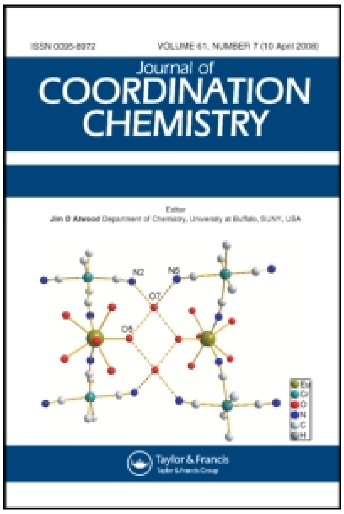

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Syntheses, structures and luminescence of three new supramolecular complexes containing *N-P*-acetamidobenzenesulfonyl-glycine acid

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A new ligand, *N-P*-acetamidobenzenesulfonyl-glycine acid (abbreviated as abglyH$_2$), and three transition metal complexes [Mn(abglyH)$_2$(bipy)(H$_2$O)$_2$]$_n$ (**1**), [Mn(abglyH)$_2$(bipy)$_2$(H$_2$O)$_2$] (**2**) and [Zn(abglyH)$_2$(H$_2$O)$_4$] (**3**) (bipy=4,4′-bipyridine) have been synthesized under mild conditions and characterized by IR, elemental analysis and X-ray diffraction analysis. Compound **1** exhibits a 1-D linear chain, which is further connected to a 3-D supramolecular network through various kinds of hydrogen bonds and p–π stacking interactions. **2** and **3** are monomeric compounds, and **2** is assembled by intermolecular hydrogen bonds and CH$\cdots\pi$ interactions into a 3-D supramolecular network, while **3** is extended into a 2-D supramolecular network through hydrogen bonds. Fluorescent analysis shows that **3** has an emissive maximum at 353 nm in the solid state at room temperature.

Keywords: *N-P*-acetamidobenzenesulfonyl-glycine acid; Supramolecular structures; Fluorescent analysis

1. Introduction

The rational design and synthesis of new extended supramolecular networks by covalent and weak intra/intermolecular interactions have brought forth frameworks with fascinating structural motifs [1–6]. In general, extended networks possessing higher dimensionalities can be obtained by assembly of coordination complexes (or polymers) with lower dimensionalities via hydrogen-bonding, π–π interaction or other intermolecular contacts [7]. Control of the formation of supramolecular complexes is a fascinating challenge. Amino acids are fundamental structure units of biomacromolecules, such as proteins and enzymes [8]. *N*-sulfonyl-amino acids reproduce the coordination behavior of peptides and their selectivity towards metal ions [9, 29–31]. *N-P*-acetamidobenzenesulfonyl-glycine acid (scheme 1) has the following advantages: (i) the substitution of a *N-P*-acetamidobenzenesulfonyl group on amine increases the number of donors in the substituted amine, which may result in different

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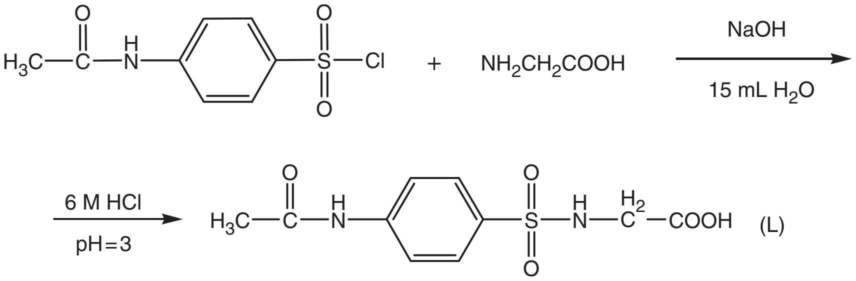

Scheme 1. Synthesis of abglyH$_2$.

coordination modes [10–13]; (ii) it can be partly or fully deprotonated (abglyH$^-$ and abgly^{2-}) as the pH value changes; (iii) it can act not only as hydrogen bond donors but also as acceptors, for construction of supramolecular structures. Herein, we report the syntheses, characterization and structures of three new complexes with the abglyH$_2$ ligand; the fluorescence for **3** has also been observed.

2. Experimental

2.1. *General*

All the reagents used in the syntheses were analytical grade. C, H and N analyses were determined on a Perkin-Elmer 240 elemental analyzer. The IR spectra were recorded in KBr discs on a Avatar^{TM} 360 E. S. P. IR spectrometer in the 4000–400 cm^{-1} range. Fluorescence experiments used a HITACHI F-4500 fluorescence spectrophotometer at room temperature.

