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Synthesis, Crystal Structure, and Characterization of a Novel Coordinated Polymer [$Cu_2I_4(Nppch)_2$]

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Solution reaction of CuI and KI in DMF/H_2O with a solution of Nppch in CH_3OH/H_2O gave rise to a three-dimensional (3D) supramolecular compound based on a binuclear [$Cu_2I_4(Nppch)_2$] unit (Nppch = *N*-(4-pyridyl) pyridinium chloride hydrochloride). The crystal structural analysis indicated that the complex crystallized in a monoclinic space group, P2(1)/n, a = 9.6821(19) Å, b = 11.414(2) Å, c = 12.096(2) Å, β = 103.17(3)°, V = 1301.6(4) Å^3, Z = 2. The complex possessed a novel three-dimensional supramolecular framework formed by hydrogen bonds among repeating [$Cu_2I_4(Nppch)_2$] binuclear units. The compound was further characterized with infrared (IR) spectra, ultraviolet spectral properties, thermal analysis, and fluorescence properties.

Keywords copper(I) complex, crystal structure, luminescent properties, thermogravimetric properties

INTRODUCTION

Since its discovery, the coordinative bond approach has attracted much attention[1] and has been widely used in the construction of supramolecular coordination compounds by self-assembly.[2] So far, a wide range of one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) infinite solid-state supramolecular coordination compounds have been synthesized and structurally characterized.[3] In recent years, the solid-metal supramolecular polymer has gradually become one of the most active research areas of chemical engineering and molecular sciences.[4–8] Furthermore, potential applications of supramolecular coordination compounds have been found in chemical sieving, sensing, and catalysis.[9] Recently, we selected transition metal iodides as reactants because the transition-metal-directed self-assembly is a highly synthesis method, and polyiodides have the ability to form various extended networks.

In this article, we report the synthesis, crystal structure, ultraviolet spectrum, and luminescent and thermogravimetric properties of a novel coordination polymer with the repeating unit [$Cu_2I_4(Nppch)_2$].

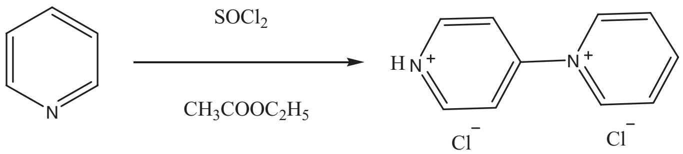
EXPERIMENTAL

General Information and Materials

Pyridine, ethyl acetate, sulfoxide chloride, and absolute ethyl alcohol were obtained from Aldrich Chemical Company. The infrared (IR) spectrum was recorded on a Shimazu IR435 spectrometer as KBr disk (4000–400 cm^{-1}). Thermal analyses were performed on a Netzsch STA 449C thermal analyzer from 30 to 600°C at a heating rate of 10°C min^{-1} in air. The ultraviolet–visible (UV-vis) spectra were measured on a Lambda 35 UV–visible spectrophotometer. Photoluminescent measurement of the compound [$Cu_2I_4(Nppch)_2$] and the cation Nppch in CH_3OH solution was conducted on a Hitachi F-4500 spectrophotometer and the data were collected at room temperature.

Synthesis of the *N*-(4-Pyridyl) Pyridinium Chloride Hydrochloride (Nppch)

Sulfoxide chloride (4.9 mL, 0.067 mol) was added to the mixture of pyridine (8.2 mL, 0.1 mol) and ethyl acetate (4.9 mL) under stirring at 0°C. The reaction was kept heating at 75–80°C and refluxing for 6 h. After reaction, the temperature was cooled to room temperature and supernatant was dumped. At last, Nppch, a yellow powder, was obtained by washing with absolute ethyl alcohol and drying. The reaction route is shown in Scheme 1.[10]



SCH. 1.

