## Accepted Manuscript

Nitrogen-rich 5-(4-pyridyl)tetrazole-2-acetic acid and its alkaline earth metal coordination polymers for potential energetic materials

Gao Wen Yang, Yuan Ting Zhang, Qi Wu, Meng Jie Cao, Jiao Wu, Qiu Yan Yue, Qiao Yun Li

PII:	\$0020-1693(16)30325-5
DOI:	http://dx.doi.org/10.1016/j.ica.2016.06.015
Reference:	ICA 17106
To appear in:	Inorganica Chimica Acta
Received Date:	28 March 2016
Revised Date:	17 May 2016
Accepted Date:	6 June 2016



Please cite this article as: G.W. Yang, Y.T. Zhang, Q. Wu, M.J. Cao, J. Wu, Q.Y. Yue, Q.Y. Li, Nitrogen-rich 5-(4-pyridyl)tetrazole-2-acetic acid and its alkaline earth metal coordination polymers for potential energetic materials, *Inorganica Chimica Acta* (2016), doi: http://dx.doi.org/10.1016/j.ica.2016.06.015

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

# Nitrogen-rich 5-(4-pyridyl)tetrazole-2-acetic acid and its alkaline earth metal coordination polymers for potential energetic materials

Gao Wen Yang, Yuan Ting Zhang, Qi Wu, Meng Jie Cao, Jiao Wu, Qiu Yan Yue, Qiao Yun Li\*

\*Qiao-Yun Li: Tel: +86-512-52251842; Fax: +86-512-52251842

Email: liqiaoyun61@126.com

Jiangsu Laboratory of Advanced Functional Material, Department of Chemistry and Material Engineering, Changshu Institute of Technology, Changshu 215500, Jiangsu, P. R. China

**Abstract:** Tetrazole and its derivatives with rich nitrogen atoms may be potential candidates for energetic materials. Alkaline earth metal coordination compounds based on such ligands are relatively less investigated. Hpytza was prepared from 4-cyanopyridine and sodium azide, ethyl bromoacetate, where Hpytza=5-(4-pyridyl)tetrazole-2-acetic acid. Hpytza and four alkaline earth metal  $[Mg(pytza)_2]_n$  (1),  $[Ca(pytza)_2(H_2O)_2]_n \cdot 3nH_2O$ coordination polymers (2), $[Sr(pytza)_2(H_2O)_2]_n$  (3) and  $[Ba(pytza)_2(H_2O)_2]_n \cdot nH_2O$  (4) were prepared under solvothermal conditions. The thermal behavior of these compounds were the (DSC) characterized by differential scanning calorimetry and thermogravimetric-differential thermogravimetric (TG-DTG) analyses. Furthermore, the critical temperature of thermal explosion and relevant thermal parameters  $\Delta S$ ,  $\Delta H$ ,  $\Delta G$  of Hpytza and polymers 1-4 were calculated, as well, indicating that these compounds are potential energetic materials.

**Keywords:** Hpytza; alkaline earth metal; luminescence; energetic material; thermal parameter

### **1. Introduction**

In recent years, the design and exploration of energetic materials has received

increasing attention due to not only the energy shortage, but also the conventional materials are neither high energetic nor environmentally friendly. Typical of energetic materials, for instance, organic compounds [1], lead salts [2] as well as coordination compounds [3] have been widely. Recently, tetrazole and its derivatives with high nitrogen percentage are acknowledged as advanced materials, in the range of luminescence, magnetism, adsorption materials, etc [4]. Besides, coordination compounds consisting of metal center and ligands usually show relatively higher thermal stability, compared with the corresponding ligands. In our previous work, we reported the synthesis and characterization of 5-[N-acetato(4-pyridyl)]tetrazole and its alkaline earth metal coordination compounds [5]. To extend our previous work and explore the relationship of the thermal stability and energetic performance, 5-(4-pyridyl)tetrazole-2-acetato, the isomer of 5-[N-acetato(4-pyridyl)]tetrazole, was chosen to be reacted with alkaline earth metal salts yielded its four new polymers  $[Mg(pytza)_2]_n$  (1),  $[Ca(pytza)_2(H_2O)_2]_n \cdot 3nH_2O$  (2),  $[Sr(pytza)_2(H_2O)_2]_n$  (3) and  $[Ba(pytza)_2(H_2O)_2]_n \cdot nH_2O$  (4). On one hand, the two isomers with abundant nitrogen and oxygen atoms tend to display various coordination modes, thus leading to structural variation. On the other hand, the different position of the carboxylate group, however, may have a fundamental effect on the resulting structures. According to the latest literature, alkaline earth metal compounds based on tetrazole-carboxylate ligands are potential energetic materials but rarely investigated [6]. Therefore, investigations on such compounds will make sense both theoretically and practically. Furthermore, TGA and DSC tests demonstrate that the four polymers can be taken advantaged of as potential explosive materials. And the relevant thermal parameters  $\Delta S$ ,  $\Delta H$  and  $\Delta G$  of polymers **1-4** are calculated, as well.



Scheme Synthetic strategy for Hpytza and polymers 1-4

### 2. Results and discussions

### 2.1 General characterization of polymers 1-4

In this work, one nitrogen rich ligand 5-(4-pyridyl)tetrazole-2-acetic acid and its alkaline earth metal coordination polymers were prepared. In the IR curve of Hpytza, the asymmetric vibration of the carboxylate group appears in the usual region  $(1730 \text{ cm}^{-1})$ . Polymers 1-4, however, show the similar peak at the region of 1640 to 1604 cm<sup>-1</sup> (1640 cm<sup>-1</sup> for 1, 1635 cm<sup>-1</sup> for 2, 1604 cm<sup>-1</sup> for 3 and 1625 cm<sup>-1</sup> for 4), whose red shift may be explained by the coordination of the carboxylate group to the metal center (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>). Peaks at 3424 cm<sup>-1</sup> for 2, 3428 cm<sup>-1</sup> for 3 and 3417 cm<sup>-1</sup> for 4, respectively, are ascribed to the O-H vibration of either coordinated water or guest water molecules. Polymer 1, however, contains neither coordinated nor guest water molecules, so it does not show a similar peak. The characteristic peaks of the C=N of both the pyridine and tetrazole rings are at 1562-1386 cm<sup>-1</sup> for 1, 1563-1403 cm<sup>-1</sup> for 2, 1462-1389 cm<sup>-1</sup> for 3 and 1528-1385 cm<sup>-1</sup> for 4, respectively, which may overlap the peaks of the symmetric vibration of the carboxylate group.