2.2. *Synthesis of* N-P-*acetamidobenzenesulfonyl-glycine acid*

Glycine (4.818 g, 0.0645 mol), NaOH (5.139 g, 0.129 mol), *N*-*P*-acetamidobenzenesulfonyl (10.000 g, 0.043 mol) and 25 mL distilled water were added to a round-bottomed flask. The reaction mixture was kept stirring for 10 h at room temperature during which it turned clear. Then the pH was adjusted to 3 by addition of 6 mol^{-1} L hydrochloric acid; the desired ligand was precipitated and removed by filtration. The product was washed with distilled water and dried in air at ambient temperature. Yield: 82.6%. Anal. Calcd (%) for $C_{10}H_{12}N_2O_5S$: C, 44.12; H, 4.41; N, 10.29. Found: C, 44.01; H, 4.36; N, 10.18.

2.3. *Synthesis of* $[Mn(abglyH)_2(bipy)(H_2O)_2]_n$ *(1)*

A mixture of $Mn(OAc)_2 \cdot 2H_2O$ (0.25 mmol, 0.061 g) and abglyH$_2$ (0.5 mmol, 0.136 g) in 10 mL aqueous solution was stirred for about 10 min to give a clear solution at 70°C. Then the pH of the reaction mixture was adjusted to 6 by slow addition of 2 mol^{-1} L NaOH solution. After 3 h of stirring at 70°C, 5 mL ethanol solution of 4,4′-bipyridine (0.25 mmol, 0.048 g) was added and the solution was stirred and heated for 4 h at 70°C, and then filtered. Well-shaped brown crystals suitable for X-ray analysis separated from the mother liquor by slow evaporation at room temperature for 15 days. Yield: 0.091 g (46%). Anal. Calcd (%) for $C_{30}H_{34}MnN_6O_{12}S_2$: C, 45.59; H, 4.31; N, 11.64. Found: C, 45.50; H, 4.23; N, 11.52.

2.4. *Synthesis of Mn(abglyH)$_2$(bipy)$_2$(H$_2$O)$_2$ (2)*

Complex **2** was prepared using a similar method to that employed for the synthesis of **1** by changing pH from 6 to 4. The primrose yellow crystal was obtained after 28 days. Yield: 0.116 g (49%). Anal. Calcd (%) for $C_{40}H_{42}MnN_8O_{12}S_2$: C, 50.75; H, 4.44; N, 11.84. Found: C, 50.69; H, 4.32; N, 11.56.

2.5. *Synthesis of Zn(abglyH)$_2$(H$_2$O)$_4$ (3)*

Compound **3** was prepared using a analogous method to that for **1** by using $Zn(OAc)_2 \cdot 2H_2O$ (0.25 mmol, 0.055 g) instead of $Mn(OAc)_2 \cdot 2H_2O$, producing colorless crystals by slow evaporation at room temperature for 40 days. Yield: 0.097 g (57%). Anal. Calcd (%) for $C_{20}\,H_{30}\,N_4O_{14}S_2$ Zn: C, 35.30; H, 4.40; N, 8.20. Found: C, 35.21; H, 4.45; N, 8.14.

2.6. *X-ray determination*

X-ray single crystal data collections for abglyH$_2$, **1**, **2** and **3** were performed with a Bruker SMART APEX II CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) by using θ/ϕ scan technique at room temperature. The structures were solved by direct methods with SHELXS-97. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [14, 15]. A summary of the crystallographic data is given in table 1. Selected bond distances and angles are given in tables 2 and 3, respectively.

3. Results and discussion

3.1. *Crystal structures of abglyH$_2$ and 1–3*

As shown in figure 1(a), carboxylate group of the abglyH$_2$ is protonated. There exists an intermolecular hydrogen bond between oxygens from acetamide groups and carboxylate oxygen atoms from amino acid motifs ($O \cdots O$ distance: 2.616 Å), forming a 1-D chain in a zigzag way arranged along the *c* axis. These chains are assembled by hydrogen bonds between sulfonamide nitrogens and sulfonamide oxygens from adjacent chains to give a 2-D layer supramolecular structure ($N \cdots O$ distance: 3.0655 Å). Adjacent layers are connected by hydrogen bonds between nitrogens of acetamide groups and carboxylate oxygens from N-protected amino acid motif to afford a 3-D supramolecular structure ($N \cdots O$ distance: 2.8898 Å), shown in figure 1(b).

The unit of **1** comprises one Mn(II) atom, two abglyH$^-$ anions, two water molecules and one bipy. As shown in figure 2(a), the Mn(II) is six-coordinate with two N atoms

Table 1. Crystallographic data and processing parameters for abglyH_2, **1**, **2** and **3**.

