

A Systematic Design and Facile Construct of Metal Pseudohalide Frameworks Directed By 1, ω -Bis(pyridinium)alkane CationsYun-Yin Niu,^{*,†} Ben-Lai Wu,[†] Xiao-Ling Guo,[†] Ying-Lin Song,[‡] Xiu-Cun Liu,[†] Hong-Yun Zhang,^{*,†} Hong-Wei Hou,[†] Cao-Yuan Niu,[†] and Seik-Weng Ng[§]*Department of Chemistry, Zhengzhou University, Zhengzhou 450052, P. R. China, School of Physical Science and Technology, Suzhou University, Suzhou 215006, P. R. China, and Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia*

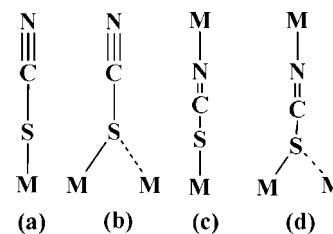
Received December 18, 2007; Revised Manuscript Received March 25, 2008

ABSTRACT: Cation-templated self-assembly of 1, ω -bis(pyridinium)alkanes ($\omega = 1-6$) with cuprous thiocyanate was studied, and six sparse polymeric thiocyanate frameworks were obtained and characterized by X-ray crystallography: $\{(\text{bpm})[\text{Cu}(\text{NCS})_4]\}_n$ (**1**), $\{(\text{bpe})[\text{Cu}_2(\text{NCS})_4]\}_n$ (**2**), $\{(\text{bpps})[\text{Cu}(\text{NCS})_3]\}_n$ (**3**), $\{(\text{bpbt})[\text{Cu}(\text{NCS})_4]\}_n$ (**4**), $\{(\text{bppt})[\text{Cu}_2(\text{NCS})_4]\}_n$ (**5**), and $\{(\text{bph})[\text{Cu}_2(\text{NCS})_4]\}_n$ (**6**) (bpm = 1,1'-bis(pyridinium)methylene, bpe = 1,2-bis(pyridinium)ethane, bpps = 1,3-bis(pyridinium)propane, bpbt = 1,4-bis(pyridinium)butane, bppt = 1,5-bis(pyridinium)pentane, bph = 1,6-bis(pyridinium) hexane). The structures consist of 0–3-dimensional frameworks with the bispyridinium cations trapped within host network cavities. Compound **1** has a 3D porous (6,3)/(6,4) joint topology structure, compounds **2** and **5** have two-dimensional polypseudorotaxane interlocked structures, compound **3** has a dimeric structure, compound **4** has a two-dimensional honeycomb structure, and compound **6** exhibits an interesting 1D hanging ladder-shaped complementary chain structure. The third-order NLO effect of **3** was studied by Z-scan techniques. The dimer exhibits self-focusing optical nonlinearities, and the effective third-order NLO refractive index (n_2) value is 3.03×10^{-11} esu.

Introduction

A bolaamphiphile is simply defined as a molecule in which two or more hydrophilic groups are connected by hydrophobic functionalities.¹ Since Fuhrhop and Mathieu reported the synthesis and self-assembly of several bolaamphiphiles, the researchers have explored applications of this basic architecture. Symmetric R, ω -bolaamphiphiles have found wide application as constituents of vesicle membranes, multilayer structures, and amphiphilic crystals.² Neve et al. has prepared the dication N,N' -dodecamethylenedipyridinium $[\text{Py-C}_{12}\text{-Py}]^{2+}$ as the bromide salt by direct alkylation of pyridine with R, ω -dibromododecane, and this was used to construct the organic–inorganic hybrid salts $[\text{Py-C}_{12}\text{-Py}][\text{MX}_4]$ (M = Pd, Cu; X = Cl, Br).^{2b} Tao et al. have also investigated the structures and host–guest interaction of cucurbiturils with 1, ω -alkylenedipyridinium.³ Li et al. use the dication 1,6-bis(4-methylpyridinio)hexane(bmph) as structure-directing agents to construct an one-dimensional hybrid polymer $[(\text{bmph})(\text{Ag}_5\text{I}_7)]_n$ with edge-sharing AgI_4 tetrahedron units.⁴