### 2.2 Crystal structure of $[Mg(pytza)_2]_n(1)$

The X-ray diffraction reveals that polymer 1 crystallizes in monoclinic space group C2/c. As shown in Fig1a, each Mg(II) ion is in a distorted octahedral coordination arrangement surrounded by two nitrogen atoms from the tetrazolyl rings and four oxygen atoms from four carboxylate groups. The Mg-O bond lengths ranging from 2.068 to 2.070Å are in excellent agreement with those of the previously reported Mg(II) compounds[5, 7a-7e]. So are the Mg-N bond lengths (2.261Å). Each pytza acts as a tridentate ligand to bridge three Mg(II) centers via one nitrogen atom of the pyridine ring and the carboxylate group in a  $\mu_{1,3}$ -COO syn-syn mode. The structure can be simplified as a  $(3^6, 4^{16}, 5^6)$  tsi network topology (Fig1b). Compared with  $[Mg(H_2O)_6](a4-ptz)_2 \cdot 2H_2O$ , where a4-ptz=5-[N-acetato(4-pyridyl)]tetrazole, the isomer of 5-(4-pyridyl)tetrazole-2-acetato, the structure is substantially different since a4-ptz is uncoordinated to the Mg(II) center, instead, they are held together by hydrogen bonds. Therefore, the structure transforms a mononuclear to a three dimensional one. Two non-classic hydrogen bonds exist between the C-H group of the tetrazolyl ring and the oxygen atom of the carboxylate group  $[C(6)-H(6A)\cdots O$ (2), O(7)—H(7A)  $\cdots$ O(1)] to stabilize the supramolecular assembly (TableS2, Fig S1).



Fig1. (a)The coordination environment of  $Mg^{2+}$  in polymer 1. Hydrogen atoms are omitted for clarity; (b)The 3D structure of polymer 1.

### 2.3 Crystal structure of $[Ca(pytza)_2(H_2O)_2]_n \cdot 3nH_2O(2)$

Polymer 2 belongs to monoclinic space group C2/c and the asymmetric unit contains half of the molecule. As shown in Fig2a, each Ca(II) center is octa-coordinated by three oxygen atoms from three water molecules and six ones from four carboxylate groups. The Ca-O bond lengths the range of 2.393 to 2.666Å are in agreement with

those of the previously reported Ca(II) compounds[5,7a,7b,7d], so the coordination arrangement can be described as an irregular square anti-prism. Compared with  $[Ca(a4-ptz)_2(H_2O)_2]_n \cdot 2nH_2O$  whose 1D chain consists of the a4-ptz which acts as a monodentate ligand via one oxygen atom of the carboxylate group and the bridging water oxygen atom, there are two kinds of coordination modes of pytza: first, adjacent two Ca<sup>2+</sup> are tetra-bridged by two oxygen atom of two water molecules and four oxygen atom of two carboxylate groups in a  $\mu_{1,3}$ -COO *syn-syn* mode to form a binuclear unit; then neighboring binuclear units are doubly bridged by the carboxylate group in a  $\mu_{1,1,3}$ -COO mode to generate a 1D zigzag chain extending along the *b* axis with Ca…Ca distance of 3.8845(15)Å and Ca…Ca…Ca angle of 143.945(31)° (Fig2b). Adjacent chains are held together by hydrogen bonds to form a 3D network structure (Table S2, Fig S2).



Fig2. (a) The coordination environment of  $Ca^{2+}$  in polymer 2; (b)The 1D chain structure of polymer 2. Hydrogen atoms are omitted for clarity.

### 2.4 Crystal structure of $[Sr(pytza)_2(H_2O)_2]_n$ (3)

The X-ray reveals that the structure of polymer **3** resembles that of polymer **2** except that it contains neither uncoordinated water molecules. Polymer **3** also displays a 1D zigzag chain extending along the *b* axis with Sr…Sr distances of 4.0409 and 4.1825 Å and Sr…Sr angle of 143.295° (FigS3). The Sr…Sr distance is larger than that of Ca…Ca, this can be explained by the fact that the metal radius of Sr<sup>2+</sup> is larger than that of Ba<sup>2+</sup>. Compared with [Sr(a4-ptz)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>·2nH<sub>2</sub>O where a4-ptz adopts a monodentate mode, pytza acts as a bidentate or tridentate ligand via the carboxylate group in a  $\mu_{1,3}$ -COO *syn-syn* or  $\mu_{1,1,3}$ -COO mode similar to that of pytza in polymer **2** (FigS4). The Sr-O bond lengths ranging from 2.518 to 2.715Å are in good agreement with those of the previously reported Sr(II) compounds[5,7b,7c,7e]. Hydrogen bonds exist between the coordinated water and nitrogen atom as well as uncoordinated water molecules, by which neighboring 1D chains are held together to form a three dimensional network (TableS2, FigS5).

