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Tetrahedral oxyanions-assisted supramolecular assemblies of pyridine-based tectons into hydrogen-bonding networks

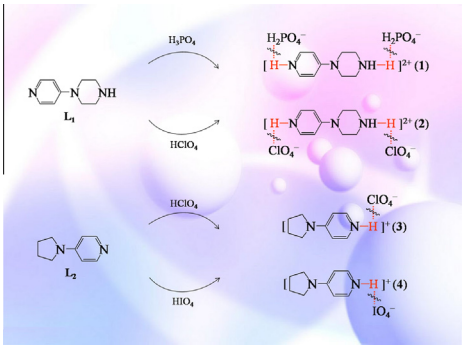
Xue-Hua Ding [a], Shi Wang [a,*], Yong-Hua Li [a], Wei Huang [a,b,*]

[a] Key Laboratory for Organic Electronics & Information Displays (KLOEID) and Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications, Nanjing 210023, China
[b] Jiangsu-Singapore Joint Research Center for Organic/Bio- Electronics & Information Displays and Institute of Advanced Materials, Nanjing University of Technology, Nanjing 211816, China

HIGHLIGHTS

- Four 3D supramolecular salts have been prepared.
- Pyridine-based L_1 and L_2 show preference for tetrahedral oxyanions.
- Robust hydrogen bonds generate various supramolecular frameworks.
- Distinctive substructures arise from $H_2PO_4^-$ anions in salts **1**.

GRAPHICAL ABSTRACT



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ABSTRACT

The systematic research has been done into structural variations of supramolecular architectures by the self assembly of two pyridine-based potential anion receptors, 1-(4-pyridyl)piperazine (L_1) and 4-pyrrolidinopyridine (L_2), and different inorganic acids (HCl, HBr, HI, HNO_3, $HClO_4$, HIO_4, H_2SO_4 and H_3PO_4). The formation of four fascinating salts, i.e. $(H_2L_1^{2+})\cdot(H_2PO_4^-)_2$ (**1**), $(H_2L_1^{2+})\cdot(ClO_4^-)_2$ (**2**), $(HL_2^+)\cdot(ClO_4^-)$ (**3**) and $(HL_2^+)\cdot(IO_4^-)$ (**4**), indicates that N-heterocyclic L_1 and L_2 are prone to cocrystallize with tetrahedral oxyanions and anionic topologies play a crucial role in the crystallization process. Structural analyses reveal that various intermolecular ring motifs have been generated by robust hydrogen-bonding interactions in compounds **1**–**4**. In particular, interesting substructures were observed in $H_2PO_4^-$ from salts **1** due to its polytopic potential hydrogen-bonding donor and acceptor oxygen atoms, including ring motifs, 1D ribbons and 2D supramolecular framework. Much to our surprise, crystal **4** proves to be a member of few supramolecular salts crystallizing with IO_4^- anion according to the Cambridge Structure Database (CSD).

Introduction

As a rapidly growing field, crystal engineering offers a rational approach to the design and synthesis of new materials with targeted structures and properties [1], which has greatly enriched supramolecular chemistry. When it comes to the purely organic

* Corresponding authors at: Key Laboratory for Organic Electronics & Information Displays (KLOEID) and Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications, Nanjing 210023, China. Tel./fax: +86 25 85866396 (S. Wang).
E-mail addresses: iamswang@njupt.edu.cn (S. Wang), iamwhuang@njtech.edu.cn (W. Huang).

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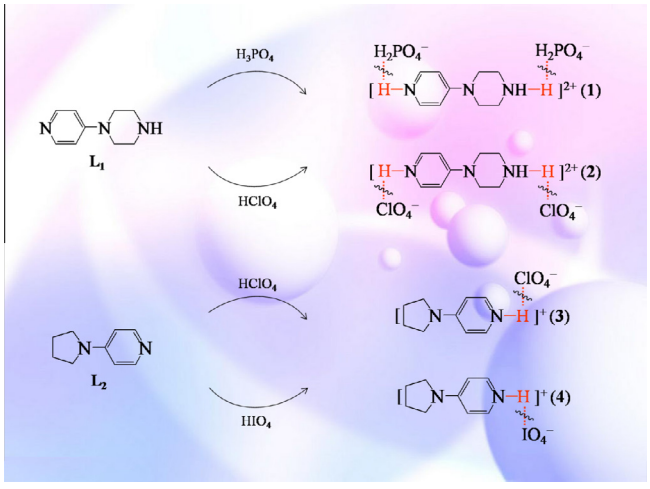
Table 1
Crystallographic data for the complex of **1**–**4**.

