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Four anthraquinone-1,5-disulfonate-based metal complexes incorporating N-heterocyclic coligands: synthesis, crystal structures, and fluorescence

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Four new anthraquinone-1,5-disulfonate (L)-based metal complexes with *N,N*-bidentate chelating coligands, $\{[\text{Pb}(\text{phen})_2(\text{L})] \cdot 4\text{H}_2\text{O}\}_n$ (**1**), $\{[\text{Mn}_2(2,2'\text{-bipy})_2(\text{H}_2\text{O})_6(\text{L})] \cdot \text{L} \cdot 6\text{H}_2\text{O}\}$ (**2**), $[\text{Co}(\text{phen})_2(\text{H}_2\text{O})(\text{L})]$ (**3**), and $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})(\text{L})]$ (**4**) (phen = 1,10-phenanthroline and 2,2'-bipy = 2,2'-bipyridine), have been hydrothermally synthesized and were structurally characterized by single-crystal X-ray diffraction, elemental analyses, FT-IR spectra, thermogravimetric curves, and solid luminescence spectra. Structural analysis suggests that **1** is a polymeric 1D zigzag chain bridged by dianionic L. In contrast, the other three complexes have discrete centrosymmetric binuclear structure for **2** and isolated isomorphous mononuclear entities for **3** and **4**, which are further assembled into 3D supramolecular networks by abundant hydrogen-bonding and/or π - π stacking interactions. Additionally, **2** and **4** exhibit favorable luminescent emissions, suggesting they are potential candidates for light emission materials.

Keywords: Anthraquinone-1,5-disulfonate; Crystal structure; Hydrogen bond; Fluorescent property

1. Introduction

Recently, organosulfonate-based metal complexes have drawn interest because of their unique architectures, intriguing topologies [1, 2], and potential applications as functional materials in catalysis [3], luminescence [3, 4], absorption [5], and magnetism [6]. As bridging ligands with binding sites up to six, organodisulfonate ligands have exhibited various coordination modes ranging from terminally monodentate to bridging hexadentate [7, 8], producing many interesting coordination frameworks with pillared layered [8], microporous [9], and/or alternating organic–inorganic layered structural motifs [10, 11]. Organic sulfonates can also behave as good hydrogen-bond acceptors, which, together with the coordination bonds, can build extended supramolecular frameworks [12, 13]. However, in contrast to the flourishing studies on the coordination behavior of carboxylate-based organic ligands, organosulfonate-based metal complexes have been investigated less due to the relatively weak coordination of

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sulfonate to metals. Very recently, by incorporating N-containing organic coligands, a series of intriguing sulfonate-based frameworks with 0D to 3D architectures have been synthesized [4, 6, 7, 14, 15]. As part of our continuing investigations on coordination and optical properties of sulfonate-based complexes [16, 17], herein, self-assembly of anthraquinone-1,5-disulfonate (L) and 1,10-phenanthroline (phen) and 2,2'-bipyridine (2,2'-bipy) coligands with different metal salts (Pb^{2+} , Mn^{2+} , Co^{2+} , and Zn^{2+}) have been carried out under controllable hydrothermal conditions. As a result, four new complexes with polymeric 1D *zigzag* chain for **1**, centrosymmetric binuclear structure for **2**, as well as isomorphous mononuclear entities for **3** and **4**, were generated. Structural analysis reveals that coordination modes of disulfonate ligand determines the overall structures and dimensionality of the target complexes. Additionally, **2** and **4** exhibit favorable luminescence properties among the four solid-state complexes with considerable thermal stability, which can be potentially used as light emission materials.

2. Experimental

2.1. Materials and methods

Commercially available chemicals were used without purification (anthraquinone-1,5-disulfonic acid disodium salt (Na_2L) was purchased from Acros and other analytical-grade reagents were obtained from Tianjin Chemical Reagent Factory). Doubly deionized water was used for conventional synthesis. Elemental analyses (C, H, and N) were carried out with a CE-440 (Leeman-Labs) analyzer. IR spectra (KBr pellets) were taken on an Avatar-370 (Nicolet) spectrometer in the range 4000 to 400 cm^{-1} . Thermogravimetric analysis (TGA) experiments were carried out on a Shimadzu simultaneous DTG-60A compositional analysis instrument from room temperature to 800°C under N_2 at a heating rate of 5°C min^{-1} . Fluorescence spectra of polycrystalline powder samples were performed on a Fluorolog-3 fluorescence spectrophotometer from Horiba Jobin Yvon at room temperature.