### 2.5 Crystal structure of $[Ba(pytza)_2(H_2O)_2]_n \cdot nH_2O$ (4)

Polymer **4** crystallizes in monoclinic space group *P*2<sub>1</sub>. As shown in Fig3, each Ba(II) center is octa-coordinated by three oxygen atoms from three water molecules, four oxygen atoms from four carboxylate groups of four pytza ligands and one nitrogen atom of the pyridyl ring, forming a distorted square antiprism coordination arrangement. The Ba-O bond lengths ranges from 2.741 to 2.861Å and that of Ba-N is 2.956Å, resembling those of the previously reported Ba(II) compounds[5,7a-7c,7e]. Compared with 1D [Ba<sub>4</sub>(a4-ptz)<sub>8</sub>(H<sub>2</sub>O)<sub>8</sub>]<sub>n</sub>·4nH<sub>2</sub>O, neighboring Ba(II) ions in polymer **4** are doubly bridged by one coordinated water and one oxygen atom of the carboxylate group in a  $\mu_{1,1}$ -COO mode to generate a 1D chain with Ba···Ba distance of 4.1511Å and Ba···Ba···Ba angle of 115.938°. Adjacent 1D chains are bridged by the tridentate pytza *via* one nitrogen atom of the pyridyl ring and the carboxylate group in a  $\mu_{1,3}$ -COO bridging mode to form a two dimensional layer extending along the *bc* plane(Fig4a). The 2D layer can be viewed as a (4,4) grid topology with

rhomboidal grids being 12.8688 and 16.4851Å, respectively (Fig4b). Adjacent 2D layers are held together by hydrogen bonds, leading to the formation of a 3D supramolecular network (TableS2, FigS6).



Fig3. The coordination environment of  $Ba^{2+}$  in polymer 4. Hydrogen atoms are omitted for clarity;



Fig4. (a)The 2D layer structure of compound 4; (b) The topology of polymer 4. Hydrogen atoms are omitted for clarity.

### 2.6 TG, DTG and DSC of Hpytza and polymers 1-4

To characterize Hpytza and polymers 1-4 in terms of thermal stability, the thermogravimetric analysis were performed from 30 to  $600^{\circ}$ C with the heating rate of  $10^{\circ}$ C·min<sup>-1</sup> under nitrogen atmosphere. As shown in Fig5, Hpytza began to decompose at 255°C and a strong exothermic peak from 262.8 to 268.2°C were observed. Polymers 1-3 began to decompose at 323, 313 and 297 respectively, leading to the collapse of the framework (Fig6). An initial mass loss of 8.85% of polymer 4 were observed, which can be ascribed to the removal of both coordinated and

uncoordinated water molecules (calculated 9.00%), further mass loss beginning at 266°C are ascribed to the decomposition of the framework structure. Drastic exothermic peaks from 326.2 to 339.1°C for polymer **1**, 316.9 to 317.4 °C for polymer **2**, 298.4 to 316.4 °C for polymer **3**, 299.8 to 315.1 °C for polymer **4** were shown in Fig7, however, one more endothermic peak from of polymer **4** was found. The comprehensive enthalpy of Hpytza and polymers **1**-**4** are calculated as -405.1, -570.1, -565.8, -467.8 and -420.4 J/g, respectively, indicating that these compounds are potential energetic materials.



Fig5. (a)The TG curves of Hpytza from 30 to  $600^{\circ}$ C with the heating rate of  $10^{\circ}$ C·min<sup>-1</sup>; (b)the DSC curves of polymers 1-4 from 30 to  $600^{\circ}$ C with the heating rate of  $10^{\circ}$ C·min<sup>-1</sup>.







Fig7. The DSC curves of polymers 1-4 from 30 to  $600^{\circ}$ C with the heating rate of  $10^{\circ}$ C·min<sup>-1</sup>; (a) for 1; (b) for 2; (c) for 3 and (d) for 4.

### 2.7 Non-isothermal kinetics of Hpytza and polymers 1-4

Tetrazole and its derivatives are nitrogen-rich compounds that can be used as potential energetic materials. To evaluate the energetic performance of Hpytza and polymers **1-4**, Kissinger's method [8] (equation1) and Ozawa's method [9] (equation2) were applied to understand the decomposition mechanism and calculate the apparent activation energy ( $E_a/kJ \cdot mol^{-1}$ ) and pre-exponential constant ( $A/s^{-1}$ ).

$$\ln(\beta/T_{p}^{2}) = \ln(RA/E_{a}) - E_{a}/(RT_{p})$$
(1)  
$$\lg\beta + 0.4567E_{a}/(RT_{p}) = C$$
(2)

Where  $T_p$  stands for the peak temperature (K); R represents the gas constant (8.314 J·mol<sup>-1</sup>·K<sup>-1</sup>);  $\beta$  is the linear heating rate (K·min<sup>-1</sup>); *C* is a constant. The peak temperature in the non-isothermal DSC curves are correspondent to the same conversion degrees at various heating rate.

The peak temperatures of Hpytza and polymers 1-4 with the linear heating rate of 5,

## 10, 15, 20 K $\cdot$ min<sup>-1</sup> are listed in Table 1.

Heating rate	5 K·min <sup>-1</sup>	10 K·min <sup>-1</sup>	15 K·min <sup>-1</sup>	20 K·min <sup>-1</sup>
compound	peak temperature			
Hpytza	533	541	546	550
1	594	604	609	613
2	584	592	597	600
3	570	578	583	586
4	568	575	582	584

Table 1 The peak temperature of Hpytza and polymers 1-4 with different heating rates

The apparent activation energy of Hpytza and polymers **1-4** calculated by Ozawa's method and Kissinger's method, the pre-exponential constant lnA and the Arrhenius equations [lnk=lnA-E/(RT)] are listed in Table **2**.