	abglyH_2	**1**	**2**	**3**
Empirical formula	$C_{10}H_{12}N_2O_5S_1$	$C_{30}H_{34}MnN_6O_{12}S_2$	$C_{40}H_{42}MnN_8O_{12}S_2$	$C_{20}H_{30}N_4O_{14}S_2Zn$
Formula weight	272.28	789.69	945.88	679.97
Temperature (K)	291(2)	291(2)	291(2)	291(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	*Pbca*	$P\bar{1}$	*P*2(1)/*n*	*C*2/*c*
Unit cell dimensions (Å, °)				
a	12.134(2)	7.6979(9)	9.9986(9)	17.663(2)
b	8.9018(15)	10.5536(13)	10.5324(10)	5.1373(6)
c	22.439(4)	11.4149(14)	20.5429(19)	30.040(4)
α		74.6 850(10)		
β		73.0200(10)	98.5450(10)	95.9000(10)
γ		77.7270(10)		
Volume (Å^3), Z	2423.7(7), 4	846.16(18), 1	2139.3(3), 2	2711.4(6), 4
D_{Calcd} (g cm^{-3})	1.492	1.550	1.468	1.666
Absorption coefficient (mm^{-1})	0.283	0.586	0.478	1.137
Index ranges	$-15 \le h \le 15$ $-11 \le k \le 11$ $-23 \le l \le 29$	$-9 \le h \le 9$ $-13 \le k \le 13$ $-14 \le l \le 14$	$-12 \le h \le 12$ $-13 \le k \le 13$ $-26 \le l \le 26$	$-21 \le h \le 22$ $-6 \le k \le 6$ $-39 \le l \le 39$
$F(000)$	1136	409	982	1408
θ Range for data collection (°)	2.47–27.50	2.46–27.50	2.42–27.49	2.32–27.50
Independent reflections	2780	3813	4897	3102
Observed reflections	2116	3321	3716	2696
Data/restraints/parameters	2780/0/165	3813/3/233	4897/0/287	3102/0/188
Goodness-of-fit on F^2	1.027	1.062	1.027	1.079
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0427$ $wR_2 = 0.1088$	$R_1 = 0.0351$ $wR_2 = 0.0903$	$R_1 = 0.0378$ $wR_2 = 0.0919$	$R_1 = 0.0440$ $wR_2 = 0.0938$
R indices (all data)	$R_1 = 0.0599$ $wR_2 = 0.1196$	$R_1 = 0.0408$ $wR_2 = 0.0957$	$R_1 = 0.0567$ $wR_2 = 0.1030$	$R_1 = 0.0440$ $wR_2 = 0.0938$
Largest diff. peak/hole (e Å^{-3})	0.518/−0.581	0.393/−0.572	0.519/−0.548	0.731/−0.487

Table 2. Selected bond lengths (Å) of abglyH_2, **1**, **2** and **3**.

S(1)–O(2)	1.4344(16)	S(1)–C(6)	1.761(2)	O(5)–C(10)	1.310(3)
S(1)–O(3)	1.4350(16)	O(1)–C(2)	1.232(3)	N(1)–C(2)	1.345(3)
S(1)–N(2)	1.6222(17)	O(4)–C(10)	1.195(3)	N(1)–C(3)	1.412(3)
N(2)–C(9)	1.464(3)	C(3)–C(8)	1.392(3)	C(6)–C(7)	1.387(3)
C(1)–C(2)	1.500(3)	C(4)–C(5)	1.376(3)	C(7)–C(8)	1.389(3)
C(3)–C(4)	1.390(3)	C(5)–C(6)	1.386(3)	C(9)–C(10)	1.511(3)
1					
Mn (1)–O(2)	2.1407(11)	Mn (1)–O(6)#1	2.1976(15)	Mn (1)–N(1)	2.3224(14)
Mn (1)–O(2)#1	2.1407(11)	Mn (1)–O(6)	2.1977(15)	Mn (1)–N(1)#1	2.3225(14)
2					
Mn(1)–O(5)#2	2.1478(14)	Mn (1)–O(6)	2.1852(15)	Mn (1)–N(3)#2	2.2761(17)
Mn (1)–O(5)	2.1479(14)	Mn (1)–O(6)#2	2.1852(15)	Mn (1)–N(3)	2.2761(17)
3					
Zn(1)–O(3)#3	2.0836(16)	Zn (1)–O(1)#3	2.0918(16)	Zn (1)–O(2)#3	2.1106(18)
Zn (1)–O(3)	2.0836(16)	Zn (1)–O(1)	2.0919(16)	Zn (1)–O(2)	2.1106(18)

Symmetry codes for **1**–**3**: #1 $-x$, $-y+2$, $-z$; #2 $-x+1$, $-y+1$, $-z$; #3 $-x+2$, $-y$, $-z+1$.

Table 3. Selected bond angles (°) of bglyH_2 and **1**–**3**.