2.2. Synthesis of $\{[\text{Pb}(\text{phen})_2(\text{L})] \cdot 4\text{H}_2\text{O}\}_n$ (**1**)

$\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ (75.9 mg, 0.2 mmol), phen (39.6 mg, 0.2 mmol), Na_2L (82.4 mg, 0.2 mmol), and doubly deionized water (10.0 mL) were sealed in a 23.0 mL teflon-lined autoclave and heated at 160°C for 2 days under autogenous pressure. After the mixture cooled to room temperature at a rate of 2.8°C h^{-1} , orange block-shaped crystals suitable for X-ray analysis were obtained (yield: 28% based on phen). Anal. Calcd for $\text{C}_{38}\text{H}_{30}\text{N}_4\text{O}_{12}\text{S}_2\text{Pb}$: C, 45.37%; H, 3.01%; and N, 5.57%. Found: C, 45.55%; H, 3.02%; and N, 5.59%. IR ($\text{KBr}, \text{cm}^{-1}$): 3401 br, 3075 w, 1682 s, 1628 s, 1605 s, 1513 w, 1490 m, 1422 m, 1226 s, 1180 s, 1140 m, 1075 m, 1020 ms, 850 m, 707 m, 630 ms, and 539 m.

2.3. Synthesis of $\{[\text{Mn}_2(2,2'\text{-bipy})_2(\text{H}_2\text{O})_6(\text{L})] \cdot \text{L} \cdot 6\text{H}_2\text{O}\}$ (**2**)

$\text{MnAc}_2 \cdot 4\text{H}_2\text{O}$ (49.0 mg, 0.2 mmol), 2,2'-bipy (31.2 mg, 0.2 mmol), Na_2L (82.4 mg, 0.2 mmol) and doubly deionized water (10.0 mL) were sealed in a 23.0 mL teflon-lined

autoclave and heated at 140°C for 2 days under autogenous pressure. After the mixture cooled to room temperature at 2.4°C h⁻¹, yellow block-shaped crystals suitable for X-ray analysis were obtained (yield: 35% based on Mn^{II}). Anal. Calcd for C₄₈H₅₂N₄O₂₈S₄Mn₂: C, 42.05%; H, 3.82%; and N, 4.09%. Found: C, 42.22%; H, 3.84%; and N, 4.11%. IR (cm⁻¹, KBr): 3460 br, 3077 w, 1688 s, 1653 m, 1572 s, 1477 m, 1437 s, 1316 s, 1269 s, 1175 s, 1093 w, 1035 s, 969 m, 823 m, 771 m, 721 m, and 612 s.

2.4. Synthesis of [Co(phen)₂(H₂O)(L)] (3) and [Zn(phen)₂(H₂O)(L)] (4)

The synthesis procedures for **3** and **4** were the same as for **2** except that 2,2'-bipy and MnAc₂·4H₂O were replaced by phen (39.6 mg, 0.2 mmol) and CoAc₂·4H₂O (49.8 mg, 0.2 mmol)/ZnAc₂·2H₂O (43.9 mg, 0.2 mmol) for **3/4**, respectively. Yellow block-shaped crystals of **3** suitable for X-ray analysis were obtained (yield: 40% based on phen). Anal. Calcd for C₃₈H₂₄N₄O₉S₂Co: C, 56.79%; H, 3.01%; and N, 6.97%. Found: C, 56.97%; H, 3.02%; and N, 7.00%. IR (KBr, cm⁻¹): 3266 br, 3069 w, 1679 s, 1628 w, 1571 m, 1515 m, 1424 s, 1308 s, 1242 s, 1180 s, 1144 s, 1023 s, 964 m, 849 m, 723 m, and 605 m. Pale-yellow prism-shaped crystals of **4** suitable for X-ray analysis were obtained (yield: 38% based on phen). Anal. Calcd for C₃₈H₂₄N₄O₉S₂Zn: C, 56.34%; H, 2.99%; and N, 6.92%. Found: C, 56.51%; H, 2.88%; N, 6.95%. IR (KBr, cm⁻¹): 3419 br, 3071 w, 1681 s, 1628 w, 1574 m, 1517 m, 1426 s, 1309 m, 1242 s, 1185 s, 1150 s, 1027 s, 966 m, 853 m, 725 m, and 609 m.

