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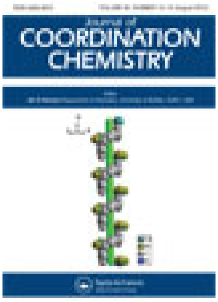

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Synthesis, structures, and properties of lead(II) and cobalt(II) metal-organic frameworks based on a flexible benzophenone-2,4′-dicarboxylic acid (H_2bpdc)

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Synthesis, structures, and properties of lead(II) and cobalt(II) metal-organic frameworks based on a flexible benzophenone-2,4′-dicarboxylic acid (H_2bpdc)

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Two new coordination polymers, $[\mathrm{Pb(bpdc)}]_n$ (**1**) and $[\mathrm{Co(bpdc)(phen)}]_n$ (**2**) [H_2bpdc = benzophenone-2,4′-dicarboxylic acid, phen = 1,10-phenanthroline], have been synthesized and structurally characterized. Hydrogen bonding and $\pi\cdots\pi$ stacking extend **1** and **2** into 3-D supramolecular architectures, where **1** exhibits a 3-D framework with 1-D hairpin-like helicates based on Pb–O covalent bonds and **2** displays a 3-D network with 1-D zipper-like chains based on Co–O and Co–N covalent bonds. The FT-IR spectra, PXRD and TG analyses are discussed for **1** and **2**. Fluorescence spectra and luminescent lifetime are studied for **1**.

Keywords: Coordination polymer; Hydrogen bonding; $\pi\cdots\pi$ Stacking; Fluorescence; Luminescent lifetime

1. Introduction

Rational design and preparation of coordination polymers (CPs) have aroused wide interest in crystal engineering and materials chemistry for their potential applications as functional solid-state materials; CPs with various helical motifs are of particular importance. The structures of ligands are crucial to construct CPs, and flexible V-shaped ketone can greatly enhance the possibility of forming helicity of the polymeric chains [1–4]. As a result, by choosing ideal ligands, several single-, double- and higher-order helical compounds have been generated in self-assembly processes. Organized by hydrogen bonding and $\pi\cdots\pi$ stacking, a few helical assemblies of purely organic molecules, as well as many inorganic helical structures, have been described [5, 6].

There are few examples of intertwining of two single-stranded helicates to form infinite double helical chains [7]. Moreover, no neutral double- or higher-order helix assembled by single-stranded helical coordination oligomers or infinite CPs directed by supramolecular interactions have been reported, although such structures may be

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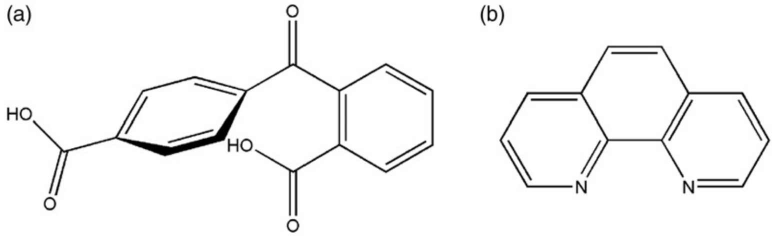

Figure 1. (a) Structure of H_2bpdc. (b) Structure of phen.

regarded as better biomimetic assemblies of nucleic acids than the polymeric helicates formed under covalent metal coordination.

Considering the flexible and rotatable features of ketones, as well as the asymmetry of the ligands, an asymmetrically V-shaped ketone, benzophenone-2,4′-dicarboxylic acid (H_2bpdc), was selected [8], as shown in figure 1(a). The chosen ligand might assemble frameworks with special properties such as interpenetration and entanglement in the presence of phen shown in figure 1(b). The phen is important in maintaining one dimensionality and may provide potential supramolecular recognition sites for aromatic $\pi\cdots\pi$ stacking to form helices [9]. The helical chains may also be paired under supramolecular recognition and attraction through $\pi\cdots\pi$ stacking and hydrogen-bonding interactions into double-stranded helices or molecular zippers, as revealed by single-crystal studies.