Table 2 The apparent activation energy of Hpytza and polymers 1-4 calculated by Kissinger's and Ozawa's methods and the Arrhenius equations

Compound	E <sub>k</sub> (kJ/mol)	E <sub>o</sub> (kJ/mol)	Arrhenius equation
Hpytza	190.75	189.94	lnk=42.15-190.34×10 <sup>3</sup> /(RT)
1	211.32	210.50	lnk=41.75-210.91×10 <sup>3</sup> /(RT)
2	252.58	249.50	lnk=51.17-251.04×10 <sup>3</sup> /(RT)
3	221.68	219.92	lnk=45.92-220.80×10 <sup>3</sup> /(RT)
4	210.63	209.32	lnk=43.68-209.98×10 <sup>3</sup> /(RT)

 $E_o(kJ \cdot mol^{-1})$ : the apparent activation energy obtained by Ozawa's method  $E_k(kJ \cdot mol^{-1})$ : the apparent activation energy obtained by Kissinger's method lnA (s<sup>-1</sup>): the pre-exponential constant in the Arrhenius equation

 $E \ (J \cdot mol^{\text{-1}})$  : the average value of  $E_k \ \text{and} \ E_o$ 

### 2.8 Critical temperature of thermal explosion of Hpytza and polymers 1-4

To discuss Hpytza and polymer 1 in terms of thermal safety, the critical temperature of thermal explosion  $(T_b)$  was calculated to obtain the lowest temperature to which a

## CCEPTED MANU

specific charge might be heated without undergoing thermal runaway. The following equations were used [10].

$$T_{pi} = T_{p0} + b\beta_i + c\beta_i^2$$
(3)  
$$T_{bp} = \{E_o - [E_o^2 - (4E_oRT_{p0})]^{1/2}\}/2R$$
(4)

The value of the peak temperatures of Hpytza and polymers 1-4 are 529, 592, 580, 569 and 568 K, respectively, when  $\beta \rightarrow 0$ , where b and c are coefficients. The corresponding critical temperatures of thermal explosion  $(T_{bp})$  of Hpytza and polymers 1-4 obtained from the above equations are 542, 607, and K, respectively, where R stands for the gas constant (8.314 J·mol<sup>-1</sup>·K<sup>-1</sup>),  $E_0$  represents the apparent activation energy calculated by Ozawa's method.

### 2.9 Thermodynamic parameters of Hpytza and polymers 1-4

The thermodynamic parameters of the decomposition of Hpytza and polymers 1-4 were calculated based on  $E_a$  and A. The entropy of activation ( $\Delta S$ ), enthalpy of activation ( $\Delta H$ ), and free energy of activation ( $\Delta G$ ) corresponding to T = T<sub>p0</sub>, E<sub>a</sub>=E<sub>K</sub>, and  $A = A_K$  obtained by the following equations [11-12].

> $A = (k_B T e^{\Delta S/R})/h$  $\Delta H = E_a - RT$  $\Delta G = \Delta H - T \Delta S$

Where  $k_B$  is the Boltzmann constant (1.3807×10<sup>-23</sup>J·K<sup>-1</sup>), and h is the Plank constant  $(6.626 \times 10^{-34} \text{ J} \cdot \text{s}^{-1})$ . These thermal parameters are listed in Table 3.

Compound	$\Delta S (J \cdot mol^{-1} \cdot K^{-1})$	ΔH (kJ/mol)	∆G (kJ/mol)
Hpytza	69.40	186.40	150.07
1	96.64	206.48	150.24
2	175.34	247.81	147.24
3	131.65	217.03	143.47
4	113.05	205.99	142.96

# 2.10 Discussion of the structure variation and the energetic performance of polymers 1-4

The work is the extension of our previous publication which reported four alkaline earth metal coordination compounds derived from 5-[N-acetato(4-pyridyl)]tetrazole (a4-ptz), the isomer of 5-(4-pyridyl)tetrazole-2-acetato[5]. The different position of the carboxylate group control the coordination modes of the ligands, thus leading to structural variation. In  $[Mg(H_2O)_6](a4-ptz)_2 \cdot 2H_2O$ , a4-ptz does not coordinated to Mg<sup>2+</sup>, instead, it plays the role of balancing the charge. In contrast, pytza acts as a tridentate bridging ligand via the nitrogen atom of the pyridine ring and the carboxylate group in a  $\mu_{1,3}$ -COO syn-syn mode; for  $[Ca(a4-ptz)_2(H_2O)_2]_n \cdot 2nH_2O$ , a4-ptz only acts as a monodentate ligand via the oxygen of the carboxylate group, but 4-pytza adopts both bidentate or tridentate in a  $\mu_{1,3}$ -COO or  $\mu_{1,1,3}$ -COO mode to form a 1D chain. However, the structure of  $[Ca(a4-ptz)_2(H_2O)_2]_n \cdot 2nH_2O$  is similar to that of  $[Sr(a4-ptz)_2(H_2O)_2]_n \cdot 2nH_2O$  while  $[Ca(pytza)_2(H_2O)_2]_n \cdot 3nH_2O$  also resembles  $[Ca(pytza)_2(H_2O)_2]_n$ ; last but not least,  $[Ba_4(a4-ptz)_8(H_2O)_8]_n \cdot 4nH_2O$  is a one dimensional chain while  $[Ba(pytza)_2(H_2O)_2]_n \cdot nH_2O$  is a two dimensional layer with (4,4) topology. It is worthwhile to point out that the pyridine-N atoms of pytza participate in the coordination to Ba<sup>2+</sup>, however, all the nitrogen atoms of a4-ptz are uncoordinated.

From the TGA, we can see that the four polymers are more stable than Hpytza, this can be explained by the coordination of the ligand to the metal center. However, polymers 1-4 tend to show less stability gradually (decomposition temperature from 323, 313, 297 to 266 °C), which is probably assigned to the larger bond length of the coordination bonds (Table 4). Polymer 1 contains neither coordinated nor uncoordinated water molecules, it only shows an exothermic peak. Polymer 2 only exhibits an endothermic peak since the loss of the uncoordinated water molecules begins at low temperature, indicating the weak interaction between the guest water molecules and the one dimensional chain. Polymer 3, however, also shows one exothermic peak since the hydrogen bonding interactions between the coordinated water molecules and the pytza ligands are strong and diverse. Polymer 4 shows both

exothermic and endothermic peaks because the loss of one uncoordinated water molecule is an exothermic process while the decomposition of the ligand is an exothermic one. For Hpytza and polymers **1-4**, the apparent activation energy obtained by Kissinger's method are similar to those of obtained by Ozawa's method. The comprehensive enthalpy of the decomposition process of polymers **1-4** are larger than Hpytza, which can be explained by the fact that the energy of the coordination bond is large. The results demonstrates that energetic performance of the coordination polymers are superior to that of Hpytza.