2.5. X-ray crystallography

Diffraction intensities for **1–4** were collected on a Bruker APEX-II CCD diffractometer equipped at 294(2) K with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) using the φ - ω scan mode. Semiempirical multi-scan absorption corrections were applied by using SADABS [18], and the program SAINT was used for integration of the diffraction profiles [19]. The structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL [20]. The final refinement was performed by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. The positions of hydrogens bonded to carbon were generated geometrically and allowed to ride on their parent carbons before the final cycle of refinement. Hydrogens attached to oxygen except for disordered water were first located in difference Fourier maps and then placed in calculated sites, and refined isotropically. One free water in **1** (O11) and three sulfonate O atoms of L ligand (O4, O5, and O6) in **4** were positionally disordered with occupation that refined to 0.6 and 0.4 for O11 and O11', as well as 0.68 and 0.32 for O4, O5, O6, and O4', O5', O6', respectively. In **1**, two free waters (O12 and O13) were site occupancy disorder with 50% occupancy. The crystallographic data and selected bond lengths and angles for **1–4** are shown in tables 1–4 and hydrogen-bond parameters are listed in table 5.

Table 1. Crystal data and structure refinement for 1–4.

	1	2	3	4
Empirical formula	$C_{38}H_{30}N_4O_{12}S_2Pb$	$C_{48}H_{52}N_4O_{28}S_4Mn_2$	$C_{38}H_{24}N_4O_8S_2Co$	$C_{38}H_{24}N_4O_8S_2Zn$
Formula weight ($g\ mol^{-1}$)	1005.97	1371.06	803.66	810.10
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions ($\text{\AA}, ^\circ$)				
a	11.7193(7)	14.6224(7)	8.8610(18)	8.816(3)
b	12.2768(7)	10.9369(6)	12.865(3)	12.864(4)
c	13.4035(8)	17.5555(9)	14.689(3)	14.757(4)
α	93.7720(10)	90	97.450(2)	97.158(4)
β	95.0310(10)	94.3980(10)	100.177(2)	100.267(4)
γ	94.8300(10)	90	92.026(2)	92.228(4)
Volume (\AA^3), Z	1908.98(19), 2	2799.3(2), 2	1631.3(6), 2	1630.7(8), 2
Calculated density ($g\ cm^{-3}$)	1.750	1.627	1.636	1.650
Absorption coefficient (mm^{-1})	4.598	0.696	0.723	0.950
$F(000)$	992	1412	822	828
Crystal size (mm^3)	$0.15 \times 0.14 \times 0.13$	$0.34 \times 0.32 \times 0.24$	$0.24 \times 0.18 \times 0.10$	$0.34 \times 0.20 \times 0.18$
Limiting indices	$-13 \leq h \leq 13$; $-14 \leq k \leq 13$; $-11 \leq l \leq 15$	$-17 \leq h \leq 17$; $-10 \leq k \leq 12$; $-20 \leq l \leq 20$	$-9 \leq h \leq 10$; $-10 \leq k \leq 15$; $-17 \leq l \leq 15$	$-10 \leq h \leq 10$; $-15 \leq k \leq 15$; $-12 \leq l \leq 17$
Reflections collected/unique	10,413/6637	14,778/4924	8990/5705	8858/5680
R_{int}	0.0166	0.0192	0.0145	0.0200
Max. and min. transmission	0.5863 and 0.5455	0.935 and 0.872	0.912 and 0.824	0.8476 and 0.7383
Data/restraints/parameters	6637/0/527	4924/0/389	5705/0/494	5680/12/515
Goodness-of-fit on F^2	1.052	1.044	1.045	1.049
Final R indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.0272$, $wR_2 = 0.0701$	$R_1 = 0.0332$, $wR_2 = 0.0896$	$R_1 = 0.0362$, $wR_2 = 0.0957$	$R_1 = 0.0355$, $wR_2 = 0.0991$
R indices (all data)	$R_1 = 0.0330$, $wR_2 = 0.0723$	$R_1 = 0.0407$, $wR_2 = 0.0934$	$R_1 = 0.0485$, $wR_2 = 0.1009$	$R_1 = 0.0448$, $wR_2 = 0.1032$