As an extension of our previous work [10], herein we report Pb(II) and Co(II) CPs, $[Pb(bpdc)]_n$ (**1**) and $[Co(bpdc)(phen)]_n$ (**2**) (H_2bpdc = benzophenone-2,4′-dicarboxylic acid, phen = 1,10-phenanthroline monohydrate).

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were commercially available and used without purification unless otherwise noted. IR spectra were recorded on a Shimadzu FT-IR 440 spectrophotometer with KBr pellets from 400–4000 cm^{-1}. Fluorescent properties of the compounds were measured with a Hitachi F-4500 FL Spectrophotometer. Luminescent lifetimes were performed on Edinburgh FLS920. The X-ray powder diffraction patterns were recorded with a Pigaku D/Max 3III diffractometer. TG measurements were performed by heating the crystalline sample from 303 to 1173 K at a rate of 5 K min^{-1} under N_2 with a NETZSCH STA 449 C microanalyzer.

2.2. *Synthesis of* $[Pb(bpdc)]_n$ *(1)*

A methanol solution (2 mL) of H_2bpdc (13.51 mg, 0.05 mmol) was slowly mixed with aqueous solution (2 mL) of $Pb(NO_3)_2$ (16.56 mg, 0.05 mmol) and then a drop of $NaHCO_3$ in aqueous solution (1 mmol mL^{-1}) was added to the mixture. The reaction mixture was heated at 413 K for 3 days followed by slowly cooling to room temperature, producing transparent crystalline products of **1**. The crystals were stable in air. Yield is 60%. FT-IR (KBr): $\nu = 3433$ (m), 3060 (m), 1668 (s), 1583 (s), 1419 (vs), 1290 (s), 1244 (s), 856 (s), 783 (s), 729 (s) cm^{-1}.

2.3. *Synthesis of [Co(bpdc)(phen)]$_n$ (2)*

A methanol solution (2 mL) of H_2bpdc (27.02 mg, 0.1 mmol) and phen (18.02 mg, 0.1 mmol) was slowly mixed with aqueous solution (2 mL) of $Co(NO_3)_2$ (9.15 mg, 0.05 mmol); afterward a drop of Na_2CO_3 in aqueous solution (1 mmol mL^{-1}) was added to the mixture. At similar conditions to **1**, pink crystals of **2** were produced. The crystals were stable in air. Yield is 75%. FT-IR (KBr): $\nu = 3440$ (m), 1686 (s), 1596 (w), 1391 (s), 1290 (s), 1233 (s), 1135 (m), 1031 (w), 879 (w), 742 (w), 642 (w) cm^{-1}.

2.4. *Crystallographic data collection and refinement*

Single-crystal diffraction data of **1** and **2** were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The structures were solved by direct methods and refined using full-matrix least-squares. All non-hydrogen atoms were anisotropically refined. All calculations were carried out using SHELXTL-97 and PLATON99. Crystal data collection and refinement parameters for **1** and **2** are given in table 1. The detailed hydrogen bonding parameters for **2** are listed in table 2.

Table 1. Crystallographic data for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{15}H_8O_5Pb$	$C_{27}H_{16}CoN_2O_5$
Formula weight	475.40	507.35
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbcn*	*P2₁/c*
Unit cell dimensions (Å, °)		
a	12.159(6)	7.7373(12)
b	6.865(4)	15.894(2)
c	29.162(16)	19.076(3)
α	90	90
β	90	102.974(5)
γ	90	90
Volume (Å^3), *Z*	2434(2), 8	2286.0(6), 4
Calculated density ($g\,cm^{-3}$)	2.595	1.474
Absorption coefficient (mm^{-1})	13.883	0.793
Crystal size (mm^3)	0.18 × 0.16 × 0.11	0.15 × 0.12 × 0.10
θ range for data collection (°)	2.18–25.10	2.19–25.48
Reflections collected	10,668	11,735
Independent reflection	2166 [*R*(int) = 0.0818]	4236 [*R*(int) = 0.0711]
Completeness to θ (%)	99.9	99.7
Goodness-of-fit on F^2	1.017	0.951
Final *R* indices $[I \geq 2\sigma(I)]^a$	$R_1 = 0.0477$, $wR_2 = 0.1206$	$R_1 = 0.0533$, $wR_2 = 0.1172$
R indices (all data)^b	$R_1 = 0.0679$, $wR_2 = 0.1364$	$R_1 = 0.1214$, $wR_2 = 0.1514$

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^b wR = [\Sigma w(F_o^2 - F_c^2)2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Parameters of hydrogen bonding for **2**.

