

## Synthesis, structure and properties of (4,4'-H<sub>2</sub>bipy)[ZnBr<sub>4</sub>]

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The compound [4,4'-H<sub>2</sub>bipy][ZnBr<sub>4</sub>] (**1**) has been synthesized via hydrothermal reaction and exhibits an isolated structure based on discrete 4,4'-H<sub>2</sub>bipy moieties and tetrahedral metal(II) centre terminally coordinated by four bromide ions. The organic moieties and the inorganic complex dianions are linked via hydrogen bonds forming a sheet structure. Optical absorption spectrum shows a band gap of 3.13 eV, indicating **1** to be a wide gap semiconductor. Luminescent investigation reveals a strong emission in blue region, which may be originating from  $\pi \rightarrow \pi^*$  charge-transfer interaction of 4,4'-H<sub>2</sub>bipy. IR, powder X-ray diffraction (PXRD) and thermogravimetry-differential thermal analyses (TG-DTA) are also reported.

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The ability of bifunctional 4,4'-bipyridine (bipy) to act as a rigid, rod-like organic building block in the self-assembly of coordination frameworks is well-known, such as, acting as a charge-compensating cation<sup>1</sup>, a pillar bonding to inorganic skeletal backbone<sup>2</sup>, an uncoordinated guest molecule and as organic template<sup>3</sup>, a bridge connecting two metal complex moieties<sup>4</sup>, or a ligand linking a metal and an inorganic framework<sup>5</sup>. Besides, bipy with delocalized  $\pi$ -electrons of the pyridyl rings has gained increased recent attention in preparing light emitting compounds in various technical applications, such as chemical sensors<sup>6</sup>, sensitizers in solar energy conversion<sup>7</sup>, and emitting materials for organic light emitting diodes<sup>8</sup>.

Recently, many structures of metal halide-bipy materials have been reported<sup>9</sup>, among which Group 12 metal halide-bipy materials are relatively rare. In fact, compounds containing Group 12 elements are particularly attractive for many reasons: the variety of coordination numbers and geometries provided by the  $d^{10}$  configuration of the Group 12 metal ions, photoelectric properties, the widespread applications of Group 12 compounds, and the essential role in biological systems of zinc, and so on. Fluorescent materials, particularly blue fluorescent materials have been of intense interest because blue fluorescence is one of the key color components required for full-color EL displays and blue fluorescent materials are still rare. Different from the neutral 4,4'-bipy which

can act as a ligand, 4,4'-H<sub>2</sub>bipy dication may usually form supramolecular frameworks through H-bonding as it cannot act as a ligand. To obtain a novel material that may possess both photoluminescent and photoelectric properties, our recent efforts in synthesizing novel Group 12-based compounds are focused largely on the systems containing 4,4'-H<sub>2</sub>bipy. We describe herein the structure and the properties of (4,4'-H<sub>2</sub>bipy)[ZnBr<sub>4</sub>] (**1**).

### Materials and Methods

All reactants (A. R. grade quality) were used without further purification. Elemental analyses of carbon, hydrogen and nitrogen were carried out with an Elementar Vario EL. The infrared spectra were recorded on a PE Spectrum-One FT-IR spectrophotometer over the frequency range 4000–400 cm<sup>-1</sup> (using the KBr pellet technique). The UV-Vis spectra were recorded at room temperature on a computer-controlled PE Lambda 35 UV-Vis spectrometer equipped with an integrating sphere in the wavelength range 190–1100 nm. BaSO<sub>4</sub> plate was used as a reference (100% reflectance), on which the finely ground powder of the samples were coated. The absorption spectra were calculated from reflection spectra by the Kubelka-Munk function<sup>10</sup>:  $\alpha/S = (1-R)^2/2R$ ,  $\alpha$  is the absorption coefficient,  $S$  is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5  $\mu\text{m}$ , and  $R$  is the reflectance.

Thermogravimetry-differential thermal analyses (TG-DTA) were performed on a NETZSCH STA 449C analyzer. Powder sample was loaded into an alumina pan and heated from 30-900 °C at the rate of 10°C/min. The fluorescent study was conducted at room temperature on a JY Fluorolog-322 fluorescence spectroscopy instrument.

