



# Dihydrogen phosphate-water tape and layers vs dihydrogen phosphate layers tuned by hydrophobic isomeric pyridine-diamine functionalized molecules



Jing Huang, Tong-Peng Liu, Li-Hua Huo, Zhao-Peng Deng<sup>\*\*</sup>, Shan Gao<sup>\*</sup>

Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, People's Republic of China

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## ABSTRACT

Assembly of six isomeric pyridine-diamine-based molecules, *N,N'*-bis(pyridin-4-ylmethyl)ethane-1,2-diamine (M1), *N,N'*-bis(pyridin-3-ylmethyl)ethane-1,2-diamine (M2), *N,N'*-bis(pyridin-2-ylmethyl)ethane-1,2-diamine (M3), *N,N'*-bis(pyridin-4-ylmethyl)propane-1,3-diamine (M4), *N,N'*-bis(pyridin-3-ylmethyl)propane-1,2-diamine (M5), and *N,N'*-bis(pyridin-2-ylmethyl)propane-1,3-diamine (M6), with phosphoric acid ( $\text{H}_3\text{PO}_4$ ) in different ratio (1:2 and 1:4), leads to the formation of nine salts,  $\text{H}_2\text{M}^{2+} \cdot 2\text{H}_2\text{PO}_4^- \cdot 4\text{H}_2\text{O}$  (1),  $\text{H}_2\text{M}^{2+} \cdot 2\text{H}_2\text{PO}_4^- \cdot 2\text{H}_2\text{O}$  (2),  $\text{H}_2\text{M}^{3^{2+}} \cdot 2\text{H}_2\text{PO}_4^- \cdot 2\text{H}_2\text{O}$  (3),  $\text{H}_4\text{M}^{4+} \cdot 4\text{H}_2\text{PO}_4^-$  (4),  $\text{H}_4\text{M}^{2^{4+}} \cdot 4\text{H}_2\text{PO}_4^-$  (5),  $\text{H}_4\text{M}^{3^{4+}} \cdot 4\text{H}_2\text{PO}_4^-$  (6),  $\text{H}_2\text{M}^{4^{2+}} \cdot 2\text{H}_2\text{PO}_4^- \cdot 3\text{H}_2\text{O}$  (7),  $2\text{H}_2\text{M}^{5^{2+}} \cdot 4\text{H}_2\text{PO}_4^- \cdot 2\text{H}_3\text{PO}_4$  (8), and  $\text{H}_2\text{M}^{6^{2+}} \cdot 2\text{H}_2\text{PO}_4^-$  (9), which have been characterized by elemental analysis, IR, TG, PL, powder and single-crystal X-ray diffraction. Structural analyses indicate that hydrogen-bonding patterns of  $\text{H}_2\text{PO}_4^-$  anions, conformation of protonated cations can effectively influence the supramolecular architectures through diverse non-covalent interactions. Hydrated salts 1–3 and 7 present 2D and 3D host-guest supramolecular networks, in which the connection of  $\text{H}_2\text{PO}_4^-$  anions and water molecules generates diverse tape and layer motifs.  $\text{H}_2\text{PO}_4^-$  anions in anhydrous salts 4–6 interconnect with each other through hydrogen bonds to form two types of layers, which are joined by discrete  $\text{H}_4\text{M}^{4+}$  cations into 3D inorganic-organic hybrid supramolecular networks. Salts 8–9 also present 2D and 3D host-guest supramolecular networks where the interconnection of  $\text{H}_2\text{PO}_4^-$  anions and its combination with  $\text{H}_3\text{PO}_4$  molecules leads to diverse layers. Luminescent analyses indicate that salts 1–9 exhibit violet and blue emission maximum in the range of 390–467 nm at room temperature.

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## 1. Introduction

Recognition of anion, initiated by Shriver and Biallas [1] as well as by Park and Simmons [2] in the late 1960s, has blossomed [3] until the 1990s and particularly the last 10 years. Worldwide chemists make their great efforts to tackle the challenges inherent in binding anions, inspired by the fundamental and vital roles of ubiquitous anions in the fields of chemistry, medicine, biology and environmental issues [3–7]. Among various anions, the recognition of tetrahedral anions, especially phosphate, is more attractive due to its occurrence in natural and biological environments and

several roles in biological systems [8]. Meanwhile, the phosphate anions generally observed are the acidic ones  $\text{HPO}_4^{2-}$  or  $\text{H}_2\text{PO}_4^-$ . Such anions interconnect with each other through strong hydrogen bonds in order to build fascinating supramolecular networks with various geometries, such as chains, ribbons, two-dimensional layers and three-dimensional networks [9]. Up to now, molecules for recognition of phosphate ions involve amine [10], amide [11], urea [12], thiourea [13], pyrrole [14], imidazole [15], pyridine/pyridinium and metal assisted organic frameworks [16] bearing multiple binding sites. Among them, our interests are mainly focused on pyridine and pyridinium heterocycles, which are frequently utilized in recognition of anion for their rigidity and influence the binding of anions. In contrast to the rigid pyridine and pyridinium-based molecules [17], the ones bearing flexible spacer are rarely reported. In 2014 [18], Hoque and co-workers reported a pyridine-urea-based molecule, (1*E*,4*E*)-5-(pyridin-2-ylmethyl)-1-(pyridin-2-