D–H···A	D···A	H···A	D–H···A (°)
C3–H3···O4	3.286(6)	2.51	141
C4–H4···O1	3.413(7)	2.58	149
C11–H11···O5	2.796(6)	2.49	100
C18–H18···O2	3.227(6)	2.49	137
C22–H22···O3	3.395(6)	2.55	151

3. Results and discussion

3.1. *Crystal structure of [Pb(bpdc)]$_n$ (1)*

The structure of **1** was characterized by X-ray single-crystal diffraction and FT-IR. X-ray single-crystal analysis reveals that **1** has a 2-D MOF structure built on inorganic rod-shaped M–O–M (Pb–O–Pb) chains. Compound **1** crystallizes in the orthorhombic space group Pbcn and the asymmetric unit consists of one Pb(II) and one deprotonated ligand. Pb1 is coordinated by seven oxygen atoms from five carboxylates of five different ligands [Pb–O = 2.422–2.800 Å], as shown in figure 2(a). The bpdc^{2-} adopted $\mu2:\eta1$, $\eta2$ and $\mu3:\eta2$, $\eta2$ bridges with five Pb ions, creating a 1-D rod-shaped Pb–O–Pb chain along the *b*-axis (figure 2b). Through hydrogen bonding [H5···O2 = 2.6016(88) Å] and an uncommon agostic bridge C–H→M (figure 2c) [11], these chains are interconnected to afford a 3-D network [Pb1···H4 = 3.1901(17) Å].

At the Pb(II) node of every rod-shaped Pb–O–Pb chain, a cyclic unit is formed by two bpdc^{2-} ligands and one Pb(II), and cyclic units stretch along the *b*-axis to form a double-stranded helical chain, which is shown in figure 3(a). Attributed to the bridging ligands, helical chains beside Pb–O–Pb exhibit left- and right-handed helical motifs to form a hairpin-like structure. Therefore, an overall mesomer is built as shown in figure 3(b).

3.2. *Crystal structure of [Co(bpdc)(phen)]$_n$ (2)*

As illustrated in figure 4, phen can optimize the influence of pH and the structure of the resulting CP through cooperation with bpdc^{2-}. The blocking of phen could control the assembly of CPs. Co1 is coordinated by four oxygen atoms from two bis(monodentate) bpdc^{2-} ligands [Co1–O1 = 2.232(3), Co1–O2 = 2.084(3), Co1–O4 = 2.109(3), Co1–O5 = 2.171(3) Å] and two nitrogen atoms from phen [Co1–N1 = 2.108(4), Co1–N2 = 2.088(4) Å] to furnish a distorted octahedron. The bpdc^{2-} bridge Co(II) into a helical chain extending along the *b*-axis with a relatively short pitch of 8.990 Å. Different from those in **1**, phen are alternately attached to both sides of a single-stranded helical chain and are orientated with a fixed angle to the chain, as illustrated in figure 5.

The angularity of phen allows pairing of two centrosymmetrically related single-stranded helical chains to generate a double-stranded, zipper-like chain with aromatic $\pi\cdots\pi$ stacking interactions between phen pairs. The face-to-face distance between the adjacent phen rings is about 3.86 Å, indicating a strong aromatic $\pi\cdots\pi$ stacking

