



## Crystal Structure and Luminescent Properties of Supramolecular Compound $[C_{12}H_{12}N_2]^{2+}[C_{16}H_8O_{10}S]^{2-}$

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A new supramolecular compound  $[C_{12}H_{12}N_2]^{2+}[C_{16}H_8O_{10}S]^{2-}$  was synthesized and characterized by elemental analysis, IR and single-crystal X-ray diffraction. In the crystal structure, multiform hydrogen bonds (N-H...O and C-H...O) lead to a three-dimensional supramolecular architecture. The luminescent properties of the compound in the solid state were investigated. The crystal belongs to monoclinic, space group C2/c,  $a = 3.039(3)$ ,  $b = 0.48803(7)$ ,  $c = 2.0251(2)$  nm,  $\beta = 100.319(2)^\circ$ ,  $Z = 4$ ,  $V = 2.955(3)$  nm<sup>3</sup>,  $R_1 = 0.0664$  and  $wR_2 = 0.1637$  (CCDC 754951).

**Key Words:** Supramolecular compound, Crystal structure, Luminescent properties.

### INTRODUCTION

Organic crystals built from acid-base complexes have received considerable attention in the predictable assembly of supramolecular architectures<sup>1,2</sup>. Weak intermolecular interactions play an important role in the formation of supramolecular structures and crystal engineering. Whereas noncovalent phenomena such as  $\pi$ - $\pi$  stacking and hydrogen bonding have been studied extensively<sup>3-6</sup>. Herein, we report the organic crystal structure of  $[C_{12}H_{12}N_2]^{2+}[C_{16}H_8O_{10}S]^{2-}$  (Fig. 1), which is a three-dimensional supramolecular architecture with hydrogen bonds interactions. The luminescent properties of the compound were also investigated.

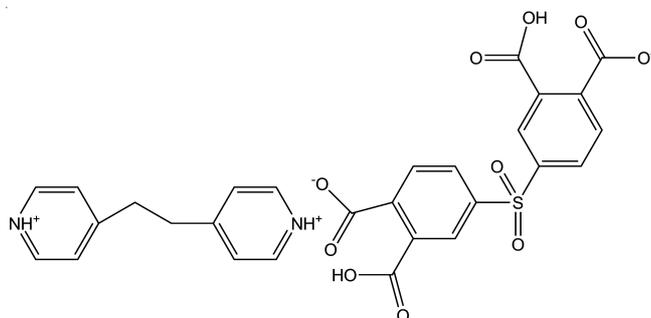


Fig. 1. Chemical structure of the title compound

### EXPERIMENTAL

All the commercially available solvents and starting materials were used as received without further purification.

The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm<sup>-1</sup> on a Bruker EQUINOX-55 spectrometer. Elemental analysis was determined on a Perkin-Elmer 2400 type elemental analyzer. Photoluminescence analyses of the solid samples were performed on an Edinburgh Instrument F920 fluorescence spectrometer at ambient temperature.

**Synthesis of the compound:** An aqueous solution (10 mL) containing 1,2-bis(4-pyridyl)ethylene (0.20 mmol), 3,3',4,4'-diphenyl sulfonetetracarboxylic acid (H<sub>4</sub>dpstc 0.20 mmol) and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.20 mmol) was stirred for 20 min. The mixture was then transferred to a 23 mL Teflon-lined autoclave and kept at 433 K for 72 h under autogenous pressure. Then the mixture was cooled to room temperature slowly. The targeted Zn<sup>2+</sup> complex was not synthesized. Unintentionally, colourless single crystals of  $[C_{12}H_{12}N_2]^{2+}[C_{16}H_8O_{10}S]^{2-}$  suitable for X-ray analysis were obtained in 48 % yield. Anal. calcd. (%) for C<sub>28</sub>H<sub>20</sub>N<sub>2</sub>O<sub>10</sub>S: C, 61.77, H, 3.70; N, 5.14. Found (%): C, 60.82; H, 3.57; N, 5.51. IR (KBr pellet,  $\nu_{max}$ , cm<sup>-1</sup>): 3430 m, 3058 s, 2428 w, 1915 s, 1668 s, 1632 s, 1602 s, 1548 s, 1421 s, 1384 vs, 1192 m, 1136 m, 1036 m, 867 m, 817 m, 776 vs, 705 s, 678 m, 622 w, 554 m, 518 w, 476 m.