Synthesis of the Compound [$Cu_2I_4(Nppch)_2$]

A solution of Nppch (0.1 mmol, 23.4 mg) in CH_3OH/H_2O (3 mL) was added to a solution of CuI (0.1 mmol, 12.2

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TABLE 1
Crystallographic data and structural refinement for compound $[Cu_2I_4(Nppch)_2]$

Empirical formula	$C_{20}H_{18}Cu_2I_4N_4$
Formula weight	949.06
Crystal system	Monoclinic
Space group	P2(1)/n
Crystal size(mm)	0.16 × 0.12 × 0.11
a (Å)	9.6821 (19)
b (Å)	11.414 (2)
c (Å)	12.096 (2)
α (°)	90
ß (°)	103.17 (3)
γ (°)	90
V (Å^3)	1301.6 (4)
Dc (mg m^{-3})	2.422
Z	2
μ (mm^{-1})	6.392
Reflections collected/unique	8304/3144
R(int)	0.0283
Final R indices	R1 = 0.0305[a], wR2 = 0.0594[a,b]
R indices (all data)	R1 = 0.0424, wR2 = 0.0642
Goodness-of-fit on F^2	1.031
Largest peak, hole (e Å^{-3})	1.527, –1.188
F(000)	872
Temperature, K	293(2)

[a] $R_1 = \|Fo| - |Fc\|/|Fo|$.
[b] $wR_2 = [w(Fo^2 - Fc^2)^2/w(Fo^2)^2]^{1/2}$.

mg) and KI (0.5 mmol, 83.0 mg) in dimethylformamide DMF/H_2O (3 mL). A little white precipitation appeared and DMF was continually added until the precitation disappeared completely. Then the mixed solution was placed in the dark. One week later, blue-green crystals were obtained at ambient temperature. Yield: 62.3%. Anal.: Calcd. for $C_{20}H_{18}Cu_2I_4N_4$: C, 25.31; H, 1.91; N, 5.90%. Found: C, 25.32; H, 1.96; N, 5.93%. IR (cm^{-1}, KBr): 3068.52(w), 3039.22(m), 1939.16(w), 1642.64(w), 1622.34(s), 1585.09(s), 1495.70(s), 1466.97(s), 1407.48(s), 1263.40(m), 1223.02(m), 1147.75(m), 1099.58(w), 1070.08(w), 1049.23(m), 1019.82(m), 964.56(w), 936.42(w), 832.43(s), 768.50(s), 667.68(s), 617.54(s), 554.49(s), 486.21(w).

X-Ray Structural Determination

Crystallographic data for $[Cu_2I_4(Nppch)_2]$ were collected at 293(2) K using Mo-Kα radiation ($\lambda = 0.71073$ Å) on a Rigaku RAXIS-IV image plate area detector. The structures were solved with the SHELX program by direct methods and expanded using the Fourier technique. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical constraints, but all the non-hydrogen atoms were treated anisotropically.

RESULTS AND DISCUSSION

Crystal Structure of the Compound $[Cu_2I_4(Nppch)_2]$

Compound $[Cu_2I_4(Nppch)_2]$ crystallizes in the monoclinic space group P2(1)/n, and crystal data and refinement details are summarized in Table 1. Selected bond lengths and bond angles were listed in Table 2.

Single-crystal x-ray diffraction analysis revealed that the compound $[Cu_2I_4(Nppch)_2]$ was a dimeric compound. As is shown in Figure 1, in this binuclear compound, the coordination circumstances of the two Cu atoms are the same and they are tetrahedrally coordinated by μ2-I, terminal atom I(2), and N(1) from cation $[Nppch]^+$. The coordination number of atom Cu is four if the Cu–Cu bond (2.84 Å) is not taken into consideration. The asymmetric unit of the compound $[Cu_2I_4(Nppch)_2]$ consists of two parts: $[Nppch]^+$ and $[Cu_2I_4]^{2-}$. In the $[Cu_2I_4]^{2-}$ part, Cu(1)–I(1)–Cu(1)#1–I(1)#1 can form a parallelogram, while the bonds of Cu(1)–I(1) and Cu(1)#1–I(1)#1 are 2.647 Å and 2.659 Å, respectively, and the angles of Cu(1)–I(1)–Cu(1)#1 and I(2)–Cu(1)–Cu(1)#1 are 68.68° and 136.96°, respectively. In the $[Nppch]^+$ part, two pyridine ring are linked by the bond N(2)–C(3), and the dihedral angle between the two pyridine rings is 38.96°.