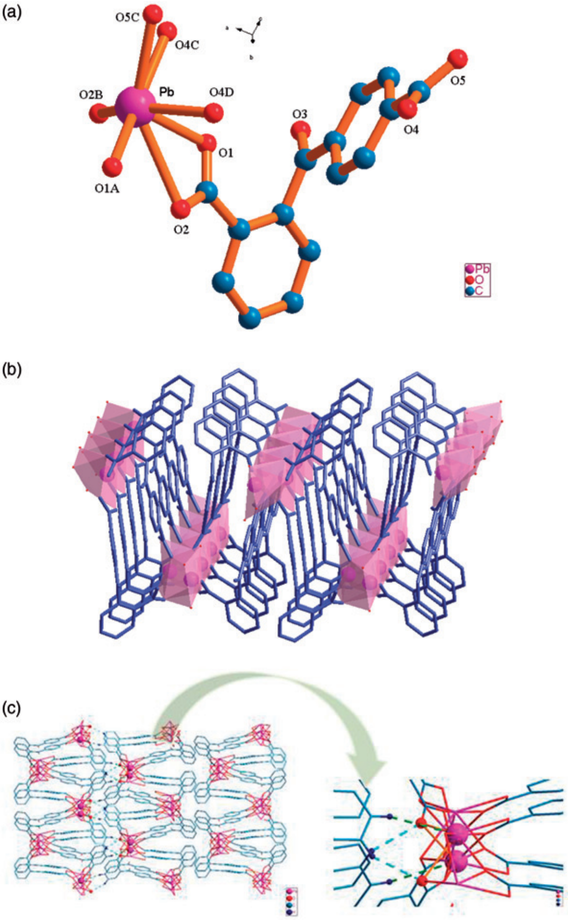

Figure 2. (a) The coordination environment of Pb(II) in **1**. Symmetry codes: (A) $-0.5+x$, $0.5-y$, $-z$; (B) $-0.5+x$, $-0.5-y$, $-z$; (C) $0.5-x$, $-0.5-y$, $-0.5+z$; (D) $-1+x$, $-y$ $-0.5+z$. (b) The 1-D rod-shaped Pb–O–Pb chain along the *b*-axis in **1**. (c) Agostic bond affording a 3-D network.

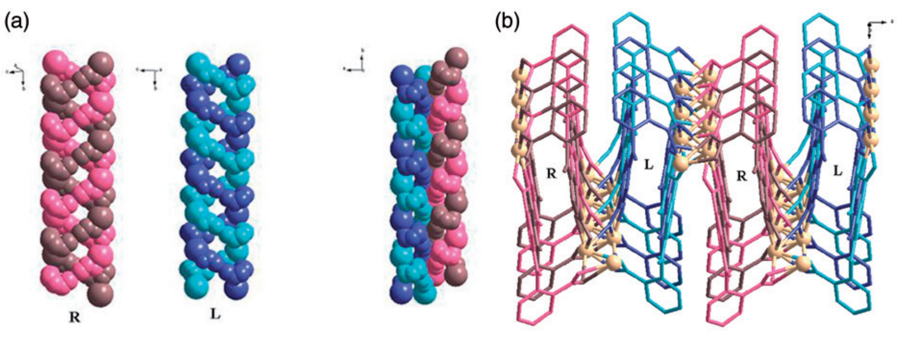

Figure 3. (a) The space-filling view of the double-stranded helical chain. (b) The left- and right-handed helical chain in the hairpin-like structure.

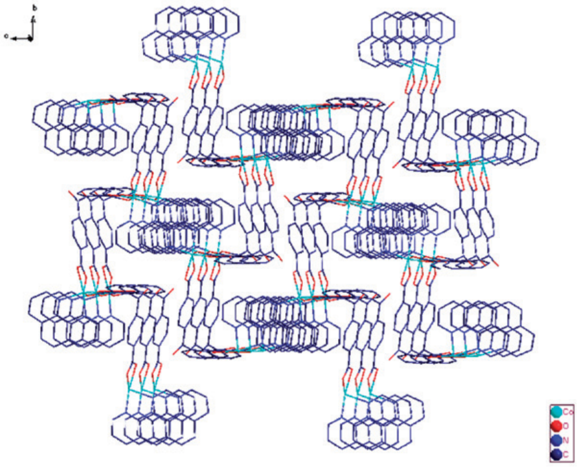

Figure 4. The 3-D packing framework of **2** like an opposite letter "Z."