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [dengzhaopeng@hju.edu.cn](mailto:dengzhaopeng@hju.edu.cn) (Z.-P. Deng), [shangao67@yahoo.com](mailto:shangao67@yahoo.com) (S. Gao).

ylmethylene)carbazone, which stabilizes dihydrogen phosphate-water trimer ( $\text{H}_2\text{PO}_4)_2\text{-H}_2\text{O}]_n^{2-}$  within its hydrophobic environment upon protonation. Owing to the weakly alkalinity of urea ( $Pk_b$ , 13.82), only the pyridyl N atoms are protonated. Meantime, the recognition of dihydrogen phosphate partially depends on the formation of  $\text{C-H}\cdots\text{O}$  hydrogen bonds which are weaker than traditional  $\text{O/N-H}\cdots\text{O}$  hydrogen bonds. In this sense, exploiting new molecules for recognition of phosphate ions through strong hydrogen bonds is still an important work.

In our previous work [19], we designed and synthesized three isomeric pyridine-ethylenediamine functionalized molecules with symmetrical  $-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-$  spacer, *N,N'*-bis(pyridin-4-ylmethyl)ethane-1,2-diamine (M1), *N,N'*-bis(pyridin-3-ylmethyl)ethane-1,2-diamine (M2), and *N,N'*-bis(pyridin-2-ylmethyl)ethane-1,2-diamine (M3) (Scheme 1), which show good recognition for chlorate, nitrate, and perchlorate anions. More importantly, they present the unique feature that the ethylenediamine unit and the pyridine unit have different alkalinity ( $Pk_{b1}$  of ethylenediamine, 4.07;  $Pk_b$  of pyridine, 8.80) and can be protonated gradually through the addition of inorganic acid, which are then beneficial to modulate the structures and properties of salts. To the tetrahedral perchlorate, its binding with doubly and quadruply protonated cations can result in different inorganic-organic hybrid and host-guest supramolecular networks [19]. In this sense, the other three isomeric pyridine-propylene diamine functionalized molecules we have reported [20], *N,N'*-bis(pyridin-4-ylmethyl)propane-1,3-diamine (M4), *N,N'*-bis(pyridin-3-ylmethyl)propane-1,2-diamine (M5), and *N,N'*-bis(pyridin-2-ylmethyl)propane-1,3-diamine (M6), can also play potential role for recognition of inorganic anions ( $Pk_{b1}$  of 1,3-propylene diamine, 3.53). Therefore, as our continuing study on the recognition of anion, we reported here the structures and properties of nine salts, namely,  $\text{H}_2\text{M1}^{2+}\cdot 2\text{H}_2\text{PO}_4^- \cdot 4\text{H}_2\text{O}$  (1),  $\text{H}_2\text{M2}^{2+}\cdot 2\text{H}_2\text{PO}_4^- \cdot 2\text{H}_2\text{O}$  (2),  $\text{H}_2\text{M3}^{2+}\cdot 2\text{H}_2\text{PO}_4^- \cdot 2\text{H}_2\text{O}$  (3),  $\text{H}_4\text{M1}^{4+}\cdot 4\text{H}_2\text{PO}_4^-$  (4),  $\text{H}_4\text{M2}^{4+}\cdot 4\text{H}_2\text{PO}_4^-$  (5),  $\text{H}_4\text{M3}^{4+}\cdot 4\text{H}_2\text{PO}_4^-$  (6),  $\text{H}_2\text{M4}^{2+}\cdot 2\text{H}_2\text{PO}_4^- \cdot 3\text{H}_2\text{O}$  (7),  $2\text{H}_2\text{M5}^{2+}\cdot 4\text{H}_2\text{PO}_4^- \cdot 2\text{H}_3\text{PO}_4$  (8), and  $\text{H}_2\text{M6}^{2+}\cdot 2\text{H}_2\text{PO}_4^-$  (9), which assemble from the above six molecules and phosphoric acid ( $\text{H}_3\text{PO}_4$ ) in different 1:2 and 1:4 ratio. The hydrogen-bonding patterns of  $\text{H}_2\text{PO}_4^-$  anions and conformations of the protonated molecules effectively influence the supramolecular architectures of the nine salts. Hydrated salts 1–3, 7 and anhydrous salts 8, 9 present 2D and 3D host-guest supramolecular networks while anhydrous salts 4–6 present 3D inorganic-organic hybrid supramolecular networks. The  $\text{H}_2\text{PO}_4^-$  anions in these nine salts take part in the

formation of diverse tape, double, sandwiched, (6,3), (4,4),  $\text{V}_2\text{O}_5$ -type and  $(6^3)_2(6^6)$  layer motifs through different hydrogen-bonding patterns. Moreover, elemental analysis, IR, TG, PXRD and luminescent properties for all the nine salts have also been performed.