TABLE 2
Selected bond lengths (Å) and angles (°) for compound $[Cu_2I_4(Nppch)_2]$

I(1)–Cu(1)	2.6467(8)	Cu(1)–N(1)	2.093(3)
I(1)–Cu(1)#1[a]	2.6589(9)	Cu(1)–I(1)#1	2.6589(9)
I(2)–Cu(1)	2.6152(8)	Cu(1)–Cu(1)#1	2.8383(12)
Cu(1)–I(1)–Cu(1)#1	64.68(2)	N(1)–Cu(1)–Cu(1)#1	115.00(10)
N(1)–Cu(1)–I(2)	108.04(10)	I(1)#1–Cu(1)–Cu(1)#1	57.45(2)
N(1)–Cu(1)–I(1)	103.99(10)	I(1)–Cu(1)–Cu(1)#1	57.87(3)
N(1)–Cu(1)–I(1)#1	102.16(10)	I(2)–Cu(1)–Cu(1)#1	136.96(4)
I(1)–Cu(1)–I(1)#1	115.32(2)	C(1)–N(1)–Cu(1)	121.5(3)
I(2)–Cu(1)–I(1)#1	113.87(2)	C(5)–N(1)–Cu(1)	121.6(3)
I(2)–Cu(1)–I(1)	112.16(3)		

[a] Symmetry transformations used to generate equivalent atoms: #1, –x, –y, –z + 2.

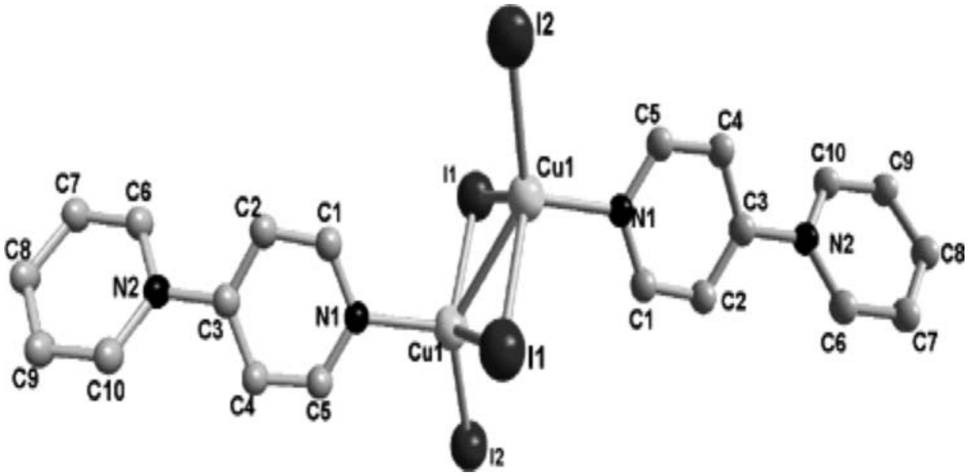

FIG. 1. The binuclear compound [$Cu_2I_4(Nppch)_2$]; the hydrogen atoms are not displayed, for clarity.