Powder X-ray diffraction (PXRD) pattern was measured on a Rigaku DMAX2500 powder diffractometer at 40 kV and 100 mA using Cu-K $\alpha$  ( $\lambda = 1.54056 \text{ \AA}$ ), with a scan speed of 0.375 s/step and a step size of 0.05°. The simulated powder pattern was calculated using single-crystal X-ray diffraction data and processed by the free Mercury v1.4 program provided by the Cambridge Crystallographic Data Centre, as shown in Fig. 1.

For synthesizing (**1**), ZnBr<sub>2</sub> (0.2 mmol, 0.045 g), 4,4'-bipy (0.2 mmol, 0.031 g) and distilled water (3 cm<sup>3</sup>) were loaded into a Teflon-lined stainless steel autoclave (25 cm<sup>3</sup>) and kept at 473 K for 3 days. After cooling slowly to room temperature at a rate of 6 K/h, colorless crystals suitable for X-ray analysis were obtained. Yield: 93% (based on zinc). Anal. Calcd for C<sub>10</sub>H<sub>10</sub>Br<sub>4</sub>N<sub>2</sub>Zn: C, 22.10; H, 1.84; N, 5.16. Found: C, 21.89; H, 2.01; N, 5.37. IR peaks (KBr, cm<sup>-1</sup>): 3218(m), 3137(m), 3079(s), 2878(m), 1635(s), 1625(s), 1600(vs), 1488(s), 1480(s), 1363(s), 1232(m), 1197(m), 1124(w), 1093 (w), 1056 (w), 999(w), 774(vs) and 705(m).

For X-ray data collection, reduction, and structure solution, the intensity data set was collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-K $\alpha$  radiation

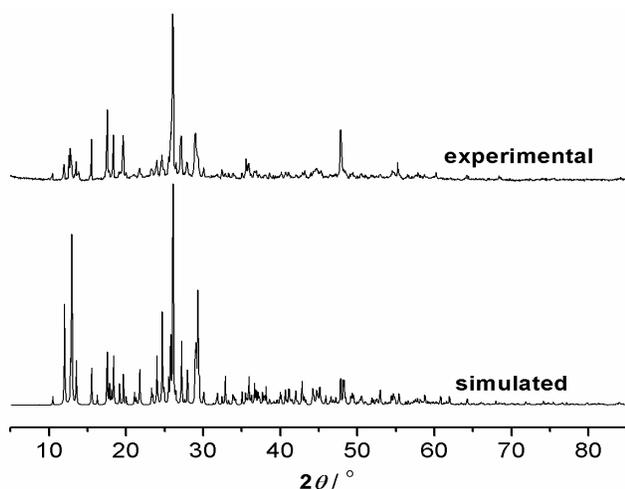


Fig. 1 — PXRD patterns for **1**.

( $\lambda = 0.71073 \text{ \AA}$ ) by using a  $\omega$  scan technique. CrystalClear software was used for data reduction and empirical absorption corrections<sup>11</sup>. The structure was solved by the direct methods using the Siemens SHELXTL™ Version 5 package of crystallographic software<sup>12</sup>. The difference Fourier maps based on these atomic positions yield the other non-hydrogen atoms. The hydrogen atom positions were generated symmetrically, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but were not refined. The structures were refined using a full-matrix least-squares refinement on  $F^2$ . All atoms except for hydrogen atoms were refined anisotropically. The crystallographic data and structure analysis are listed in Table 1.

## Results and Discussion

X-ray diffraction analysis reveals that compound **1** exhibits an isolated structure, consisting of 4,4'-H<sub>2</sub>bipy dication and tetrabromo-zinc dianions, as shown in Fig. 2. Selected bond distances and bond angles are given in Table 2. The tetrahedral zinc atom is coordinated by four terminal bromine atoms with the bond lengths of Zn1-Br1, Zn1-Br2, Zn1-Br3 and Zn1-Br4 being 2.2996(9), 2.3481(9), 2.3665(9) and 2.4153(7) Å, respectively. The Zn-Br distances are in the normal range and comparable with those reported in literature<sup>13</sup>. The bond angles of Br-Zn-Br are in the