**Crystal structure determination:** A single crystal having dimension of 0.38 mm × 0.18 mm × 0.15 mm was chosen for X-ray diffraction studies. X-Ray diffraction intensities for the compound were collected at 298(2) K on a Bruker Apex CCD area-detector diffractometer (MoK $\alpha$ ,  $\lambda = 0.071073$  nm). Absorption corrections were applied by using multi-scan program SADABS. The structure was solved with direct methods and

refined with full-matrix least-squares technique using the SHELXTL program package<sup>7</sup>. Anisotropic thermal parameters were applied to all of the non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C-H: 0.093 nm). A hydrogen atom on oxygen atom was located from difference maps. A calculation of the solvent-accessible volume yielded  $130 \text{ \AA}^3$  of empty space per unit cell in the structure<sup>8,9</sup>. This is consistent with the final Fourier difference map, which shows no peak greater than  $130 \text{ \AA}^3$  after the final refinement. The vacant regions may arise from geometrical packing constraints. Crystal data as well as details of data collection and refinements for the compound are summarized in Table-1. Selected bond distances and bond angles are listed in Table-2. CCDC: 754951.

## RESULTS AND DISCUSSION

**Crystal structure of complex 1:** The asymmetric unit of the title compound consists of a 1,2-*bis*(4-pyridyl)ethylene cation and a 3,3',4,4'-diphenylsulfonetetracarboxylic acid anion ( $H_2dpstc$ ) (Fig. 1), which is similar to that of reported co-crystal 1,3-di-4-pyridylpropane-4,4'-oxydibenzoic acid<sup>10</sup>. The two carboxyl groups of  $H_2dpstc$  are deprotonated and two pyridyl rings accept the protons to produce the 1,2-*bis*(4-pyridyl)ethylene cation. The dihedral angle between the two

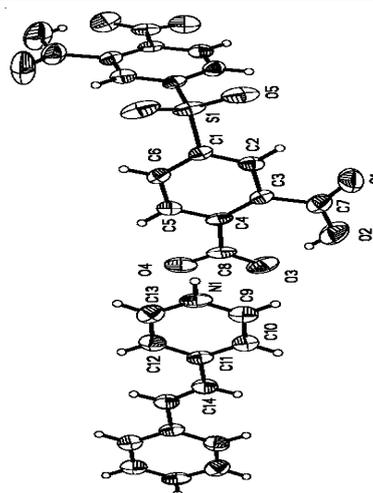


Fig. 1. ORTEP drawing of the title compound with atom labeling (thermal ellipsoids 30 %)

benzene rings of the flexible  $H_2dpstc$  molecule is  $75.46^\circ$ . There are several kinds of hydrogen bonding are present in the structure: (a) hydrogen bonds between the pyridyl N atoms of the 1,2-*bis*(4-pyridyl)ethylene and carboxylate O atoms of the  $H_2dpstc$  with the N1-H1...O4 distance of  $0.2638(4) \text{ nm}$ ; (b) hydrogen bonds between two carboxyl groups of the  $H_2dpstc$

TABLE-1  
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE COMPOUND

Empirical formula	$C_{28}H_{20}N_2O_{10}S$	$D_c$ (Mg $m^{-3}$ )	1.296
Formula weight	576.53	$\theta$ range for data collection ( $^\circ$ )	2.04-25.01
Crystal system	Monoclinic	Indices range (h, k, l)	$-31 \leq h \leq 36, -5 \leq k \leq 5, -24 \leq l \leq 16$
Space group	C2/c	$\lambda$ (MoK $\alpha$ ) (nm)	0.071073
a (nm)	3.039(3)	Reflections collected	6357
b (nm)	0.48803(7)	Independent reflections	2583
c (nm)	2.0251(2)	Data/restraints/parameters	2583/0/186
$\alpha$ ( $^\circ$ )	90	$F_{(000)}$	1192
$\beta$ ( $^\circ$ )	100.319(2)	Goodness-of-fit on $F^2$	0.967
$\gamma$ ( $^\circ$ )	90	Final R	$R_1 = 0.0664, wR_2 = 0.1637$
V ( $nm^3$ )	2.955(3)	R Indices (all data)	$R_1 = 0.1198, wR_2 = 0.1812$
Z	4	Largest diff. peak and hole ( $e \text{ nm}^{-3}$ )	0.678, -0.430