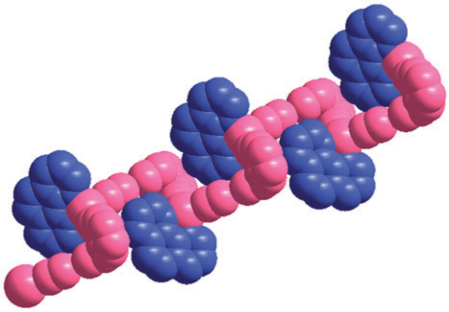

Figure 5. The phen ligands are alternately attached to both sides of the 1-D single-stranded helical chain.

interaction [12], shown in figure 6. The V-shaped bpdc^{2-} ligands interconnect Co(II) to furnish chiral helices along the *b*-axis.

3.3. *Powder X-ray diffractions*

To check phase purity of samples, powder X-ray diffractions at room temperature were carried out. Although there are a few differences in the position, intensity, and width of the diffraction peaks of simulated and experimental patterns, match of the key positions indicates pure phase of **1** and **2** and that the as-synthesized crystalline materials are homogeneous.

3.4. *IR spectral studies*

In IR spectra of **1** and **2**, absorptions of skeletal vibrations for the aromatic ring are at 1400–1600 cm^{-1}. Bands of carboxylate are at 1571 cm^{-1} for **1** and 1581 cm^{-1} for **2** for antisymmetic stretching and at 1380 cm^{-1} for **1** and 1415 cm^{-1} for **2** for

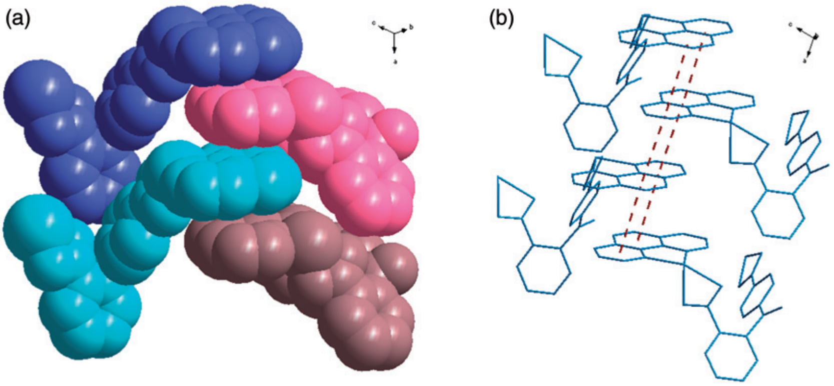

Figure 6. Aromatic $\pi \cdots \pi$ stacking interactions between phen pairs in **2**: (a) The space-filling views of $\pi \cdots \pi$ stacking interactions in **2**. (b) The perspective views of $\pi \cdots \pi$ stacking interactions in **2**.

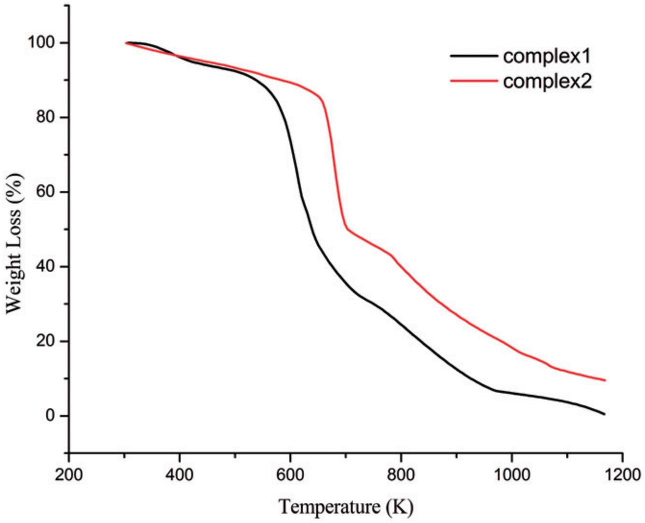

Figure 7. The TG curves of **1** and **2**.

symmetric stretching. A series of bands from 900 to 650 cm^{-1} are from H_2bpdc and phen. Peaks at 3600–3400 cm^{-1} can be attributed to the O–H stretch of lattice water.

3.5. *Thermogravimetric analyses*

TG experiment was carried out under N_2 at heating rate of 5 K min^{-1} from 303–1173 K. As illustrated in figure 7, below 540 K, **1** exhibits weight loss of 10.25%, attributed to release of three lattice water molecules. There are no indications of lattice water in X-ray single-crystal analysis indicating disorder. Endothermic weight loss of 46.48% (Calcd 46.84%) from 540 to 661 K can be ascribed as decomposition of organic ligands.