^a $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o^2)]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Pb(1)–N(1)	2.557(4)	Pb(1)–N(3)	2.628(4)
Pb(1)–N(4)	2.578(4)	Pb(1)–O(1)	2.692(3)
Pb(1)–N(2)	2.603(4)	Pb(1)–O(5)	2.729(3)
N(1)–Pb(1)–N(4)	75.72(11)	N(2)–Pb(1)–O(1)	114.91(11)
N(1)–Pb(1)–N(2)	64.20(12)	N(3)–Pb(1)–O(1)	74.02(11)
N(4)–Pb(1)–N(2)	83.25(12)	N(1)–Pb(1)–O(5)	126.74(12)
N(1)–Pb(1)–N(3)	85.68(12)	N(4)–Pb(1)–O(5)	69.74(11)
N(4)–Pb(1)–N(3)	63.51(12)	N(2)–Pb(1)–O(5)	72.44(11)
N(2)–Pb(1)–N(3)	140.15(12)	N(3)–Pb(1)–O(5)	111.93(11)
N(1)–Pb(1)–O(1)	70.00(12)	O(1)–Pb(1)–O(5)	161.57(12)
N(4)–Pb(1)–O(1)	126.56(11)		

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Mn(1)–O(10)	2.1484(17)	Mn(1)–O(1)	2.2220(17)
Mn(1)–O(9)	2.1557(17)	Mn(1)–N(1)	2.254(2)
Mn(1)–O(11)	2.1730(17)	Mn(1)–N(2)	2.281(2)
O(10)–Mn(1)–O(9)	103.44(7)	O(11)–Mn(1)–N(1)	100.65(7)
O(10)–Mn(1)–O(11)	85.13(7)	O(1)–Mn(1)–N(1)	94.26(7)
O(9)–Mn(1)–O(11)	88.57(7)	O(10)–Mn(1)–N(2)	91.13(8)
O(10)–Mn(1)–O(1)	82.87(7)	O(9)–Mn(1)–N(2)	164.55(8)
O(9)–Mn(1)–O(1)	83.03(7)	O(11)–Mn(1)–N(2)	87.56(7)
O(11)–Mn(1)–O(1)	163.34(6)	O(1)–Mn(1)–N(2)	104.17(7)
O(10)–Mn(1)–N(1)	162.09(8)	N(1)–Mn(1)–N(2)	72.36(8)
O(9)–Mn(1)–N(1)	93.71(8)		

Table 4. Selected bond lengths (Å) and angles (°) for **3** and **4**.

	3	4
M(1)–O(1)	2.1740(18)	2.2077(19)
M(1)–O(9)	2.060(2)	2.078(2)
M(1)–N(1)	2.139(2)	2.130(2)
M(1)–N(2)	2.108(2)	2.160(2)
M(1)–N(3)	2.132(2)	2.125(2)
M(1)–N(4)	2.125(2)	2.164(2)
O(9)–M(1)–N(3)	170.05(9)	99.06(8)
O(9)–M(1)–N(1)	87.77(10)	92.71(9)
N(3)–M(1)–N(1)	96.83(8)	167.27(9)
O(9)–M(1)–N(2)	98.37(9)	168.47(8)
N(3)–M(1)–N(2)	91.22(8)	91.13(8)
N(1)–M(1)–N(2)	78.23(8)	77.67(9)
O(9)–M(1)–N(4)	92.71(10)	89.46(9)
N(3)–M(1)–N(4)	77.98(9)	77.93(8)
N(1)–M(1)–N(4)	97.43(8)	97.45(8)
N(2)–M(1)–N(4)	167.88(9)	97.99(8)
O(9)–M(1)–O(1)	89.52(9)	88.01(8)
N(3)–M(1)–O(1)	87.37(7)	91.84(7)
N(1)–M(1)–O(1)	170.11(7)	93.42(8)
N(2)–M(1)–O(1)	92.77(8)	86.28(7)
N(4)–M(1)–O(1)	92.20(8)	168.94(7)

Table 5. Hydrogen-bonding parameters (Å, °) for **1–4**.