abglyH_2					
O(2)–S(1)–O(3)	118.96(10)	O(2)–S(1)–C(6)	107.40(10)	C(2)–N(1)–C(3)	130.09(19)
O(2)–S(1)–N(2)	107.54(10)	O(3)–S(1)–C(6)	109.51(10)	C(9)–N(2)S–(1)	119.05(13)
O(3)–S(1)–N(2)	106.00(9)	N(2)–S(1)–C(6)	106.84(9)	O(1)–C(2)–N(1)	122.9(2)
1					
O(2)–Mn(1)–O(2)#1	180.0	O(6)–#–1Mn(1)–O(6)	179.999(1)	O(2)–Mn(1)–N(1)#1	92.46(5)
O(2)–Mn(1)–O(6)#1	93.12(5)	O(2)–Mn(1)–N(1)	87.54(5)	O(2)#–1Mn(1)–N(1)#1	87.54(5)
O(2)#–1Mn(1)–O(6)#1	86.88(5)	O(2)#–1Mn(1)–N(1)	92.46(5)	O(6)#–1Mn(1)–N(1)#1	88.68(6)
O(2)–Mn(1)–O(6)	86.88(5)	O(6)#–1Mn(1)–N(1)	91.32(6)	O(6)–Mn(1)–N(1)#1	91.32(6)
O(2)#–1Mn–(1–O(6)	93.12(5)	O(6)–Mn(1)–N(1)	88.68(6)	N(1)–Mn(1)–N(1)#1	180.00(8)
2					
(5)#2–Mn(1)–O(5)	179.999(1)	O(6)–Mn(1)–O(6)#2	180.0	O(5)#2–Mn(1)–N(3)	88.91(6)
O(5)#2–Mn(1)–O(6)	91.00(6)	O(5)#2–Mn(1)–N(3)#2	91.09(6)	O(5)–Mn(1)–N(3)	91.09(6)
O(5)–Mn(1)–O(6)	89.00(6)	O(5)–Mn(1)–N(3)#2	88.91(6)	O(6)–Mn(1)–N(3)	89.61(6)
O(5)#2–Mn(1)–O(6)#2	89.00(6)	O(6)–Mn(1)–N(3)#2	90.39(6)	O(6)#2–Mn(1)–N(3)	90.39(6)
O(5)–Mn(1)–O(6)#2	91.00(6)	O(6)#2–Mn(1)–N(3)#2	89.61(6)	N(3)#2–Mn(1)–N(3)	180.0
3					
O(3)#3–Zn(1)–O(3)	179.999(1)	O(1)#3–Zn(1)–O(1)	179.999(1)	O(3)#3–Zn(1)–O(2)	90.63(7)
O(3)#3–Zn(1)–O(1)#3	88.48(6)	O(3)#3–Zn(1)–O(2)#3	89.37(7)	O(3)–Zn(1)–O(2)	89.37(7)
O(3)–Zn(1)–O(1)#3	91.52(7)	O(3)–Zn(1)–O(2)#3	90.63(7)	O(1)#3–Zn(1)–O(2)	85.09(7)
O(3)#3–Zn(1)–O(1)	91.52(7)	O(1)#3–Zn(1)–O(2)#3	94.91(7)	O(1)–Zn(1)–O(2)	94.91(7)
O(3)–Zn(1)–O(1)	88.48(7)	O(1)–Zn(1)–O(2)#3	85.09(7)	O(2)#3–Zn(1)–O(2)	180.0

Symmetry codes for **1**–**3**: #1 $-x$, $-y+2$, $-z$; #2 $-x+1$, $-y+1$, $-z$; #3 $-x+2$, $-y$, $-z+1$.

from two different 4,4′-bipyridine ligands and four oxygen atoms from two abglyH^- anions and two water molecules to give a slightly distorted octahedron; the bond angles around Mn(II) range from 86.88(5)° to 93.12(5)°. The Mn–N bond distance is 2.3224(14) Å, slightly longer than previous Mn(II) complexes containing Mn–N bonds (2.2448(17) 2.2946(16) Å) and the Mn–O bond distances range from 2.1407(11) to 2.1977(15) Å, in the normal range of Mn–O bonds (2.1268(13) 2.2843(15) Å) [17]. In **1**, the carboxylate groups from abglyH^- are monodentate and each bipy is μ_2-bridging

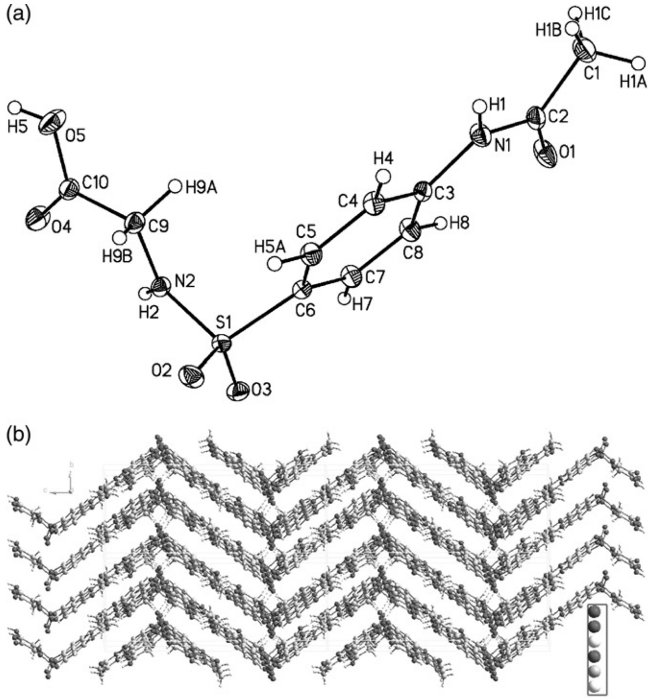

Figure 1. (a) Molecular structure of abglyH$_2$; (b) a perspective view of the 3-D structure through hydrogen bonds in abglyH$_2$.

connecting two Mn(II) atoms. As a result, **1** is extended into a 1-D chain running along the *a* axis. These chains have abglyH$^-$ ligands dendritic at the two sides and the pyridine rings of bipy at each chain are arranged in a nearly parallel fashion with an inter-ring distance of 10.5536 Å.