On the other hand, some anionic halogen/pseudohalogenoocuprates(I) have been reported to exhibit solid state fluorescence⁵ or ambient pressure superconductivity.⁶ Of most interest is the observation that halogen/pseudohalogenoocuprates(I) exhibit varieties of extended motifs. In contrast to the well-studied polymeric frameworks of halogenocuprates(I), there are fewer examples of thiocyanatocuprates extended structures. Raston et al. prepared a pyridinium of copper(I) thiocyanate, $[\text{C}_5\text{H}_6\text{N}]^+[\text{Cu}_2(\text{SCN})_3]^-$: the structure comprises a three-dimensional network of copper(I) atoms linked by bridging thiocyanate groups, the pyridinium counterions occupying sites in the network cavities.⁷ In the mixed-valence complex $[\text{Cu}^{\text{II}}(\text{DMF})_4][\text{Cu}^{\text{I}}(\text{SCN})_4(\text{CN})_2]$, there exist polymeric $[\text{CuL}_4(\text{SCN})_4(\text{CN})_2]^{2-}$ anionic layers.⁸ G. Thiele et al. have studied the effects of the counter cations on the structure of the isolated or polymeric 0–3D thiocyanatometallate anions of d¹⁰ metals, as well

Scheme 1. Schematic Representation of the Bonding Modes of NCS^- ^a

^a (a) Terminal (t -) mode; (b) end-on μ_2 -bridging mode; (c) end-to-end μ_2 -bridging mode; (d) 1,1,3- μ_3 -bridging mode.

as the properties of SCN as a multidentate ligand; and the results reflect that smaller cations facilitates the formation of a closely anionic packing.⁹

The most widespread method for the preparation of halogen/pseudohalogenoocuprates(I) is the reaction between a Cu^+ (or Cu^0) and a halide salt of the appropriate cation dissolved in an organic solvent.¹⁰ However, the use of 1, ω -bis(pyridinium)alkane cation-templated synthesis in the construction of polymer thiocyanate frameworks has not been reported. We report here a variation of above studies presenting the new hybrids containing thiocyanatometallate together with bolaamphiphiles. The cation of choice, the bolaamphiphilic 1, ω -bis(pyridinium)alkane ($\omega = 1-6$), was utilized in order to explore the possible size effects from cations on the polymeric anionic skeletons. NCS^- group was selected for its various bonding modes (Scheme 1, t -, μ -, μ_3 -)¹¹ and possible coligand effects. Based on the important experimental facts of above two fields we reasoned that the combination of these two components might lead to hybrid materials with potentially distinctive properties. This article is attributed to some of the intrinsic properties of cation-templated synthesis in the construction or modification of inorganic thiocyanate assemblies. All the hybrid salts $[\text{Py-C}_x\text{-Py}]^{2+}[\text{Cu}_y(\text{NCS})_z]$ ($x = 1-6$; $y = 1, 2$; $z = 3, 4$; Scheme

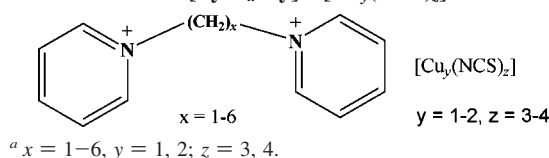
* To whom correspondence should be addressed. E-mail: wzhy917@zzu.edu.cn; niuyy@zzu.edu.cn. Tel: +86 371-67763675. Fax: +86 371-67763675.

[†] Zhengzhou University.

[‡] Suzhou University.

[§] University of Malaya.

Scheme 2. Schematic Representation of the Titled Hybrid Salts [Py-C_x-Py]²⁺[Cu_y(NCS)_z]^a



2) were structurally characterized, and the NLO properties of soluble compound **3** in DMF are reported.