### **3.**Experimental section

### 3.1 Synthesis and characterization of 5-(4-pyridyl)tetrazole-2-acetic acid

5-(4-pyridyl) tetrazole (Hpytz) was prepared by [2+3] cycloaddition reactions, by treating 4-cyanopyridine with  $NaN_3$  in toluene in the presence of triethylammonium chloride. A mixture of ethyl bromoacetate (12.53 g, 0.075 mol), Hpytz (7.35 g, 0.05 mol), and potassium hydroxide (5.61 g, 0.10 mol) in methanol/  $H_2O$  (5:1) was refluxed 24 hour at 70 °C. After cooling to room temperature, the precipitate was filtered off, washed with 2×30 mL methanol and dried to give mostly H(tetrazole)-substituted products 5-(4-pyridyl)tetrazole-2-acetato potassium salt. Then HCl (12M) added, concentrated was forming the precipitate 5-(4-pyridyl)tetrazole-2-acetic acid. The precipitate was washed with distilled water and then dried. Yield: 67% based on Hpytz. <sup>1</sup>HNMR (DMSO- $d_6$ ,  $\delta ppm$ ):5.81(2H, -CH<sub>2</sub>), 8.01(2H,=CH), 8.81(2H,=CH), 11.95(1H, COO-); <sup>13</sup>CNMR (DMSO-*d*<sub>6</sub>, δppm): 54.39, 78.97, 120.91, 134.55, 151.33, 162.83. Anal. Calcd for C<sub>8</sub>H<sub>7</sub>N<sub>5</sub>O<sub>2</sub>: C: 46.83, H: 3.44, N: 34.13%; Found: C: 46.65, H: 3.54, N: 34.68%; IR (KBr, cm<sup>-1</sup>): 3426(m), 1730(s), 1449(m), 1420(m), 1396(m), 1257(s), 906(m), 868(m).

### 3.2 Synthesis of $[Mg(pytza)_2]_n(1)$

Hpytza (0.0205g, 0.1mmol) was dissloved in 1 mL distilled water and the pH value was adjusted to 5 with KOH (0.2M), then ethanol (5 mL) and Mg(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$ 

(0.0256 g, 0.1 mmol) were added. The solution was sealed in a 25 mL telfon stainless steel and heated at 120°C for 48h. After cooling to room temperature, light yellow block crystals were obtained. Yield: 45% based on Mg<sup>2+</sup>. Anal. Calcd for C<sub>16</sub>H<sub>12</sub>MgN<sub>10</sub>O<sub>4</sub>: C, 44.42; H, 2.80; N, 32.38%. Found: C, 44.25; H, 2.88; N, 32.33%. IR (KBr, cm<sup>-1</sup>): 1687(w), 1640(s), 1562(w), 1458(w), 1429(m), 1386(s), 1299(w), 1220 (w), 1124(w), 1056(w), 1009(w), 823(w), 755(w), 724(m), 685(m).

### 3.3 Synthesis of $[Ca(pytza)_2(H_2O)_2]_n \cdot 3nH_2O(2)$

A similar method to that of polymer **1** was adopted to prepare polymer **2** except that the solvent was changed to a mixture of distilled water (1mL) and ethanol (3mL). Yield: 40% based on Ca<sup>2+</sup>. Anal. Calcd for C<sub>16</sub>H<sub>22</sub>CaN<sub>10</sub>O<sub>9</sub>: C, 35.69; H, 4.12; N, 26.01%. Found: C, 35.25; H, 4.18; N, 26.33%. IR (KBr, cm<sup>-1</sup>): 3424(m), 1635(s), 1563(w), 1457(w), 1426(s), 1403(s), 1307(w), 1291(w), 1217(w), 1052(w), 1007(w), 826(m), 752(w), 722(m), 677(m).

### 3.4 Synthesis of $[Sr(pytza)_2(H_2O)_2]_n$ (3) and $[Ba(pytza)_2(H_2O)_2]_n \cdot nH_2O(4)$

Similar methods to that of polymer **2** were adopted to prepare polymers **3** and **4** except that the solvent was changed to a mixture of distilled water (4mL) and ethanol (1mL). For **3**, yield: 42% based on  $Sr^{2+}$ . Anal. Calcd for  $C_{16}H_{16}SrN_{10}O_6$ : C, 36.12; H, 3.03; N, 26.33%. Found: C, 36.25; H, 3.08; N, 26.52%. IR (KBr, cm<sup>-1</sup>): 3428(m), 1604(s), 1462(w), 1429(m), 1389(s), 1313(w), 1222(m), 1206 (w), 1013(w), 846(w), 823(m), 729(s), 683(w). For **4**, yield: 40% based on Ba<sup>2+</sup>. Anal. Calcd for  $C_{16}H_{18}BaN_{10}O_7$ : C, 32.04; H,3.03; N, 23.36%. Found: C, 32.25; H, 3.12; N, 23.23%. IR (KBr, cm<sup>-1</sup>): 3417(m), 1625(s), 1528(w), 1459(w), 1425(m), 1385(s), 1307(m), 1212 (w), 1127(w), 1050(w), 1000(w), 836(m), 752(w), 723(m), 683(w).

### 3.5 X-Ray crystallography

Single crystal X-ray crystal data were collected on a Rigaku SCX mini CCD diffractometer equipped with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The intensity data were collected by the  $\omega$  scan technique and were reduced using

the Crystal-Clear program [13], and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined on F<sup>2</sup> by full matrix least squares using SHELXTL [14]. All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they were bonded. Selected bond lengths and angles are listed in Table **4**. Crystallographic data are summarized in Table **S1**. Hydrogen-bonding parameters are given in Table **S2**. Polymers **1-4** are deposited with CCDC number 1426716-1426719.