## 2. Experimental

### 2.1. Materials and methods

All chemicals were of A. R. grade and used without further purification in the syntheses. Molecules M1-M6 were synthesized according to the previous reported method [19]. Elemental analyses were carried out with a Vario MICRO from Elementar Analysensysteme GmbH, and the infrared spectra (IR) were recorded from KBr pellets in the range of  $4000\text{--}400\text{ cm}^{-1}$  on a Bruker Equinox 55 FT-IR spectrometer. Powder X-ray diffraction (PXRD) patterns for the three complexes were measured at 293 K on a Bruker D8 diffractometer (Cu  $K\alpha$ ,  $\lambda = 1.54059\text{ \AA}$ ). The TG analyses were carried out on a Perkin Elmer TG/DTA 6300 thermal analyzer under flowing  $\text{N}_2$  atmosphere, with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . Luminescence spectra were measured on a Perkin Elmer LS 55 luminescence spectrometer.

### 2.2. Syntheses

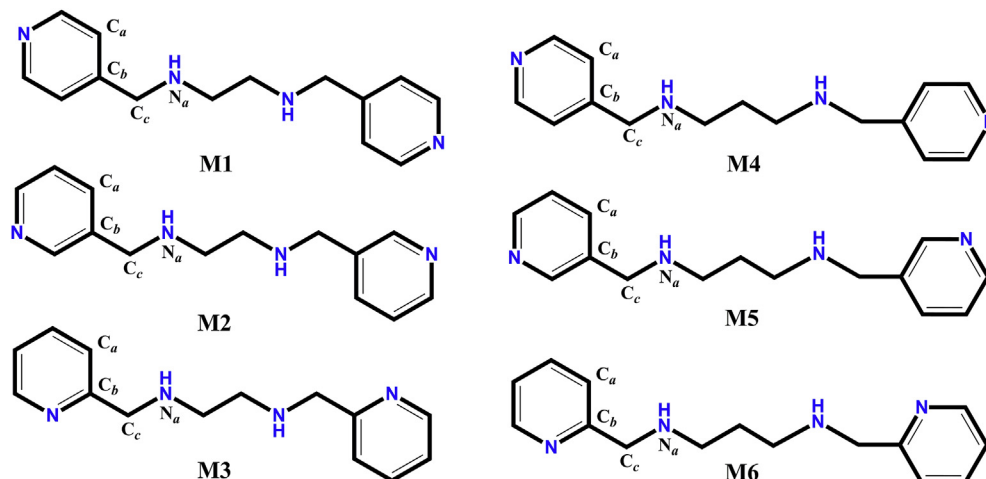
#### 2.2.1. Synthesis of salts 1–6

4 mmol  $\text{H}_3\text{PO}_4$  (85 wt%, the amount of the acid is calculated from their massfraction, volume, density and molecular weight) was added to the methanol solution of 2 mmol M1-M3 for 1–3 and 1 mmol M1-M3 for 4–6, and then the mixture was stirred at room temperature for 10 min. Single crystals of salts 1–6 were isolated from the filtrate after several days.

Compound 1: Yield: 85%. Elemental analysis calcd (%) for  $\text{C}_{14}\text{H}_{32}\text{N}_4\text{O}_{12}\text{P}_2$ : C 32.95, H 6.32, N 10.98; found: C 32.98, H 6.36, N 10.94. IR ( $\nu/\text{cm}^{-1}$ ): 3430m, 3041–2865br,s, 1606s, 1523m, 1456s, 1432m, 1110s, 1027s, 988m, 923s.

Compound 2: Yield: 87%. Elemental analysis calcd (%) for  $\text{C}_{14}\text{H}_{28}\text{N}_4\text{O}_{10}\text{P}_2$ : C 35.45, H 5.95, N 11.81; found: C 35.42, H 5.90, N 11.83. IR ( $\nu/\text{cm}^{-1}$ ): 3321m, 3062–2783br,m, 1604m, 1527m, 1488m, 1432m, 1110s, 1054m, 1025m, 951s.

Compound 3: Yield: 82%. Elemental analysis calcd (%) for  $\text{C}_{14}\text{H}_{28}\text{N}_4\text{O}_{10}\text{P}_2$ : C 35.45, H 5.95, N 11.81; found: C 35.48, H 5.99, N 11.83. IR ( $\nu/\text{cm}^{-1}$ ): 3382m, 3037–2805br,s, 1599m, 1477m, 1446m, 1094s, 1049s, 978m, 950s.



Scheme 1. Schematic representation of the two series of isomeric pyridine-diamine functionalized molecules used in this work.

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