Table 1 — Crystallographic data and structure analysis for **1**

Formula	C <sub>10</sub> H <sub>10</sub> Br <sub>4</sub> N <sub>2</sub> Zn
$F_w$	543.21
Colour	colourless
Crystal size/mm <sup>3</sup>	0.37 0.20 0.14
Crystal system	monoclinic
Space group	$P2_1/c$
$a$ (Å)	7.7444(4)
$b$ (Å)	20.212(2)
$c$ (Å)	9.7494(4)
$\beta$ (°)	108.148(6)
$V$ (Å <sup>3</sup> )	1450.2(2)
$Z$	4
$2\theta_{\max}$ (°)	50.7
Reflections collected	9318
Independent, observed reflections ( $R_{\text{int}}$ )	2599, 1135 (0.0577)
$d_{\text{calcd}}$ (g/cm <sup>3</sup> )	2.488
$\mu$ (mm <sup>-1</sup> )	12.694
$T$ (K)	293(2)
$F(000)$	1016
$R_1, wR_2$	0.0669, 0.1329
$S$	0.961
Largest and Mean $\Delta/\sigma$	0.001, 0
$\Delta\rho$ (max/min) (e/Å <sup>3</sup> )	1.972/-1.171

range of 106.90(3)–111.20(3)°, which are close to those in a regular tetrahedron. The charge of [ZnBr<sub>4</sub>] moiety must be –2 due to the oxidation state of Zn and Br are +2 and –1, respectively. For the requirement of charge balance, the nitrogen atoms of the 4,4'-bipy ligand must be protonated, as the cases found in many other compounds<sup>1</sup>. The two pyridyl rings of the 4,4'-bipy ligand are slightly twisted with a small dihedral angle of *ca.* 4.42°, which is comparable with that previously documented<sup>9b</sup>. In the title compound, no  $\pi \dots \pi$  stacking interactions were established between the 4,4'-bipy ligands. The 4,4'-H<sub>2</sub>bipy moieties and tetrabromo-zinc dianions are linked by Br...C and Br...N hydrogen bonds, yielding a 2-D supramolecular sheet. The hydrogen bonds and electrostatic interactions between the (4,4'-H<sub>2</sub>bipy)<sup>2+</sup> dications and the [ZnBr<sub>4</sub>]<sup>2-</sup> dianions contribute to the stabilization of the crystal packing of the title compound (Fig. 3).

To our knowledge, some analogs have been documented, of which only four are isostructural with the title compound, i.e. (4,4'-H<sub>2</sub>bipy)[ZnCl<sub>4</sub>] (**2**), (4,4'-H<sub>2</sub>bipy)[HgCl<sub>4</sub>] (**3**), (4,4'-H<sub>2</sub>bipy)[CoCl<sub>4</sub>] and (4,4'-H<sub>2</sub>bipy)[CoBr<sub>4</sub>], and **2** and **3** are Group 12 metal halides with 4,4'-H<sub>2</sub>bipy<sup>1</sup>. The very analogous compound, (4,4'-H<sub>2</sub>bipy)[ZnCl<sub>4</sub>] (**2**), features a

Table 2 — Selected bond lengths (Å) and bond angles (°)

Zn1-Br1	2.2996(9)	Br1-Zn1-Br3	106.95(3)
Zn1-Br2	2.3481(9)	Br1-Zn1-Br4	106.90(3)
Zn1-Br3	2.3665(9)	Br2-Zn1-Br3	109.97(3)
Zn1-Br4	2.4153(7)	Br2-Zn1-Br4	111.00(3)
Br1-Zn1-Br2	111.20(3)	Br3-Zn1-Br4	110.70(3)