Table 4. Selected bond distances (Å) and angles (°) for polymers 1-4

$[Mg(pytza)_2]_n(1)$			
Mg(1)-O(1)	2.070(3)	Mg(1)-O(2)	2.068(3)
Mg(1)-N(5)	2.261(3)		
O(1)–Mg (1)–O(1A)	90.35(15)	O(1)-Mg(1)-O(2C)	179.70(11)
O(1A)-Mg (1)-O(2C)	89.89(9)	O(2C)-Mg (1)-O(2B)	89.87(15)
O(1)-Mg (1)-N(5D)	94.99(11)	O(1A)-Mg (1)-N(5E)	88.68(10)
O(2C)-Mg (1)-N(5D)	84.84(11)	O(2B)-Mg (1)-N(5D)	91.48(11)
N(5D)-Mg (1)-N(5E)	174.80(18)		

[Ca(	pytza	$l)_2(H)$	$_{2}O)_{2}]_{n}$	$\cdot 3nH_2O$	(2)
	( '				

Ca(1)–O(3B)	2.393(4)	Ca(1)–O(2)	2.428(4)
Ca(1)–O(1A)	2.426(4)	Ca(1)–O(6)	2.437(4)
Ca(1)–O(5)	2.445 (4)	Ca(1)–O(4)	2.505(4)
Ca(1)–O(5A)	2.561 (4)	Ca(1)–O(3)	2.666(4)
O(3B)-Ca(1)-O(1A)	123.58 (14)	O(3B)-Ca(1)-O(2)	79.89(13)
O(1A)-Ca(1)-O(2)	140.45(13)	O(3B)-Ca(1)-O(6)	72.10(13)
O(1A)-Ca(1)-O(6)	71.27(14)	O(2)-Ca(1)-O(6)	147.35(13)
O(3B)–Ca(1)–O(5)	85.04(13)	O(1A)-Ca(1)-O(5)	74.84(13)

O(2)–Ca(1)–O(5)	76.50(13)	O(6)–Ca(1)–O(5)	116.43(13)
O(3B)-Ca(1)-O(4)	121.33 (14)	O(1A)-Ca(1)-O(4)	96.38(14)
O(2)-Ca(1)-O(4)	95.79(14)	O(5A)-Ca(1)-O(5)	78.24(13)
O(5)-Ca(1)-O(4)	151.25(13)	O(3B)-Ca(1)-O(5A)	150.19(12)
O(1A)-Ca(1)-O(5A)	75.57(12)	O(2A)–Ca(1)–O(5)	72.34(12)
O(6A)-Ca(1)-O(5)	137.59(13)	O(6)-Ca(1)-O(4)	85.04(14)
O(4A)-Ca(1)-O(5)	73.04(13)	O(3B)-Ca(1)-O(3)	71.72(14)
O(6A)-Ca(1)-O(5)	137.59 (13)	O(5A)–Ca(1)–O(5)	78.24(13)
O(4A)-Ca(1)-O(5)	73.04(13)	O(3B)–Ca(1)–O(3)	71.72(14)
O(1A)-Ca(1)-O(3)	136.29(13)	O(2)–Ca(1)–O(3)	78.16(12)
O(6)-Ca(1)-O(3)	77.40(13)	O(5)–Ca(1)–O(3)	148.14(12)
O(4)-Ca(1)-O(3)	50.51(12)	O(5A)-Ca(1)-O(3)	111.81(12)
$[Sr(pytza)_2(H_2O)_2]_n$ (3)		X	

$[Sr(pytza)_2(H_2O)_2]_n$ (3)			
Sr(1)–O(5A)	2.608(2)	Sr(1)–O(3)	2.518(2)
Sr(1)–O(3B)	2.715(3)	Sr(1)–O(2A)	2.542(3)
Sr(1)–O(6)	2.570(3)	Sr(1)–O(1)	2.582(3)
Sr(1)–O(4)	2.643(3)	Sr(1)–O(5)	2.6718(24)
O(3B)–Sr(1)–O(2A)	123.34(9)	O(3B)-Sr(1)-O(6)	71.66(8)
O(3B)–Sr(1)–O(6)	72.64(9)	O(3B)–Sr(1)–O(1)	79.73(9)
O(2A)-Sr(1)-O(1)	138.91(9)	O(6)–Sr(1)–O(1)	147.11(8)
O(3B)–Sr(1)–O(5A)	84.12(8)	O(2A)-Sr(1)-O(5A)	74.62(8)
O(6)-Sr(1)-O(5A)	116.79(8)	O(1)-Sr(1)-O(5A)	74.91(8)
O(3B)–Sr(1)–O(4)	121.07(9)	O(2A)-Sr(1)-O(4)	95.31(9)
O(6)-Sr(1)-O(4)	81.97(9)	O(1)–Sr(1)–O(4)	99.84(9)
O(5A)–Sr(1)–O(4)	153.45(8)	O(3B)–Sr(1)–O(3)	73.96(8)
O(2A)–Sr(1)–O(3)	136.23(8)	O(6)-Sr(1)-O(3)	77.39(9)
O(1)-Sr(1)-O(3)	79.42(8)	O(5A)–Sr(1)–O(3)	148.76(7)
O(4)-Sr(1)-O(3)	48.87(8)		