Donor–H... Acceptor	<i>d</i> (D–H)	<i>d</i> (H... A)	<i>d</i> (D... A)	∠DHA
1				
O10–H10A... O6 ^{#2}	0.85	2.36	2.877(1)	119
O10–H10B... O7 ^{#1}	0.85	2.17	3.020(8)	173
2				
O9–H9A... O13	0.85	2.05	2.755(6)	140
O9–H9B... O14	0.85	1.90	2.703(3)	158
O10–H10A... O3 ^{#1}	0.85	2.08	2.835(9)	147
O10–H10B... O12 ^{#2}	0.85	1.92	2.740(9)	162
O11–H11A... O6 ^{#2}	0.85	1.89	2.734(8)	170
O11–H11B... O7 ^{#3}	0.85	1.85	2.702(3)	175
O12–H12A... O5	0.85	2.22	2.982(8)	150
O12–H12B... O2 ^{#4}	0.85	2.03	2.835(9)	158
O13–H13A... O2 ^{#4}	0.85	1.97	2.806(3)	167
O13–H13B... O3	0.85	1.95	2.773(9)	163
O14–H14A... O5	0.85	2.04	2.869(4)	166
O14–H14B... O6 ^{#3}	0.85	2.36	3.154(4)	155
O14–H14B... O7 ^{#3}	0.85	2.26	2.961(8)	140
3				
O9–H9A... O2	0.90	1.91	2.714(4)	147
O9–H9B... O5 ^{#1}	0.74	2.51	3.107(4)	138
O9–H9B... O6 ^{#1}	0.74	2.18	2.880(2)	158
4				
O9–H9''... O3	0.85	1.92	2.723(2)	157
O9–H9'... O4' ^{#1}	0.85	2.37	3.212(8)	172
O9–H9'... O5' ^{#1}	0.85	2.38	2.919(0)	122

Symmetry codes for **1**: ^{#1}1–*x*, 1–*y*, –*z*; ^{#2}*x*–1, *y*, *z*; for **2**: ^{#1}1–*x*, *y*+1/2, 1/2–*z*; ^{#2}*x*, *y*+1, *z*; ^{#3}–*x*, *y*+1/2, 1/2–*z*, ^{#4}1–*x*, *y*–1/2, 1/2–*z*; for **3**: ^{#1}*x*, *y*+1, *z*; for **4**: ^{#1}*x*, *y*–1, *z*.

3. Results and discussion

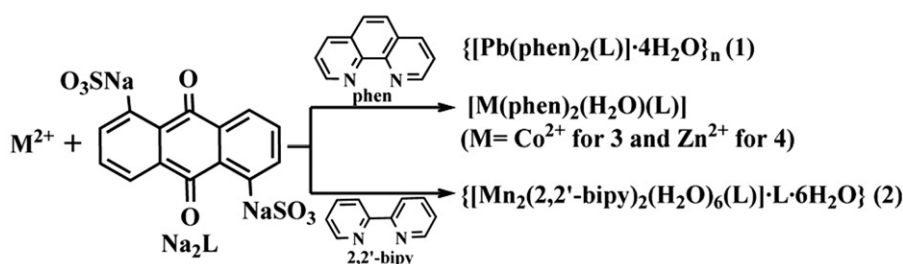
3.1. Syntheses and general characterization

Complexes **1–4** were synthesized by controllable hydrothermal reactions of Na₂L, phen for **1**, **3**, and **4** and 2,2'-bipy for **2**, and metal salts with a molar ratio of 1:1:1 (scheme 1). The reaction temperature and cooling rate of the mixture were important for the final crystalline products. Complex **1** was obtained at 160°C with the cooling rate of 2.8°C h⁻¹, while **2–4** were obtained at 140°C with the cooling rate of 2.4°C h⁻¹. Complexes **1–4** are air stable, insoluble in commonly organic solvents, and retain their crystalline integrity at ambient conditions for a considerable length of time.

In IR spectra, broad bands corresponding to O–H stretch are centered at 3401, 3460, 3266, and 3419 cm⁻¹ for **1–4**, respectively, indicating the presence of water. Weak absorption at 3069–3077 cm⁻¹ is assigned to aromatic ν_{C–H}. Vibrations of the aromatic ring in **1–4** are observed in the range 1600–1400 cm⁻¹. The strong absorption for ketone of anthraquinone appears at ~1680 cm⁻¹, and the stretching vibrations for sulfonates are found at 1270–1180 (ν_{as}) and ~1030 (ν_s) cm⁻¹ for **1–4**.

3.2. Structural description of {[Pb(phen)₂(L)]·4H₂O}_n (**1**)

Complex **1** crystallizes in the triclinic *P* $\bar{1}$ space group with an infinite 1D zigzag chain alternately bridged by two chemically equivalent but crystallographically unique L and



Scheme 1. Syntheses of complexes 1–4.