In the solid-state structure, there exists only one type of intermolecular interactions From the packing diagram of the compound [$Cu_2I_4(Nppch)_2$] (as shown in Figure 2), it is shown that hydrogen bonds (C–H···I) exit between atom I of each construction unit and the H atom from cation [Nppch]$^+$ of the neighboring construction unit. Although the C–H···I hydrogen bonds (as shown in Table 3) are relatively weak, they play a very important role in holding the crystal framework. The structure is formed by a layer accumulation with an arrangement in opposite directions. As a result of these C–H···I inducing contacts, the repeating [$Cu_2I_4(Nppch)_2$] construction unit grows infinitely in the a, b, and c directions, and then a final supramolecular

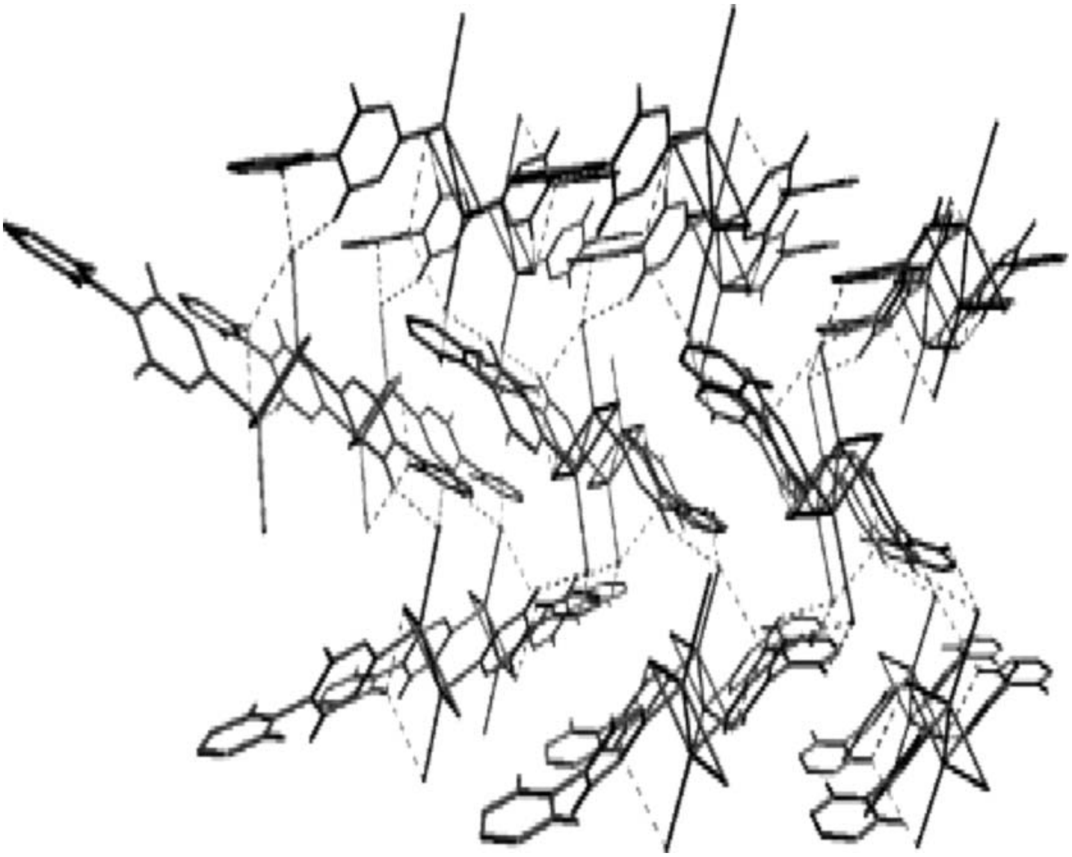

FIG. 2. Three-dimensional supramolecular framework of compound [$Cu_2I_4(Nppch)_2$] (along *a* axis) with C–H···I interaction shown by the dotted lines.

TABLE 3
D–H···A interactions and their distances and angles parameters for the compound

D–H···A interaction	$D_{D\cdots A}$ (Å)	$D_{H\cdots A}$ (Å)	∠DHA (°)
C(2)–H(2A)···I(2)	3.938	3.100	150.93
C(6)–H(6A)···I(2)	3.934	3.127	146.06
C(10)–H(10A)···I(2)	3.789	3.053	137.28
C(4)–H(4A)···I(1)	4.003	3.087	168.58
C(10)–H(10A)···I(1)	3.797	3.151	128.21

structure is built (Figure 2). Indeed, all these intermolecular interactions are weak, undeniably, but that may make this binuclear complex increase its melting point and become stable.