In these adjacent chains, there exists p–π stacking interaction along the *b* axis through mutual-nesting between the acetamide groups of the lateral ligands and the pyridine rings in a parallel way. The dihedral angle between two planes is 2.393(78)° and the distance between C7 of acetamide and the central pyridine ring is 3.6491(22) Å (shown in figure 2c). Complex **1** is dominated by three different types of intermolecular hydrogen bonds in the solid state. N(3)H(3N) $\cdots$ O(3) forms 8-membered hydrogen bonded rings, O(6)H(1W) $\cdots$ S(1) and O(6)H(1W) $\cdots$ O(3) constitute 18-membered hydrogen bonded rings. These rings are alternately repeated in the lattice by translation along the *b* axis. The *c* direction is characterized by the formation of similar 22-membered rings comprised of the interactions N(2)H(2N) $\cdots$ O(1). Consequently, a 3-D network is formed via the interplay of hydrogen bonds (shown in figure 2b).

To explore the influence of pH on the supramolecular structure, we synthesized **2** by changing pH. As shown in figure 3(a), **2** is a centrosymmetric mononuclear structure. The center Mn(II) is six-coordinate with two nitrogens from two monodentate bipy ligands and four oxygens from two water molecules and a pair of carboxylate groups of two different abglyH$^-$ anions. The Mn–N distance is 2.2761(17) Å, shorter than that in **1**. The Mn(1)–O(5) and Mn(1)–O(6) distances are 2.1479(14) and 2.1852(15) Å, respectively. The bond angles around Mn(II) range from 88.91(6)° to 91.09(6)°, close to octahedral.

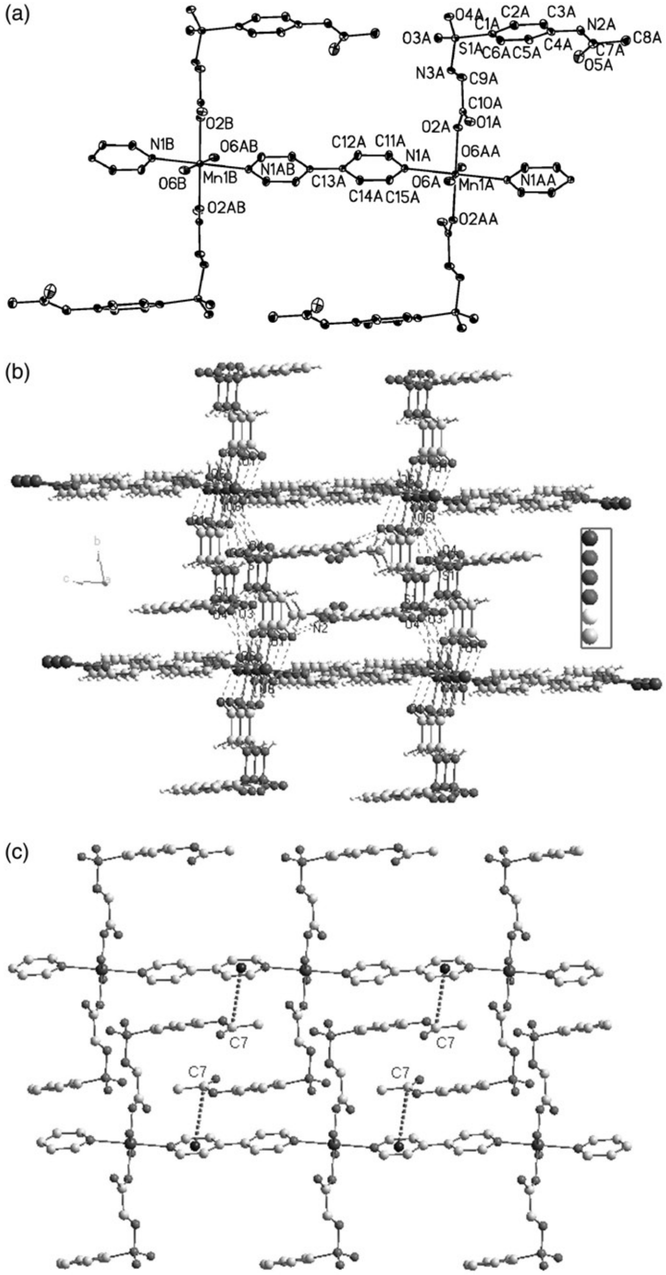

Figure 2. (a) ORTEP view of the building block of **1** with atomic labeling (hydrogen atoms are omitted for clarity); (b) packing diagrams for **1**, showing hydrogen-bonded network; (c) view of the interchain *p*–π interactions indicated by the black dashed lines in **1** (hydrogen atoms are omitted for clarity).