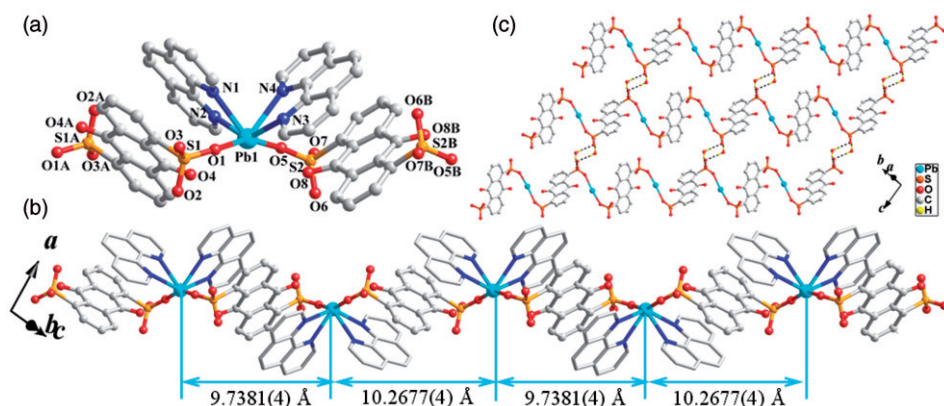


Figure 1. (a) Local coordination environment of Pb^{II} in **1** with atomic labels in the asymmetric unit (symmetric codes: $A = 1 - x, -y, -z$; $B = 2 - x, 1 - y, 1 - z$). (b) 1D zigzag chain of **1** alternately bridged by two crystallographically unique L. (c) 2D wavy layer of **1** formed by intermolecular O–H \cdots O hydrogen-bonding interaction (phen ligands omitted for clarity).

some lattice waters. As depicted in figure 1(a), the Pb^{II} in **1** is six-coordinate with N1, N2, N3, and N4 from two chelating phen and two sulfonate donors from two separated L ligands. The Pb–O bond distances are slightly longer than those of Pb–N (table 2), although they all fall within normal values [16, 17, 21, 22].

In contrast to the two asymmetric bidentate chelating phen, both L with different inversion centers present their deprotonated sulfonates as bidentate bridges to link neighboring Pb^{II} ions into an infinite 1D zigzag chain (figure 1b). The Pb \cdots Pb separations across the two L's are 9.7381(4) and 10.2677(4) Å, respectively. Furthermore, hydrogen-bonding bridging waters extend the adjacent 1D chains into a 2D wave-like layer by twofold O–H \cdots O hydrogen bonds with uncoordinated sulfonate oxygens (figure 1c and table 5).

3.3. Structural description of $\{[\text{Mn}_2(2,2'\text{-bipy})_2(\text{H}_2\text{O})_6(\text{L})]\cdot\text{L}\cdot 6\text{H}_2\text{O}\}$ (**2**)

Different from polymer **1**, **2** contains a centrosymmetric binuclear cation, six lattice waters, and one free, centrosymmetric L dianion for charge compensation. As shown in