Ultraviolet Spectrum Properties

The UV-vis absorption of compound Nppch and $[Cu_2I_4(Nppch)_2]$ in CH_3OH solution is shown in Figure 3 and Figure 4. The electronic spectra of cation Nppch and compound $[Cu_2I_4(Nppch)_2]$ showed bands at 203 nm and 257 nm, and at 241 nm and 273 nm. By comparison, it is known that these bands at 241 nm and 273 nm of compound $[Cu_2I_4(Nppch)_2]$, are probably dominated by $\pi\cdots\pi$ transfer, while accompanied by a red shift due to coordinating of the metal atoms and organic ligands and the introduction of auxochrome I.

Luminescent Properties

The study of luminescent properties of metal–organic frameworks (MOFs) is of great interest owing to their higher thermal stability than the pure organic ligand and the ability to affect the emission wavelength and intensity of the organic material by metal coordination.[11] The fluorescence spectra of cation Nppch and compound $[Cu_2I_4(Nppch)_2]$ are shown in Figure 5. When the excitation wavelength was set at 325 nm, the emission wavelength of organic cation Nppch were 380 nm and 500 nm, while the maximum emission wavelength of $[Cu_2I_4(Nppch)_2]$ was 365 nm when the maximum excitation wavelength was set at 330 nm. By comparison, we observe that the emission wavelength of compound exhibited a blue shift, which is tentatively assumed as the metal-to-ligand charge transfer transition.[12]

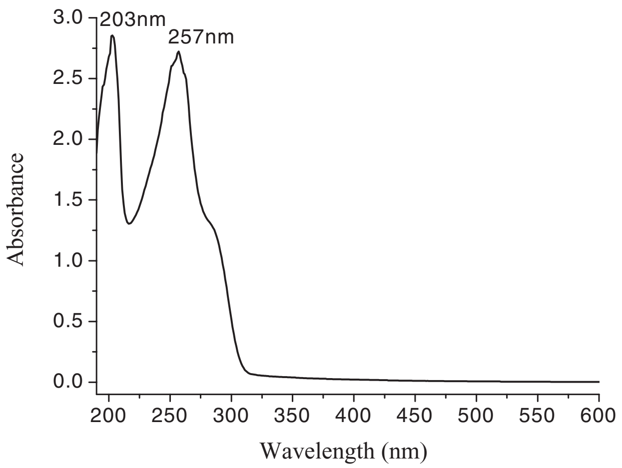

FIG. 3. Ultraviolet and visible spectra of Nppch.

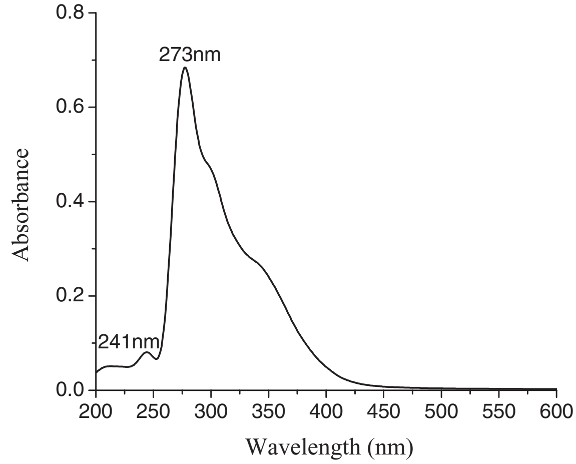

FIG. 4. Ultraviolet and visible spectrogram of compound $[Cu_2I_4(Nppch)_2]$.