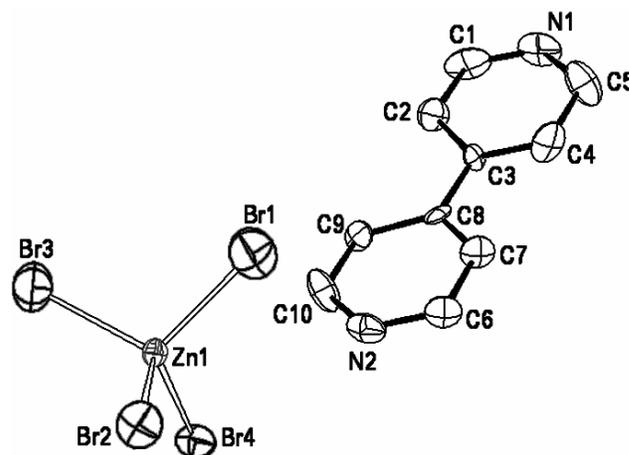
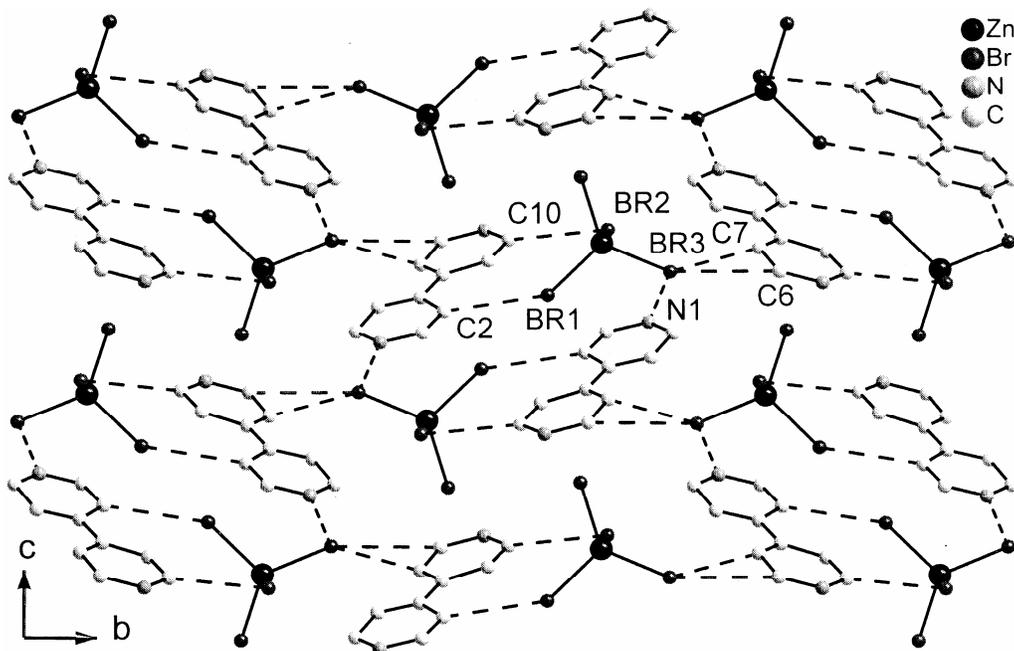
Fig. 2 — ORTEP drawing of **1** with 40% thermal ellipsoids (hydrogen atoms omitted for clarity).

Fig. 3 — Packing diagram of **1** with the dashed lines representing Br...N and Br...C hydrogen bonds, respectively. Hydrogen bonds (Å): Br1...C2#1 3.476(5), Br2...C10#1 3.555(5), Br3...N1#2 3.215(4), Br3...C6#3 3.468(5) and Br3...C7#3 3.551(5) (Symmetry codes: #1 1+x, y, z; #2 -x, 1-y, -z; #3 1-x, -0.5+y, -0.5-z).

hydrogen bonded dimeric ring motif containing two hydrogen bonds. However, in the title compound, there are five hydrogen bonds that link the dications and dianions to form a 2-D supramolecular sheet. **1** and the analogous **2**, adopt very different structural motifs even though there is only minor difference in chemical formula—different halide atoms, indicating that halide atoms play a vital role in structural motifs. For these analogs, besides the structural motif of **2**, there are two other motifs, namely, hydrogen bonded polymeric ribbon structure and hydrogen bonded sheet motif in which the tetrachlorometallate anions polymerise to form a one-dimensional chain<sup>14</sup>. Therefore, the structural motif of the title compound may be classified as the fourth type.