Compounds	**1**	**2**	**3**	**4**
Formula	$C_9H_{19}N_3O_8P_2$	$C_9H_{15}Cl_2N_3O_8$	$C_9H_{13}ClN_2O_4$	$C_9H_{13}IN_2O_4$
Formula weight	359.21	364.14	248.66	340.11
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pbca*	*C*2/*c*	$P2_1/c$	$P2_1/c$
a (Å)	17.989(5)	18.575(11)	7.5245(15)	7.4795(14)
b (Å)	7.572(5)	11.181(7)	16.342(3)	15.981(3)
c (Å)	20.891(5)	14.201(8)	9.3839(19)	10.2199(19)
α (°)	90.00(5)	90.00	90.00	90.00
β (°)	90.00(5)	96.122(6)	107.815(2)	108.386(2)
γ (°)	90.00(5)	90.00	90.00	90.00
V (Å^3)	2846(2)	2933(3)	1098.6(4)	1159.2(4)
D_x (Mg m^{-3})	1.677	1.65	1.503	1.949
μ (mm^{-1})	0.35	0.49	0.35	2.76
Z	8	8	4	4
T (K)	293	296	296	296
F (000)	1504	704	520	664
θ range for data collection (°)	2.3–28.3	2.1–28.3	2.5–28.3	2.5–28.4
Index ranges	$-24 \leqslant h \leqslant 24$, $-10 \leqslant k \leqslant 10$, $-27 \leqslant l \leqslant 25$	$-23 \leqslant h \leqslant 24$, $-13 \leqslant k \leqslant 14$, $-11 \leqslant l \leqslant 18$	$-10 \leqslant h \leqslant 9$, $-21 \leqslant k \leqslant 21$, $-10 \leqslant l \leqslant 12$	$-9 \leqslant h \leqslant 9$, $-21 \leqslant k \leqslant 21$, $-11 \leqslant l \leqslant 13$
Measured reflections	23,105	7665	9368	9574
Independent reflections	3533	3479	2745	2892
R_{int}	0.051	0.04	0.028	0.05
Reflections with $I > 2\sigma(I)$	2778	2138	1992	2043
R_1 [$I > 2\sigma(I)$]	0.038	0.076	0.048	0.054
wR_2 (all data)	0.101	0.231	0.13	0.094
S	1.05	1.05	1.03	1.32



Scheme 1. Structures of the proton-transfer supramolecular salts **1**–**4**.

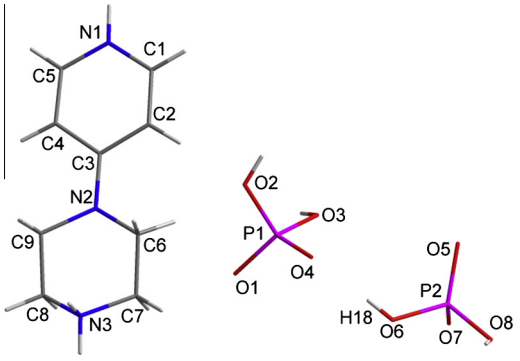


Fig. 1. View of the asymmetric unit for **1** with the labelled atoms.

supramolecular synthesis, noncovalent interactions have been widely exploited, like hydrogen bonding (H-bonding), electrostatic interactions and van der Waals forces [2]. Dominant among them

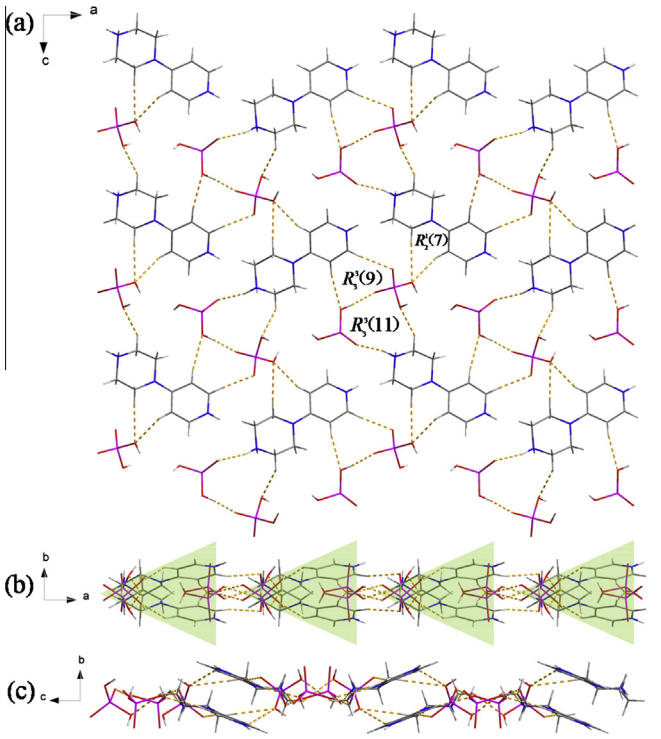


Fig. 2. Crystal structure of **1**. (a) 2D layer structure parallel to the *ac*-plane, where three kinds of ring motifs form. (b) The chain constructed by arrowhead-like repeating units along the *c*-axis. (c) View of crystal structure along the *a*-axis. Hydrogen bonds are shown by dashed lines in light orange. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)