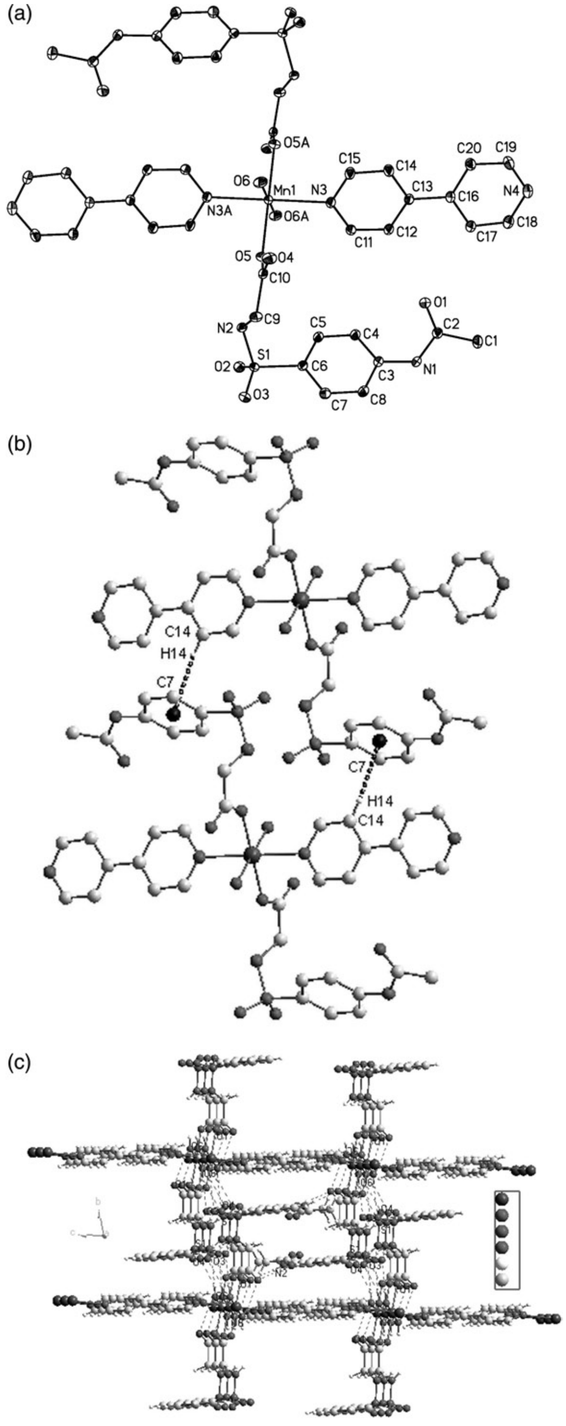

Figure 3. (a) ORTEP view of the Mn environment in **2** with the atom-numbering scheme (hydrogen atoms are omitted for clarity); (b) view of the intermolecular C–H $\cdots \pi$ interactions indicated by the black dashed lines in **2** (hydrogen atoms except H(14) are omitted for clarity); (c) a view of the 3-D supramolecular network formed by strong intermolecular hydrogen bonds.

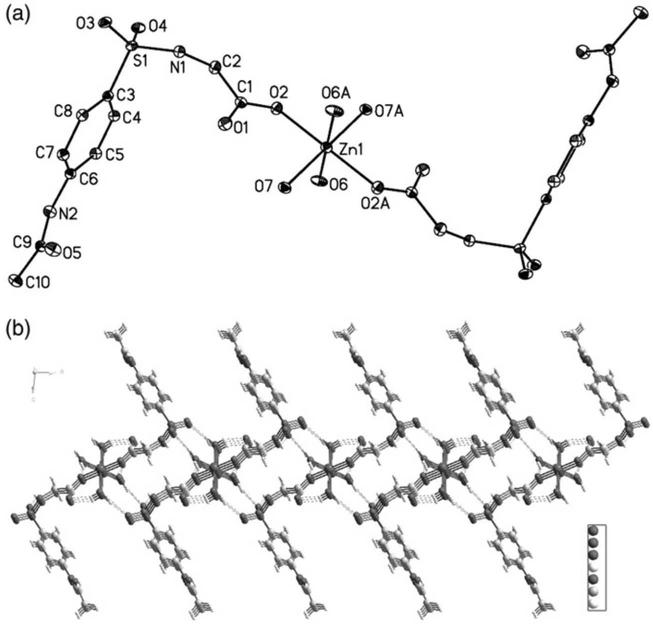

Figure 4. (a) The Zn environment in **3** with atom-numbering scheme (hydrogen atoms are omitted for clarity); (b) view of the 2-D network structure (along *ab* plane) with hydrogen bonds shown as dashed lines for **3**.