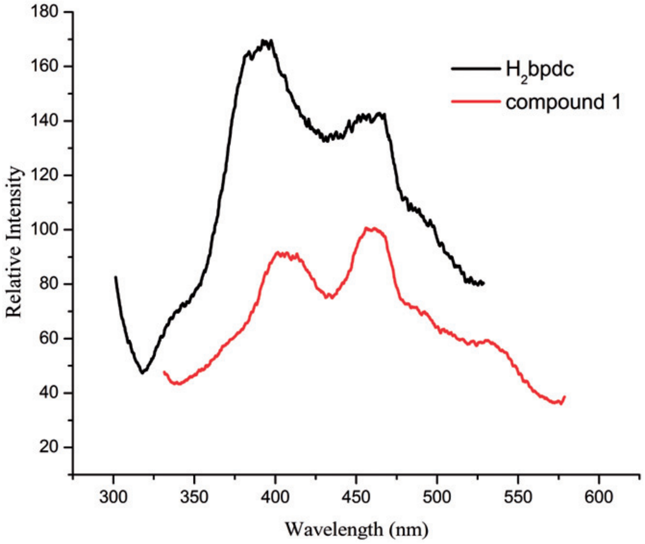

Figure 8. Fluorescence spectra of H_2bpdc and **1** in the solid state at room temperature.

Similarly for **2**, the first weight loss of 12.74% (Calcd 12.79%) between 303 and 633 K corresponds to release of four free water molecules. Then the TG curve of **2** shows a rapid drop which is attributed to decomposition of the organic framework.

3.6. *Fluorescent properties*

The fluorescent properties of free H_2bpdc and **1** are tested in the solid state at room temperature (figure 8). Upon excitation at 310 nm, H_2bpdc displays emission peaks at 392 and 464 nm while **1** exhibits emission peaks at 402 and 456 nm. Since it is difficult to oxidize and reduce Pb^{2+}, the observed emission for **1** is not metal-to-organic charge transfer or ligand-to-metal charge transfer [13]. It is probably due to intraligand π–π^* fluorescent emissions [14]. Compared with free H_2bpdc, significant shifted emission maxima for **1** should be assigned to the deprotonation of the H_2bpdc ligand and the influence of the coordination of the ligand to metal [15].

3.7. *Luminescent lifetime of 1*

The decay lifetime curve of **1** can be well fitted with double-exponential decay, giving two lifetimes, $\tau_1 = 1.03$ ns and $\tau_2 = 5.13$ ns ($\chi_2 = 1.061$), which suggest fluorescence [16]. The values are comparable with those observed in various Pb-MOFs [17].

4. Conclusions

We synthesized and characterized two new metal-carboxylate frameworks, $[Pb(bpdc)]_n$ (**1**) and $[Co(bpdc)(phen)]_n$ (**2**). Structural studies show hydrogen bonding and $\pi\cdots\pi$

stacking exist in **1** and **2**; there is an uncommon agostic C–H → M bond in **1**. **1** exhibits excellent fluorescence, indicating that it may be a photoactive material. In **1**, two stranded helical chains were formed by Pb(II) and carboxylic groups of bpdc^{2-}. **2** exhibits a new helical pattern, in which end-sealing phen provides us with a new strategy in the design of 1-D helical chains. Compound **2** shows strong coordination ability of Co(II), which can be reflected in structures reported [18]. Continued efforts to explore the construction of novel MOFs with interesting properties incorporating polycarboxylates are underway.

Supplementary material

Copies of crystallographic data as .cif files for the structures of **1** and **2** with CCDC Nos. 866316 (**1**) and 866317 (**2**) are offered in the supplementary material. Selected bond lengths (Å) and angles (°) for **1** and **2** are shown in table S1. XPRD patterns of **1** and **2** at room temperature can be found in figures S1 and S2 and luminescent lifetime curve for **1** in figure S3. Crystallographic data for structures of **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-866316 and CCDC-866317 (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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