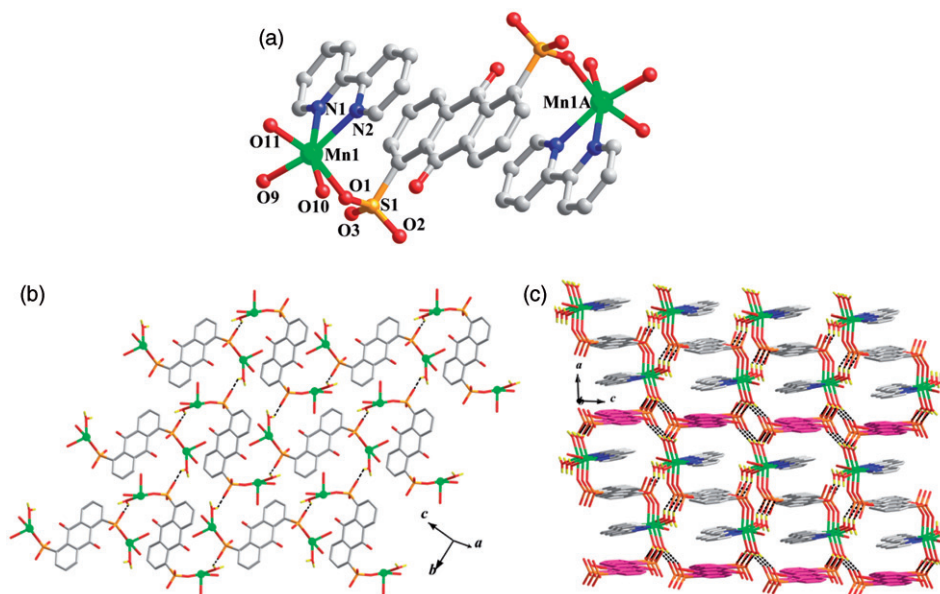


Figure 2. (a) Binuclear entity of **2** with atomic labels in the asymmetric unit (symmetric codes: $A = 1 - x, 2 - y, -z$). (b) 2D sheet of **2** arranged by intermolecular O–H \cdots O hydrogen-bonding interaction (phen ligands omitted for clarity). (c) 3D packing structure of **2** through free L, highlighted in purple.

figure 2(a), the crystallographically unique Mn^{II} is six-coordinate in distorted octahedral coordination geometry. The equatorial plane of the octahedral Mn^{II} is one chelating 2,2'-bipy ligand and two waters. Axial positions are occupied by two oxygens from another coordinated water and one sulfonate of L anion with Mn–O and Mn–N distances varying from 2.1484(17) to 2.281(2) Å (table 3). One centrosymmetric L dianion is a bidentate bridging ligand to aggregate two symmetry-related Mn^{II} ions (Mn1 and Mn1A) through two sulfonate donors, leading to a discrete binuclear structure of **2** with Mn \cdots Mn distance of 10.3027(6) Å.

As shown in figure 2(b), the discrete binuclear units are further connected into a 2D supramolecular sheet through a pair of O–H \cdots O hydrogen-bonding interactions between the bridging sulfonate of L and a coordinated water (table 5). Furthermore, the free L behaves as H-bonded bridges, extending the 2D non-covalent layer into a 3D supramolecular network by O–H \cdots O (figure 2c and table 5). Lattice waters can also be entrapped in the supramolecular framework by O–H \cdots O hydrogen-bonding interactions (figure S1 and table 5).

3.4. Structural description of [Co(phen)₂(H₂O)(L)] (**3**) and [Zn(phen)₂(H₂O)(L)] (**4**)

Replacement of Pb^{II} in **1** by Co^{II} or Zn^{II} generated two isostructural mononuclear entities, **3** and **4**. Due to their analogous structure, only the description of **3** is presented herein; the structure of **4** is shown in figure S2 in the supporting information.

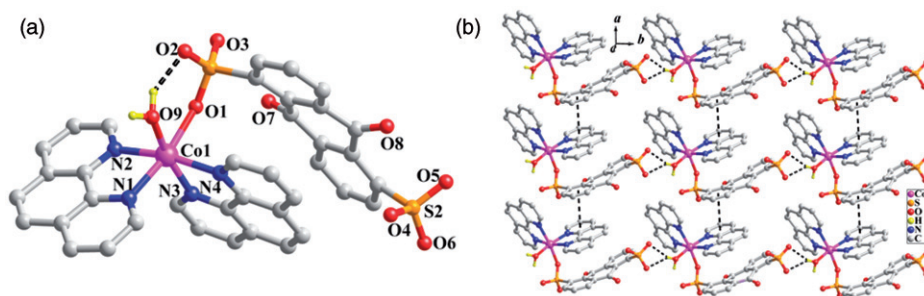


Figure 3. (a) Mononuclear structure of **3** with intramolecular hydrogen-bonding interaction. (b) 2D supramolecular sheet of **3** assembled by hydrogen-bonding and π - π stacking interactions.

As shown in figure 3(a), the crystallographically independent Co^{II} in **3** is bound to two phen molecules, one unidentate sulfonate of L^{2-} , and one coordinated water, forming a distorted octahedral coordination geometry (table 4). Rather than being a bidentate connector to aggregate neighboring metal ions as in **1** and **2**, L in **3** is terminally monodentate to complete the metal coordination sphere. There is an intramolecular non-covalent $\text{O}-\text{H}\cdots\text{O}$ interaction between coordinated water and sulfonate of L (table 5), which helps to consolidate the mononuclear fragment. Acting as a typically asymmetric chelating ligand, phen binds to Co^{II} with the $\text{Co}-\text{N}$ bond distances being between 2.108(2) and 2.139(2) Å (table 4).