Experimental Section

Materials and Methods. The dication bpm²⁺ dichloride was prepared from the improved refluxing reaction of 7 mL of CH₂Cl₂ with 30 mL of pyridine under 90 °C.^{12a} The dications [Py-(CH₂)_n-Py]²⁺ ($n = 2-5$) were prepared as the bromide salt by direct alkylation of pyridine with 1,ω-dibromoalkane (pyridine also served as the solvent for the reaction).^{12b} Other chemicals were obtained from commercial sources and used as received without further purification. The IR spectrum was recorded on a Shimadzu IR435 spectrometer as KBr disk (4000–400 cm⁻¹). Carbon, hydrogen and nitrogen analyses were performed with a Perkin-Elmer 240C instrument.

Complex Synthesis. {(bpm)[Cu(NCS)₄]}_n (**1**). A methanol solution of bpm·Cl₂ (0.243 g, 1 mmol) was added to a stirring colorless solution of CuNCS (0.121 g, 1.0 mmol) dissolved in 10 mL of DMF/H₂O (volume ratio of 4:1) in the presence of excess KNCS (0.194 g, 2.0 mmol). The solution was then filtered and slowly evaporated in a vial at room temperature. Dark red crystals of **1** suitable for X-ray analysis were obtained after 5 days in about 51% yield. The product is not soluble in common solvents. Anal. Calcd for C₁₅H₁₂Cu₂N₆S₄: C, 33.89; H, 2.28; N, 15.81. Found: C, 33.75; H, 2.16; N, 15.86%. IR (KBr, cm⁻¹): $\nu = 3051.15w, 2075.62s, 1623.51m, 1482.57m, 1181.78m, 757.26m, 671.87m, 558.7w$.

{(bpe)[Cu₂(NCS)₄]}_n (**2**). Compound **2** was obtained as pink red crystals by a similar reaction procedure. Yield: 62%. The product is not soluble in common solvents. Anal. Calcd for

C₈H₇CuN₃S₂: C, 35.22; H, 2.59; N, 15.40. Found: C, 35.25; H, 2.55; N, 15.06%. IR (KBr, cm⁻¹): $\nu = 3445.84b, 2361.96m, 2077.56s, 1626.58m, 1548.01w, 1485.43w, 1271.10w, 1191.07w, 769.47w, 674.61m, 491.97w, 454.18w$.

{(bppp)[Cu(NCS)₃]}_n (**3**). Poor yellow crystals. Yield: 74%. A week later red block crystals were obtained in 42% yield. The product is only soluble in hot DMF. Anal. Calcd for C₁₆H₁₆CuN₅S₃: C, 43.87; H, 3.68; N, 15.99. Found: C, 43.85; H, 3.55; N, 15.86%. IR (KBr, cm⁻¹): $\nu = 3437.45b, 2362.07m, 2095.78s, 1628.04s, 1482.60m, 1273.82w, 1168.77w, 758.06m, 675.19m, 447.52w$.

{(bpbp)[Cu(NCS)₄]}_n (**4**). Poor yellow crystals. Yield: 70%. The product is not soluble in common solvents. Anal. Calcd for C₁₈H₁₈Cu₂N₆S₄: C, 37.68; H, 3.16; N, 14.65. Found: C, 37.52; H, 3.07; N, 14.25%. IR (KBr, cm⁻¹): $\nu = 3435.98b, 2078.16s, 1629.04m, 1485.10w, 1121.58m, 766.13w, 676.20w, 616.79w$.

{(bppt)[Cu₂(NCS)₄]}_n (**5**). Poor yellow crystals. Yield: 64%. The product is not soluble in common solvents. Anal. Calcd for C₁₉H₂₀Cu₂N₆S₄: C, 38.83; H, 3.43; N, 14.30. Found: C, 38.63; H, 3.35; N, 14.28%. IR (KBr, cm⁻¹): $\nu = 3050.79w, 2114.58s, 2088.07s, 1626.46m, 1481.64m, 1173.27m, 759.64m, 682.78m, 450.11w$.