Conventional strong hydrogen bonds and intermolecular C–H $\cdots\pi$ interactions play a major role in stabilizing **2** in the solid state. Intermolecular hydrogen bond N(2)–H(1W) $\cdots$ O(2) forms a linear array along the *b* axis, O(6)–H(1W) $\cdots$ N(4) forms a plane (in *bc* plane) along the *a* axis, while the remaining intermolecular hydrogen bond N(1)–H(1) $\cdots$ O(4) forms a 3-D network. Additionally, intermolecular C–H $\cdots\pi$ weak interactions (shown in figure 3b) exist between C(14)–H(14) and benzene rings of the ligands in neighboring coordinated molecules, with distance between C(14) and the central benzene ring of 3.697 Å. The weak interactions (shown in figure 3c) mentioned above provide extra opportunities to produce supramolecular architectures of the higher dimensions [18].

To explore the influence of metal ion on the formation of supramolecular structure, we synthesized **3** by utilizing Zn of Mn. As illustrated in figure 4(a), Zn(II) serves as a central metal with four water molecules and two abglyH$^-$ anions in octahedral geometry. The carboxylate group is monodentate with Zn(1)–O(3) distance of 2.0835(16) Å, slightly longer than reported Zn–O distances (1.968 and 2.011 Å) [19, 20]. The Zn(1)O$_{H_2O}$ bond lengths are 2.0919(16) and 2.1106(18) Å, slightly longer than 2.0835(16) Å of Zn(1)–O(3). The coordination geometry of Zn(1) is slightly distorted with angles ranging from 85.09(7)° (O(1)–Zn(1)–O(2)#1, $\#1=-x+2$, $-y$, $-z+1$) to 94.91(7)° (O(1)#1Zn(1)O(2)#1, $\#1=-x+2$, $-y$, $-z+1$).

As shown in table 4, there are some hydrogen bonding interactions. H $\cdots$ A(O or S) separations are in the 1.89–2.92 Å region and the bond angles range between 147.1° and 177.0°, in the normal range [21]. These different kinds of hydrogen bonding D–H $\cdots$ A (D=O or N) interactions extend the mononuclear complex into a 2-D supramolecular pattern (in *ab* plane, figure 4b), further stabilizing the 2-D supramolecular packing.

Table 4. Details of the hydrogen bonds for abglyH_2 and **1**–**3**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
abglyH_2				
N(2)–H(2)···O(2)#1	0.86	2.56	3.065(2)	118.8
N(1)–H(1)···O(4)#2	0.86	2.04	2.890(2)	168.7
O(5)–H(5)···O(1)#3	0.82	1.81	2.616(2)	165.9
1				
O(6)–H(2W)···O(1) #1	0.84	2.05	2.7693(19)	144.1
O(6)–H(1W)···S(1)#2	0.83	2.92	3.6806(15)	154.3
O(6)–H(1W)···O(3)#3	0.83	2.21	2.979(2)	154.5
N(3)–H(3N)···O(3)#4	0.86	2.49	3.132(2)	132.4
N(2)–H(2N)···O(1)#5	0.86	2.09	2.953(2)	177.9
2				
O(6)–H(2W)···O(4)#1	0.97	1.83	2.715(2)	150.8
O(6)–H(1W)···N(4)#2	0.76	2.23	2.951(2)	156.9
N(2)–H(2)···O(2)#3	0.86	2.55	3.144(2)	127.0
N(1)–H(1)···O(4)#4	0.86	2.03	2.892(2)	175.4
3				
O(1)–H(1W)···O(6)#2	0.83	2.02	2.846(2)	177.0
O(1)–H(2W)···O(4)#1	0.83	1.89	2.672(3)	155.1
O(2)–H(3W)···O(5)#2	0.83	2.08	2.904(2)	172.6
O(2)–H(3W)···S(1)#2	0.83	2.92	3.6842(18)	153.9
O(2)–H(4W)···O(3)#3	0.83	1.92	2.741(2)	173.8
N(1)–H(1)···O(5)#3	0.86	2.31	3.071(3)	147.1
N(2)–H(2)···O(7)#4	0.86	2.15	2.962(3)	157.6

Symmetry transformations used to generate equivalent atoms: abglyH_2: #1 $-x+2$, $y-1/2$, $-z+3/2$; #2 $x-1/2$, y, $-z+3/2$; #3 x, $-y+3/2$, $z+1/2$.
1: #1 $-x$, $-y+2$, $-z$; #2 $x+1$, $-y+2$, $-z-1$; #3 x, $y+1$, z; #4 $-x$, $-y+1$, $-z$; #5 $-x$, $-y+1$, $-z+1$.
2: #1 $-x+1$, $-y+1$, $-z$; #2 $x+1/2$, $-y+1/2$, $z-1/2$; #3 $x+1$, $-y+2$, $-z$; #4 $x+3/2$, $y+1/2$, $-z+1/2$.
3: #1 $-x+2$, $-y$, $-z+1$; #2 $-x+3/2$, $-y+1/2$, $-z+1$; #3 x, $y-1$, z; #4 x, $y+1$, z.

