy})_2(\text{dcbpy})\}_4(\text{NO}_3)(\text{H}_2\text{O})_4]\cdot2\text{CH}_3\text{OH}\cdot2.5\text{H}_2\text{O}$ (**Ir₄Yb₂**) is as follows. $\text{Ir}(\text{ppy})_2(\text{Hdcbpy})$ (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 $\text{Yb}(\text{NO}_3)_3\cdot6\text{H}_2\text{O}$ (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 $C_{138}H_{110}\text{N}_{17}\text{Yb}_2\text{Ir}_4\text{O}_{28.5}$, 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 $[\text{Gd}_2(\text{OH})\{\text{Ir}(\text{ppy})_2(\text{dcbpy})\}_4(\text{NO}_3)(\text{H}_2\text{O})_4]\cdot2\text{CH}_3\text{OH}\cdot2.5\text{H}_2\text{O}$ (**Ir₄Gd₂**): yield: 15%. Elemental analyses (%) calcd for $C_{138}H_{110}\text{N}_{17}\text{Gd}_2\text{Ir}_4\text{O}_{28.5}$, 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 $[\text{Dy}_2(\text{OH})\{\text{Ir}(\text{ppy})_2(\text{dcbpy})\}_4(\text{NO}_3)(\text{H}_2\text{O})_4]\cdot2\text{CH}_3\text{OH}\cdot2.5\text{H}_2\text{O}$ (**Ir₄Dy₂**): yield: 26%. Elemental analyses (%) calcd for $C_{138}H_{110}\text{N}_{17}\text{Dy}_2\text{Ir}_4\text{O}_{28.5}$, 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 $[\text{Er}_2(\text{OH})\{\text{Ir}(\text{ppy})_2(\text{dcbpy})\}_4(\text{NO}_3)(\text{H}_2\text{O})_4]\cdot3\text{CH}_3\text{OH}\cdot2.5\text{H}_2\text{O}$ (**Ir₄Er₂**): yield: 28%. Elemental analyses (%) calcd for $C_{139}H_{114}\text{N}_{17}\text{Er}_2\text{Ir}_4\text{O}_{29.5}$, 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 **Ir₄Gd₂**, **Ir₄Dy₂** and **Ir₄Yb₂** (Fig. S33†), which is in agreement with the release of two CH_3OH and $2.5\text{H}_2\text{O}$ molecules (calcd 3.0–3.1%). The weight loss for **Ir₄Er₂** is 4.1%, corresponding to the release of three CH_3OH and $2.5\text{H}_2\text{O}$ molecules (calcd 3.9%). The number of solvent molecules for **Ir₄Yb₂** 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 ($\lambda = 0.71073\text{ \AA}$) 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 \AA^3) 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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