$[Ba(pytza)_2(H_2O)_2]_n \cdot nH_2O(4)$			
Ba(1)–O(1)	2.741(2)	Ba(1)–O(6B)	2.7474(19)
Ba(1)-O(4A)	2.807(3)	Ba(1)–O(2B)	2.8278(19)
Ba(1)–O(4)	2.840(3)	Ba(1)–O(6)	2.850(2)
Ba(1)–O(5)	2.861(2)	Ba(1)–N(5C)	2.956(3)
O(1)-Ba(1)-O(6B)	145.27(7)	O(1)-Ba(1)-O(4A)	69.39(7)
O(6B)-Ba(1)-O(4A)	84.52(7)	O(1)-Ba(1)-O(2B)	111.43(6)
O(6B)-Ba(1)-O(2B)	74.10(6)	O(4A)-Ba(1)-O(2B)	63.73(7)
O(1)-Ba(1)-O(4)	130.10(7)	O(6B)–Ba(1)–O(4)	84.45(6)
O(4A)-Ba(1)-O(4)	132.82(4)	O(2B)-Ba(1)-O(4)	69.12(7)
O(1)-Ba(1)-O(6)	67.18(6)	O(6B)-Ba(1)-O(6)	133.64(2)
O(4A)-Ba(1)-O(6)	83.19(6)	O(2B)–Ba(1)–O(6)	60.38(6)
O(4)-Ba(1)-O(6)	72.22(7)	O(1)-Ba(1)-O(5)	77.49(8)
O(6B)-Ba(1)-O(5)	74.55(7)	O(4A)-Ba(1)-O(5)	77.12(7)
O(2B)-Ba(1)-O(5)	131.36(7)	O(4)-Ba(1)-O(5)	141.83(7)
O(6)-Ba(1)-O(5)	143.80(7)	O(1)-Ba(1)-N(5C)	68.02(7)
O(6B)-Ba(1)-N(5C)	131.70(7)	O(4A)-Ba(1)-N(5C)	137.27(7)
O(2B)–Ba(1)–N(5C)	137.92(7)	O(4)-Ba(1)-N(5C)	80.06(7)
O(6)-Ba(1)-N(5C)	83.71(6)	O(5)-Ba(1)-N(5C)	90.47(8)

Symmetry code: For 1: A:-x,y,0.5-z; B: -x.1-y,-z; C: x,1-y,0.5+z; D: 0.5-x,0.5+y,0.5-z; E: -0.5+x, 0.5+y, z; For 2: A: -x, 1-y, 1-z; B: -x, 2-y, 1-z; For 3: A: 2-x, 2-y, 1-z; B: 2-x, 1-y, 1-z; For 4: A: 2-x, -0.5+y, 1-z; B: 2-x, 0.5+y, 1-z; C: 2-x, 0.5+y, -z.

### 4. Conclusions

In summary, Hpytza and its four alkaline earth metal compounds have been reported for the first time. It is worthwhile to point out that the position of the carboxylate group has a substantial effect on the crystal structures of such compounds, compared with the compounds based on 5-[N-acetato(4-pyridyl)tetrazole]. In addition, the four polymers show blue light emission at room temperature in the solid state. Our

research results show that the energetic performance of the polymers are closely related to the structures of the polymers and the coordination of the metal ions may enhance the energetic performance of the such compounds. The four polymers may be used as potential energetic materials.

### Acknowledgment

The authors acknowledge financial support from the Natural Science Foundation of Ji

angsu Province (Grant No. BK2012210), the Natural Science Foundation of the Jiang

su Higher Education Institutions of China

(Grant No.10KJB430001) and the Opening Fund of Jiangsu Key Laboratory of Advan

ced Functional Materials (Grant No.12KFJJ010).

### **Caption list**

Table **S1** Selected crystallographic data and structure refinement for polymers **1-4**. Table **S2** Hydrogen parameters for polymers **1-4** 

Fig.S1 The coordination environment of  $Sr^{2+}$  in polymer 3. Hydrogen atoms are omitted for clarity.

Fig.S2 The The 1D chain structure of polymer 3. Hydrogen atoms are omitted for clarity.

Fig.S3 The 3D network structure of polymer 2 formed via hydrogen bonds.

Fig.S4 The 3D network structure of polymer 3 formed via hydrogen bonds.

Fig.**S5** The 3D network structure of polymer **4** formed via hydrogen bonds.

### References

[1](a)Y.H. Joo, H.X. Gao, D.A. Parrish, S.G. Cho, E.M. Goh, J.M. Shreeve, J.

Mater. Chem., 22 (2012) 6123-6130;

(b)L. Liu, Y.Q. Zhang, Z.M. Li, S.J. Zhang, J. Mater. Chem. A., 3 (2015) 14768-14778;

(c)R.H. Wang, Y. Guo, Z. Zeng, B. Twamley, J.M. Shreeve., *Chem. Eur. J.*, 15 (2009) 2625-2634;

(d)T.M. Klapötke, D.G. Piercey, Inorg. Chem., 50 (2011) 2732-2734;

(e) Y.C. Li, C. Qi, S.H. Li, H.J. Zhang, C.H. Sun, Y.Z. Yu, S.P. Pang, J. Am. Chem.

Soc., 132 (2010) 12172-12173.

[2]Singh, G; Prem Felix, S. J. Hazard. Mater., A90, (2002) 1.

[3](a)B.D. Wu, G.T. Zhang, T.L. Zhang, L.Yang, J.G. Zhang, Z.N. Zhou, K.B. Yu, *Chinese J. Struct. Chem.*, 30 (2011) 431-437;

(b)Z.M. Li, T.L. Zhang, G.T. Zhang, Z.N. Zhou, L. Yang, J.G. Zhang, K.B. Yu, J. Coord. Chem., 66 (2013) 1276-1286;

[4](a) M. Wriedt, A.A. Yakovenko, G.J. Halder, A.V. Prosvirin, Kim R. MDunbar, H.C. Zhou, *J. Am. Chem. Soc.*, 135 (2013) 4040-4050;

(b)M. Wriedt, J.P. Sculley, A.A. Yakovenko, Y.G Ma, G. J. Halder, P.B. Balbuena, H.C. Zhou, *Angew. Chem. Int. Ed.*, 51 (2012) 9804-9808;

(c)Z.M. Li, G.T. Zhang, T.L. Zhang, J.G. Zhang, L. Yang, Z.N. Zhou, S.Y. Qi, K.B. Yu,

F.Q. Zhao, J.H. Yi, S.Y. Xu, H.X. Gao, Acta Chim. Sinica., 69 (2011) 10, 1253-1258;

(d)G.W. Yang, F.F. Zhang, Q. Wu, M.J. Cao, Y. Bai, Q.Y. Li, B. Wei, J.H. Zou, *RSC Adv.*, 5 (2015) 84439-84445;

(e) D.Y. Chen, J.H. Zou, W.X. Li, B. Xu, Q.Y. Li, G.W. Yang, J. Wang, Y.M. Ding, Y. Zhang, X.F. Shen, *Inorg. Chem. Comm.*, 40 (2014) 35-38;