TABLE-2  
SELECTED BOND LENGTHS (nm) AND BOND ANGLES ( $^\circ$ ) OF THE TITLE COMPOUND

N(1)-C(13)	0.1313(4)	C(5)-C(6)	1.372(5)	C(3)-C(4)	1.401(5)
N(1)-C(9)	0.1317(5)	C(9)-C(10)	1.358(5)	C(3)-C(7)	1.515(6)
O(1)-C(7)	0.1190(5)	C(14)-C(14B)	1.294(7)	C(4)-C(5)	1.380(5)
O(2)-C(7)	1.265(5)	S(1)-C(1)	1.765(4)	C(10)-C(11)	1.370(5)
O(3)-C(8)	1.241(5)	C(1)-C(2)	1.357(5)	C(11)-C(12)	1.377(5)
O(4)-C(8)	1.236(5)	C(1)-C(6)	1.367(5)	C(11)-C(14)	1.478(5)
O(5)-S(1)	1.431(3)	C(2)-C(3)	1.390(5)	C(12)-C(13)	1.367(5)
C(4)-C(8)	1.527(5)	-	-	-	-
C(13)-N(1)-C(9)	122.5(4)	O(4)-C(8)-O(3)	122.4(4)	C(3)-C(4)-C(8)	126.9(4)
O(5A)-S(1)-O(5)	118.8(3)	O(4)-C(8)-C(4)	116.4(4)	C(6)-C(5)-C(4)	122.4(3)
O(5A)-S(1)-C(1A)	107.72(17)	O(3)-C(8)-C(4)	121.1(5)	C(1)-C(6)-C(5)	118.7(3)
O(5)-S(1)-C(1A)	108.52(16)	N(1)-C(9)-C(10)	120.0(4)	O(1)-C(7)-O(2)	120.0(5)
O(5A)-S(1)-C(1)	108.52(16)	C(9)-C(10)-C(11)	120.3(4)	O(1)-C(7)-C(3)	119.4(5)
O(5)-S(1)-C(1)	107.72(17)	C(14B)-C(14)-C(11)	124.3(5)	O(2)-C(7)-C(3)	120.7(5)
C(1A)-S(1)-C(1)	104.5(2)	C(2)-C(3)-C(4)	118.0(3)	C(10)-C(11)-C(12)	117.4(4)
C(2)-C(1)-C(6)	120.4(3)	C(2)-C(3)-C(7)	113.1(4)	C(10)-C(11)-C(14)	118.5(4)
C(2)-C(1)-S(1)	119.2(3)	C(4)-C(3)-C(7)	128.9(4)	C(12)-C(11)-C(14)	124.1(4)
C(6)-C(1)-S(1)	120.4(3)	C(5)-C(4)-C(3)	118.5(3)	C(13)-C(12)-C(11)	120.4(4)
C(1)-C(2)-C(3)	122.0(3)	C(5)-C(4)-C(8)	114.6(4)	N(1)-C(13)-C(12)	119.3(4)

Symmetry transformations used to generate equivalent atoms: (A)  $-x, y, -z + 1/2$ ; (B)  $-x + 1/2, -y + 5/2, -z$ .

with the O2-H2...O3 distance of 0.2379(5) nm; (c) hydrogen bonds between C atoms of the bpe and carboxyl groups of the H<sub>2</sub>dpstc with C14-H14...O1 distances of 0.3317(6) nm (Table-3). Strong intermolecular N-H...O hydrogen bonds link the ions into the one-dimensional chains and the adjacent chains are further connected by intermolecular C-H...O hydrogen bonds to afford a three-dimensional supramolecular architecture with one-dimensional open channels (Fig. 2).

D-H...A	D-H	H...A	D...A	D-H...A
N1-H1-O4 <sup>i</sup>	0.086	0.178	0.2638(4)	176.3
O2-H2-O3	0.082	0.158	0.2379(5)	165.5
C14-H14-O1 <sup>ii</sup>	0.093	0.243	0.3317(6)	158.6

Symmetry code: (i) x, -1+y, z; (ii) 1/2-x, 1/2+y, 1/2-z.