{(bph)[Cu₂(NCS)₄]}_n (**6**). Colorless crystals. Yield: 55%. The product is not soluble in common solvents. Anal. Calcd for C₂₀H₂₂Cu₂N₆S₄: C, 39.92; H, 3.68; N, 13.97. Found: C, 39.78; H, 3.61; N, 13.88%. IR (KBr, cm⁻¹): $\nu = 3439.60b, 2093.69vs, 1627.69m, 1489.10m, 1167.85m, 761.58m, 673.79m, 436.00w$.

Nonlinear Optical Measurements. The optical measurements were performed with linearly polarized 8 ns pulses at 532 nm generated from a frequency-doubled Q-switched Nd:YAG laser. This wavelength is of paramount practical importance in the field of optical nonlinearity as well as the design and fabrication of resonance cavities of lasers. The spatial profiles of the pulses were nearly Gaussian after a spatial filter was employed. A DMF solution of compound **3** was placed in a 1 mm thick quartz cell for optical limiting measurements. Crystalline samples of **3** are stable toward oxygen, moisture, and laser light. The laser pulse was focused into the cells containing the nonlinear medium with a 250 mm focal length

Table 1. Crystal Data and Structure Refinement Details for 1–6

	1	2	3	4	5	6
formula	C ₁₅ H ₁₂ Cu ₂ N ₆ S ₄	C ₈ H ₇ CuN ₃ S ₂	C ₁₆ H ₁₆ CuN ₅ S ₃	C ₁₈ H ₁₈ Cu ₂ N ₆ S ₄	C ₁₉ H ₂₀ Cu ₂ N ₆ S ₄	C ₂₀ H ₂₂ Cu ₂ N ₆ S ₄
formula wt	531.63	272.83	438.06	573.70	587.73	601.76
cryst size/mm	0.24 × 0.11 × 0.12	0.20 × 0.17 × 0.16	0.31 × 0.17 × 0.15	0.37 × 0.32 × 0.10	0.20 × 0.18 × 0.17	0.20 × 0.18 × 0.17
temp/K	273(2)	298(2)	291(2)	293(2)	291(2)	291(2)
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	P2(1)/c	P2(1)/c	P $\bar{1}$	C/c	P2(1)/c	P2(1)/n
<i>a</i> /Å	7.1820(14)	8.3845(9)	7.9960(11)	5.9102(7)	16.120(3)	5.8763(5)
<i>b</i> /Å	31.815(6)	17.7398(19)	9.7315(13)	27.551(3)	9.1088(18)	11.8384(9)
<i>c</i> /Å	8.5950(17)	7.0820(8)	13.5102(19)	7.4596(9)	17.478(4)	18.140(1)
α /deg	90.00	90.00	97.456(2)	90	90	90
β /deg	96.59(3)	103.849(2)	91.516(2)	112.032(2)	106.71(3)	95.748(0)
γ /deg	90.00	90.00	112.988(2)	90	90	90
vol/Å ³	1951.0(7)	1022.75(19)	956.2(2)	1125.9(2)	2458.1(8)	1255.6(2)
<i>Z</i>	4	4	2	2	4	2
<i>D</i> /g cm ⁻³	1.810	1.772	1.522	1.692	1.588	1.592
μ /mm ⁻¹	2.621	2.503	1.478	2.278	2.089	2.047
<i>F</i> (000)	1064	548	448	580	1192	612
rls collected	18615	4040	7158	3540	15286	8020
unique rlns	3476	1749	3529	1832	5738	2893
<i>R</i> _{int}	0.0525	0.0458	0.0204	0.0213	0.0654	0.0182
GOF	1.139	1.000	1.043	1.075	1.069	1.026
<i>R</i> ₁ ^a (<i>I</i> > 2σ(<i>I</i>))	0.0471	0.0408	0.0318	0.0524	0.0358	0.0370
w <i>R</i> ₂ ^a (all data)	0.1269	0.0777	0.0716	0.1379	0.0754	0.0904
Δρ _{max} /Δρ _{min} (e Å ⁻³)	0.405/−0.583	0.350/−0.423	0.273/−0.347	0.951/−0.790	0.332/−0.408	0.617/−0.668

^a $R_1 = \|F_o\| - \|F_c\| / \|F_o\|$; $wR_2 = [w(F_o^2 - F_c^2)^2 / w(F_o^2)]^{1/2}$.