Complexes **1**–**3** were synthesized under mild conditions, and their formations were strongly influenced by pH values and metal ions. In the assembly of **1** and **2**, factors such as the abglyH_2 ligand, auxiliary bipy, solvent, metal/ligand ratio and reaction time are kept constant and only the pH was varied (6 for complex **1** and 4 for complex **2**); in the assembly of **1** and **3**, all factors are kept constant except the metal ion (Mn(II) for **1** and Zn(II) for **3**). Thus, two key factors affect the formation of **1**–**3**, the pH values and the nature of the metal ion. The abglyH_2 ligand exhibits the same coordination mode in complexes **1**–**3**, coordination of carboxyl oxygen to the metal, consistent with the reported cases where *N*-benzenesulfonylamino acids behave as simple carboxylate ligands at low pH. When the pH value increases, it switches to dianionic *N*,*O*-bidentate chelating due to deprotonation of amide nitrogen giving an additional donating site [22–27]. Further study of the coordination chemistry of this ligand at higher pH is ongoing, which may offer new metal-organic supramolecular assembly.

3.2. *Infrared spectra*

Comparing infrared spectra of the free ligand to those of its complexes provides information about the coordination of the ligand. Complexes **1**–**3** show similar infrared bands in the range 4000–400 cm^{-1}, which are different from the free ligand. The ν(NH) of the ligand (3245 cm^{-1}) and its complexes (3225–3234 cm^{-1}) show only minor shifts in excellent agreement with the fact that this group is not coordinated. Bands assigned to

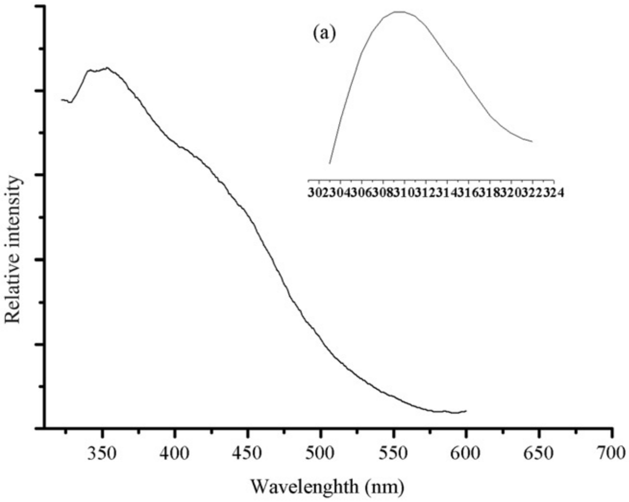

Figure 5. The emission spectra of **3** in the solid state at room temperature; (a) the excitation spectra of **3** in the solid state at room temperature.

$\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, which are observed for the free ligand at 1720 cm^{-1} and 1498 cm^{-1}, respectively, shift to 16261–635 cm^{-1} and 1384–1412 cm^{-1} in **1**–**3**, indicating that deprotonation of the carboxylate groups occurred upon coordination. The difference between the asymmetric and symmetric stretches, $\Delta(\nu_{as}(COO^-) - \nu_s(COO^-))$, was greater than 200 cm^{-1}, indicating monodentate carboxylate [16]. The $\nu_{as}(\text{–}SO_2\text{–})$ (1328–1361 cm^{-1}) and $\nu_s(\text{–}SO_2\text{–})$ (11561–163 cm^{-1}) show little change (1345 and 1159 cm^{-1}), suggesting that this group does not coordinate. All these spectroscopic features of abglyH$_2$ and **1**–**3** are consistent with the crystal structure determinations.

3.3. *Fluorescence of 3*

The luminescence of **3** was investigated in the solid state at room temperature. The fluorescence spectrum of **3** is shown in figure 5 and exhibits an emission band in the range 325–570 nm with a maximum at 353 nm upon excitation at 308 nm. In comparison to the emission at 401 nm for free abglyH$_2$ in the solid state at room temperature, the fluorescence may be assigned to the metal-perturbed π^*–π transition of the ligand. Generally, the rigidity of the ligand increases in a complex, giving enhanced fluorescence efficiency. However, fluorescence intensity observed in **3** is not as strong as expected, perhaps from coordination of water to Zn(II) since water molecules possessing high-energy OH-vibrations ($\nu = 3700\,cm^{-1}$) are efficient quenchers [28]. The luminescence of **3** indicates that metal coordination affects the emission wavelength and intensity of the organic material.

4. Conclusion

In summary, the new ligand abglyH$_2$ and its three coordination complexes with different structural motifs have been synthesized and characterized. All the complexes display supramolecular structures in the solid state by intermolecular hydrogen bonding or/and aromatic π–π interactions. The pH and metal ion play important roles in the formation of the complexes. Complex **3** exhibits luminescence in the solid state at room temperature. Efforts to investigate other luminescent metal complexes and coordination polymers with N-protected amino acids are underway in our laboratory.

Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 660387 (abglyH_2), 652616 (**1**), 652615 (**2**), 649503 (**3**) and copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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