In the packing structure of **3**, individual monomer is arranged into a 1D chain along the crystallographic b direction through $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions between the uncoordinated sulfonate (O4, O5) and coordinated water (O9) (figure 3b and table 5). Adjacent chains were further stacked into a 2D supramolecular layer through π - π stacking interactions between phen and benzene rings of L, in which the centroid-to-centroid distance and the dihedral angle of the two rings are 3.559(5) Å and $3.217(7)^\circ$, respectively (figure 3b).

3.5. Thermal stability

TGA were carried out to explore the thermal stability of **1-4** (figure 4). For **1**, one weight-loss process with a total weight loss of 76.5% was observed from room temperature to 593°C , ascribed to slow release of lattice water as well as collapse of the chain-like framework (Calcd: 77.8%). The final residue was PbO (expt: 23.6%, Calcd: 22.2%). An obvious weight-loss stage between 30°C and 97°C was observed for **2**, corresponding to loss of lattice and coordinated water (expt: 15.0%, Calcd: 15.8%). The second weight loss occurred between 320°C and 520°C due to the decomposition of the ligands; the final product was MnO_2 (expt: 12.4%, Calcd: 12.7%). Complexes **3** and **4** have similar one-step weight-loss behavior with different temperature ranges, 245°C ending at 520°C for **3** and 245°C ending at 624°C for **4**, leaving CoO (expt: 9.0%, Calcd: 9.3%) and ZnO (expt: 8.7%, Calcd: 10.0%) for **3** and **4** as the final products, respectively.

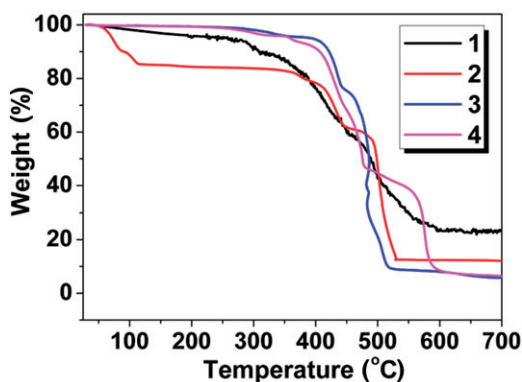
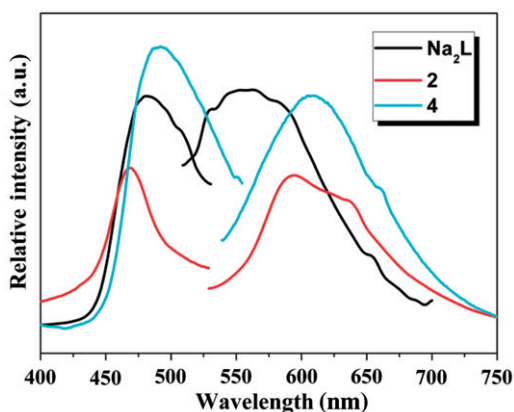


Figure 4. TG curves for 1–4.

Figure 5. Solid-state excitation and emission spectra of 2, 4 and Na₂L at room temperature.

3.6. Luminescent properties

Solid excitation and emission spectra of 1–4 were measured at room temperature to explore their applications as functional materials (figure 5). Complexes 1 and 3 are non-fluorescent while 2 and 4 display emissions at 594 and 607 nm upon excitation at *ca.* 468 and 490 nm, respectively. Under similar experimental conditions, the Na₂L can exhibit emission at 557 upon excitation at 480, which should be from $\pi-\pi^*$ transition. Neutral phen molecule can exhibit emission at 400 and 450 nm [23]. Thus, the fluorescent behavior of the two complexes can be assigned to intraligand charge transfer and the shift of the emission bands should be ascribed to the chelating coordination of L.

4. Conclusion

Four new anthraquinone-1,5-disulfonate-based metal complexes were isolated by incorporating *N,N*-chelating coligands. Tuned by the selectively bidentate bridging or

terminally monodentate mode of anthraquinone-1,5-disulfonate, these complexes exhibit 1D infinite chain, discrete binuclear and mononuclear structures. Complexes **2** and **4** exhibit intense fluorescence with favorable thermal stability, suggesting their potential applications as light-emitting materials.

Supplementary material

Crystallographic data (excluding structure factors) for the crystal structures reported in this article have been deposited with the Cambridge Crystallographic Data Center (CCDC nos. 789704–789707). This material can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk). The supplementary figures (S1 and S2) can be obtained from the authors.

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