Table 2. Bond Lengths (Å) and Angles (deg) for 1–6^a

Compound 1					
Cu1–N3	1.834(3)	Cu(1)–S(1)	2.5659(16)	Cu(1)–S(3)#1	2.6008(15)
Cu1–S2	2.431(1)	Cu(2)–N(2)	1.724(4)	Cu(2)–N(1)#2	1.980(4)
Cu(2)–N(4)#3	2.356(4)	Cu(2)–S(4)	2.4415(13)		
N(3)–Cu(1)–S(2)	124.07(11)	N(3)–Cu(1)–S(1)	85.29(12)	S(2)–Cu(1)–S(1)	115.97(5)
N(4)#3–Cu(2)–S(4)	112.61(12)	N(3)–Cu(1)–S(3)#1	111.02(11)	S(2)–Cu(1)–S(3)#1	99.93(6)
N(2)–Cu(2)–N(4)#3	112.63(16)	S(1)–Cu(1)–S(3)#1	122.22(5)	N(2)–Cu(2)–N(1)#2	111.04(16)
N(1)#2–Cu(2)–N(4)#3	94.52(16)	N(2)–Cu(2)–S(4)	103.78(13)	N(1)#2–Cu(2)–S(4)	122.45(10)
Compound 2					
Cu(1)–N(3)#1	1.981(3)	Cu(1)–N(2)#2	2.013(3)	Cu(1)–S(1)	2.3609(9)
Cu(1)–S(2)	2.4042(1)				
N(3)#1–Cu(1)–N(2)#2	110.87(12)	N(3)#1–Cu(1)–S(1)	121.65(9)	N(2)#2–Cu(1)–S(1)	106.72(8)
N(3)#1–Cu(1)–S(2)	102.13(10)	N(2)#2–Cu(1)–S(2)	117.93(10)	S(1)–Cu(1)–S(2)	97.56(4)
Compound 3					
Cu(1)–N(3)	1.983(2)	Cu(1)–N(4)	1.987(2)	Cu(1)–N(5)#1	1.997(2)
Cu(1)–S(3)	2.4653(8)				
N(3)–Cu(1)–N(4)	112.65(9)	N(3)–Cu(1)–N(5)#1	111.35(10)	N(3)–Cu(1)–S(3)	104.08(7)
N(4)–Cu(1)–N(5)#1	113.93(10)	N(5)#1–Cu(1)–S(3)	106.43(7)	N(4)–Cu(1)–S(3)	107.64(7)
Compound 4					
Cu1–N2	1.943(7)	Cu1–N1#1	1.960(6)		
Cu1–S1	2.364(2)	Cu1–S1#2	2.481(2)		
N2–Cu1–N1#1	118.9(3)	N2–Cu1–S1	114.2(3)	N1#1–Cu1–S1	108.1(2)
N2–Cu1–S1#2	110.9(3)	N1#1–Cu1–S1#2	99.0(2)	S1–Cu1–S1#2	103.67(5)
Compound 5					
Cu(1)–N(6)#1	1.972(2)	Cu(1)–N(3)	1.997(2)	Cu(1)–S(3)	2.3651(8)
Cu(1)–S(2)	2.4373(8)	Cu(2)–N(5)	1.964(2)	Cu(2)–N(4)#2	1.977(2)
Cu(2)–S(4)	2.3492(8)	Cu(2)–S(1)#2	2.4623(8)		
N(6)#1–Cu(1)–N(3)	112.01(9)	N(6)#1–Cu(1)–S(3)	119.02(7)	N(3)–Cu(1)–S(3)	105.16(7)
N(6)#1–Cu(1)–S(2)	107.62(7)	N(3)–Cu(1)–S(2)	106.69(7)	S(3)–Cu(1)–S(2)	105.57(3)
N(5)–Cu(2)–N(4)#2	117.07(9)	N(5)–Cu(2)–S(4)	117.54(7)	N(4)#2–Cu(2)–S(4)	105.19(7)
N(5)–Cu(2)–S(1)#2	103.90(7)	N(4)#2–Cu(2)–S(1)#2	106.09(7)	S(4)–Cu(2)–S(1)#2	106.00(3)
Compound 6					
Cu(1)–N(3)	1.908(3)	Cu(1)–N(2)#1	1.936(2)	Cu(1)–S(1)	2.3006(9)
N(3)–Cu(1)–N(2)#1	122.12(12)	N(3)–Cu(1)–S(1)	123.19(10)	N(2)#1–Cu(1)–S(1)	110.14(8)
C(10)–S(1)–Cu(1)	106.21(10)				