(f)M.F. Wu, Z.F. Liu, S.H. Wang, J. Chen, G. Xu, F.K. Zheng, G.C. Guo, J.S. Huang, *CrystEngComm.*, 13 (2011) 6386;

(g) J.H. Zou, D.L. Zhu, F.F. Li, F.S. Li, H. Wu, Q.Y. Li, G.W. Yang, P. Zhang, Y.X.Miao, J. Xie, Z. Anorg. Allg. Chem., 640 (2014) 2226-2231;

(h)J.H. Zou, D.Y. Chen, G.W. Yang, Q.Y. Li, J. Yang, L. Shen, *RSC Adv.*, 5 (2015) 27887-27890;

(i)G. Aromi, L.A. Barrios, Ol. Roubeau, P. Gamez, *Coord. Chem. Rev.*, 255 (2011) 485-546;

(j)S.H. Wang, F.K. Zheng, M.J. Zhang, Z.F. Liu, J. Chen, Y. Xiao, A.Q. Wu, G.C. Guo, J.S. Huang, *Inorg. Chem.*, 52 (2013) 10096-10104;

(k)J. Chen, S.H. Wang, Z.F. Liu, M.F. Wu, Y. Xiao, F.K. Zheng, G.C. Guo, J.S. Huang, *New J. Chem.*, 38 (2014) 269-276

(1)A. Karmakar, G.M.D.M. Rubio, M.F.C. GuedesdaSilva, S. Hazra, A.J.L. Pombeiro, *Cryst. Growth Des.*, 15(9) (2015) 4185-4197

(m)D.S. Liu, Y. Sui, W.T. Chen, P.Y. Feng, Cryst. Growth Des., 15(8) (2015) 4020-4025.

[5]Y. Zhou, G.W. Yang, Q.Y. Li, K. Liu, G.Q. Gu, Y.S. Ma, R.X. Yuan, *Inorg. Chim. Acta.*, 362 (2009) 1723-1729.

[6](a)H.S. Huang, Z.M. Li, G.T. Zhang, T.L. Zhang, S.T. Zhang, L. Yang, J.G. Zhang, Z.N. Zhou, *Main Group Chem.*, 12 (2013) 197-208;

(b) Z.M. Li, T.L. Zhang, L. Yang, Z.N. Zhou, J.G. Zhang, *J. Coord. Chem.*, 65 (2012) 143-155.

[7](a)J. Yang, Q.Y. Li, L. Shen, G.W. Yang, X.Y. Tang, C. Zhai, H.D. Ding, J.N. Jin, W. Shen, *J Chem Crystallogr.*, 41 (2011) 1483-1489;

(b)G.W. Yang, B.J. Wang, Z.T. Shen, Q.Y. Li, C. Ji, X.F. Shen, M.H. He, *J. Coord. Chem.*, 65 (2012) 2657-2670;

(c)Q.Y. Li, G.W. Yang, L. Shen, M.H. He, W. Shen, K. Gu, J.N. Jin, Z. Anorg. Allg. Chem., 638 (2012) 826-831;

(d)B. J. Wang, J. H. Zou, W. X. Li, Z. Wang, B. Xu, S. Li, Y.S. Zhai, D. L. Zhu, Q. Y. Li, G. W. Yang, *J. Organomet. Chem.*, 749 (2014) 428-432

(e)J.H. Zou, H.J. Cui, B. Xu, D.L. Zhu, Q.Y. Li, G.W. Yang, Y.C. Hua, *Inorg. Chim.* Acta., 423 (2014) 430–434

[8]H.E. Kissinger, Anal. Chem., 19 (1957) 1702-1706.

[9](a)T. Ozawa, Bull. Chem. Soc. Jpn., 38(1965), 1881-1886;

(b)J.H. Flynn and L.A. Wall, J Polym Sci, Part B: Polym. Phys., 4 (1966) 323-328.

[10]T.L. Zhang, R.Z. Hu, Y. Xue, F.P. Li, *Thermochim Acta.*, 244 (1994) 171-175.

[11] R.Z. Hu, S.P. Chen, S.L. Gao, F.Q. Zhao, Y. Luo, H.X. Gao, Q.Z. Shi, H.A. Zhao,

P. Yao, J. Li, J. Hazard. Mater., 117 (2005) 103-110.

[12] J.H. Yi, F.Q. Zhao, B.Z. Wang, Q. Liu, C. Zhou, R.Z. Hu, Y.H. Ren, S.Y. Xu, K.Z.Xu, X.N. Ren, *J. Hazard. Mater.*, 181 (2010) 432-439.

[13] Rigaku CrystalClear. Rigaku Corporation, Tokyo, Japan, (2005).

[14] G.M. Sheldrick, Acta. Cryst. A64 (2008) 112.

# Nitrogen-rich 5-(4-pyridyl)tetrazole-2-acetic acid and its alkaline

earth metal coordination polymers for high performance

### energetic materials

Gao Wen Yang, Yuan Ting Zhang, Qi Wu, Meng Jie Cao, Jiao Wu, Qiu Yan Yue, Qiao Yun Li\*

\*Qiao-Yun Li: Tel: +86-512-52251842; Fax: +86-512-52251842

Email: liqiaoyun61@126.com

Jiangsu Laboratory of Advanced Functional Material, Department of Chemistry and Material Engineering, Changshu Institute of Technology, Changshu 215500, Jiangsu, P. R. China

5-(4-pyridyl)tetrazole-2-acetic acid and its four alkaline earth metal compounds were prepared. The structural variation was assigned to not only the isomer, but also the radius of the metal ion. These coordination compounds are superior to the ligand in terms of thermal stability and energetic performance.



Corresponding author. Tel.: +86-18762987673; fax: +86-52251842 E-mail address: Qiao Yun Li <u>(liqiaoyun61@126.com)</u> Jian Hua <u>Zou(zoujh93@126.com)</u>