Thermogravimetric Properties

The thermal gravimetry–differential scanning calorimetry (TG-DSC) curve for compound $[Cu_2I_4(Nppch)_2]$ is shown in Figure 6. From TG, it is observed that the decomposition process of the compound $[Cu_2I_4(Nppch)_2]$ contains two stages. The first stage took place in the range of 227.0–567.4°C and total weight loss is 50.04% (theoretical weight loss 46.50%), which probably corresponded to the elimination of organic cations and some I atoms. The second stage mainly involved burning of the inorganic framework, that is, odd I atoms, while total weight loss is 17.20%. From the preceding data, we tentatively assume that the last product is CuO. DSC analysis of compound $[Cu_2I_4(Nppch)_2]$ showed a small and narrow endothermic peak

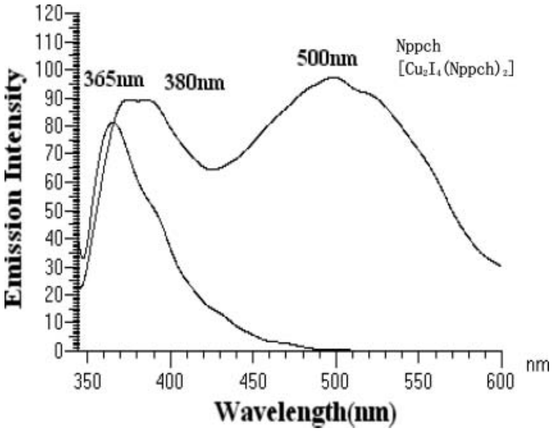

FIG. 5. Solid-state fluorescence spectra of compound $[Cu_2I_4(Nppch)_2]$ and Nppch at room temperature.

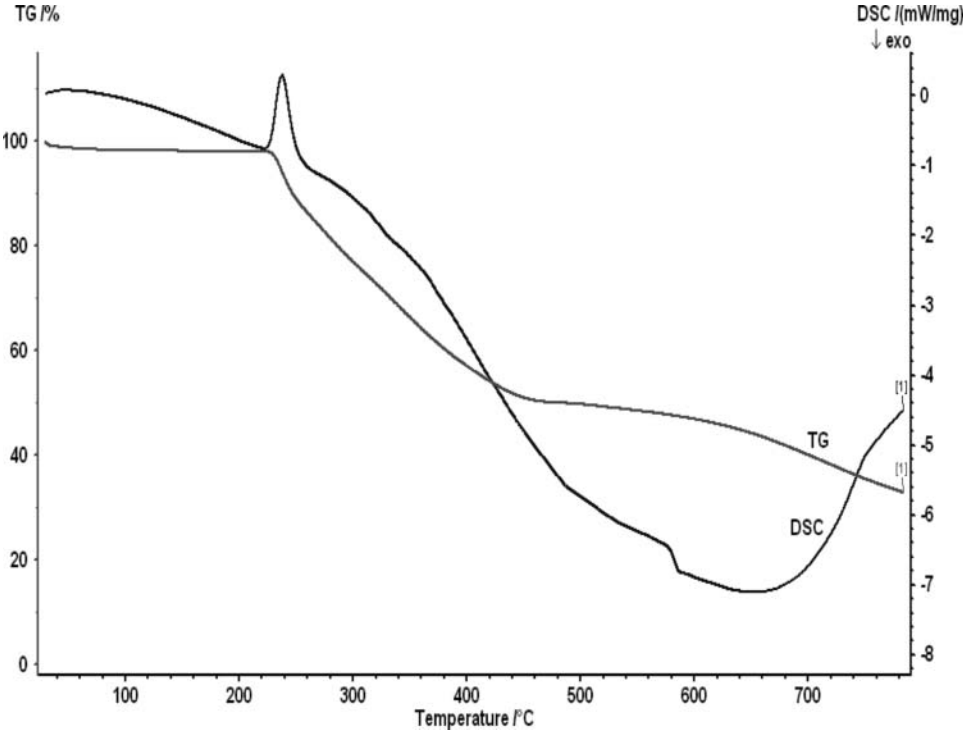

FIG. 6. TG-DSC curve of the compound [$Cu_2I_4(Nppch)_2$].

around 238.1°C and a large and broad exothermic peak around 653.3°C.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC number. 816382. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; or www: http://www. ccdc. cam.ac.uk).

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