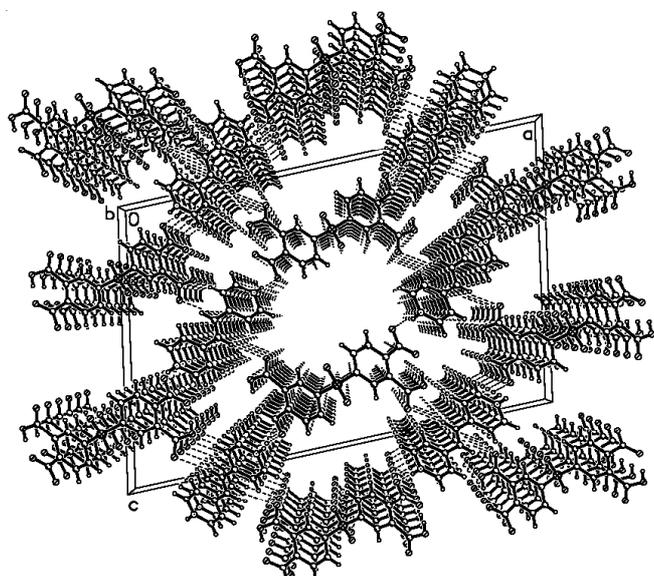


Fig. 2. Stacking of 3D supramolecular architecture in the title compound, viewed down the b axis. Dashed lines denote hydrogen bonds

**Luminescent properties:** The emission spectra of [C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>]<sup>2+</sup>[C<sub>16</sub>H<sub>8</sub>O<sub>10</sub>S]<sup>2-</sup> and the H<sub>4</sub>dpstc ligand in the solid state at room temperature are shown in Fig. 3. It could be observed that the compound exhibits preferably photoluminescence with an emission maximum at ca. 436 nm ( $\lambda_{\text{ex}} = 351$  nm). In order to understand the nature of the emission band, the photoluminescence properties of the free H<sub>4</sub>dpstc ligand were analyzed. It was found that an intense emission maximum at ca. 461 nm ( $\lambda_{\text{ex}} = 430$  nm) could be observed and the emission of the free H<sub>4</sub>dpstc ligand may be attributed to  $\pi$ - $\pi^*$  transitions within the molecular orbital manifolds of phenyl rings, while free 1,2-bis(4-pyridyl)ethylene ligand presents largely weak photoluminescence emission. Comparison with

the H<sub>4</sub>dpstc ligand, the emission maxima of the compound is red-shifted and may be related to the multiform hydrogen bonds between the H<sub>2</sub>dpstc anion and 1,2-bis(4-pyridyl)-ethylene cation.

## Conclusion

In summary, we have prepared and characterized a new supramolecular compound [C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>]<sup>2+</sup>[C<sub>16</sub>H<sub>8</sub>O<sub>10</sub>S]<sup>2-</sup>. The compound exhibits a three-dimensional supramolecular architecture, basing on the multiform hydrogen bonds. The luminescent properties of the compound were investigated and indicated it was a preferable new fluorescence material.

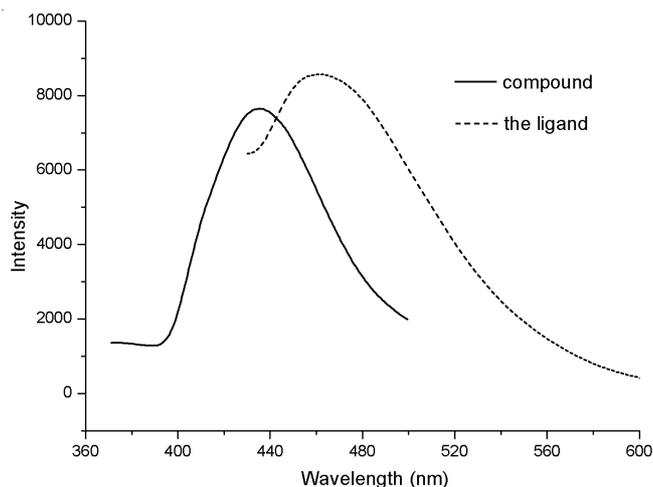


Fig. 3. Luminescence spectrum of the compound (—) and the H<sub>4</sub>dpstc ligand (-----) at the room temperature

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