#### UV-vis spectroscopy

Optical absorption spectrum of **1** reveals the presence of an optical gap of 3.13 eV, which suggests that compound **1** is probably a semiconductor and is consistent with the yellow color of the crystal, as for the case reported already<sup>15</sup>. The gradual slope of the optical absorption edge for **1** is indicative of the existence of indirect transitions<sup>16</sup>. The optical absorption of **1** is likely to have originated from the charge-transfer excitations mainly from the valence band of the bromine atoms to the conduction band of the zinc center.

#### Fluorescent properties

The solid state emission spectrum of **1** is investigated at room temperature (Fig. 4). The fluorescent spectrum study shows a broad and strong emission with a maximum wavelength of 567 nm upon photo-excitation at 408 nm. The emission may be assigned to the  $\pi \rightarrow \pi^*$  charge-transfer interaction of the 4,4'-H<sub>2</sub>bipy moieties.

#### TG-DTA studies

TG-DTA study shows that compound **1** underwent a two-step decomposition process, as shown in Fig. 5. From 30–410 °C, the TG curve displays an initial mass loss of 28.35% (calcd 29.10%) with a small endothermic peak centred at 335°C, corresponding to the loss of 4,4'-H<sub>2</sub>bipy moiety. A second weight loss of 71.65% (calcd 70.90%) is found in the temperature range 410–900 °C, in accordance with the loss of ZnBr<sub>4</sub> moiety. The results are consistent with the X-ray structures.

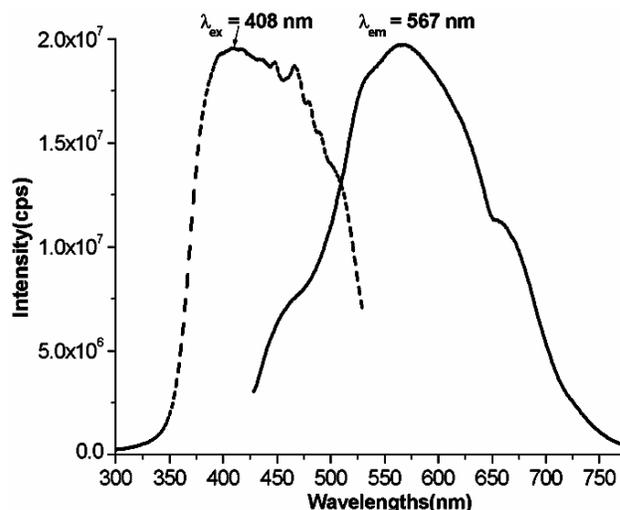


Fig. 4 — Solid-state emission and excitation spectra of **1** at room temperature (Solid line: emission spectrum; Dashed line: excitation spectrum).

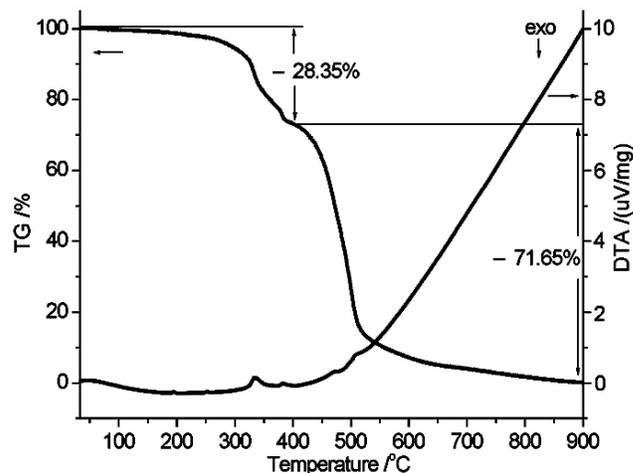


Fig. 5 — TG-DTA diagram showing the weight loss of **1**.

Thus, using hydrothermal reaction of ZnBr<sub>2</sub> with 4,4'-bipy, the title compound (4,4'-H<sub>2</sub>bipy)[ZnBr<sub>4</sub>] is obtained. Optical absorption spectrum shows that the title compound may be a candidate for potential photoelectric material. This compound exhibits a broad and strong fluorescent emission band, and it may be used as a blue-light material. It is believed that more and more Group 12 metal halide-bipy compounds with good photoluminescent and photoelectric properties can be developed.

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