^a Symmetry codes for **1**: #1 $-x + 2, -y, -z + 2$; #2 $x + 1, y, z$; #3 $x, -y + 1/2, z + 1/2$. Symmetry codes for **2**: #1 $x, -y + 3/2, z - 1/2$; #2 $-x + 1, -y + 1, -z + 1$; #3 $x, -y + 3/2, z + 1/2$; #4 $-x + 1, -y + 2, -z + 1$. Symmetry codes for **3**: #1 $-x, -y + 1, -z$. Symmetry codes for **4**: #1 $x + 1, y, z$; #2 $x + 1/2, -y + 3/2, z + 1/2$. Symmetry codes for **5**: #1 $x, y - 1, z$; #2 $x, -y + 1/2, z - 1/2$; #3 $x, -y + 1/2, z + 1/2$; #4 $x, y + 1, z$. Symmetry codes for **6**: #1 $x - 1, y, z$; #2 $x + 1, y, z$; #3 $-x + 1, -y + 1, -z + 1$.

lens. The laser beam was divided into two beams. One was used to monitor the incident laser energy meter, and the other was focused onto the sample cell. The input and the output energies of the beams were measured with an energy meter (Laser Precision Rjp-735), which was linked to a computer by an IEEE interface.¹³ The experimental data were collected utilizing a single shot at a rate of 1 pulse per minute to avoid the influence of thermal effects.

X-ray Crystallography. Polymer **1** measurements were made on a MART APEX II CCD diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). Crystallographic data for the compounds **2–6** was collected on a Bruker APEX-II area-detector diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied by using SADABS. The structures were solved with direct methods and refined with full-matrix least-squares techniques on F^2 using the SHELXTL program package.¹⁴ All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restraints. Data affected by the bad quality of crystal **4** caused some difficulties in the crystal structure solution. The cation in **4**, which is disordered about a general position, was refined as a cationic species of 0.5 site occupancy. The two pyridyl rings were refined rigid hexagons of 1.39 Å sides; the C–N distances were restrained to 1.45 ± 0.01 Å and the C–C distances to 1.50 ± 0.01 Å. The cation in **6**, which lies about

a center-of-inversion, is disordered in four of the six methylene carbon atoms; the methyl carbon atoms bonded to the pyridyl rings are ordered. The disordered atoms were refined with 0.25 site occupancy. The C–N distances were restrained to 1.45 ± 0.01 Å and the C–C distances to 1.54 ± 0.01 Å. Additionally, the 1,3-related C $\cdots$ C distances were restrained to 2.51 ± 0.01 Å. Crystal data for **1–6** are summarized in detail in Table 1. Selected bond lengths and bond angles are put in Table 2. CCDC-623355 (for **2**), 622700 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax, (+44)-1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

Results and Discussion

Synthesis. The preparation of the compounds is straightforward, and the yields were more than 42%. Upon the addition of a methanol solution of quaternary ammonium salt of [Py-C $_x$ -Py]²⁺ ($x = 1–5$) to a DMF solution of the CuNCS with excess KNCS salt crystal precipitation was observed in 2–10 h. The precipitates were filtered, washed with DMF/CH₃OH and dried *in vacuo* to give pure complexes **1–6**. Repeat preparation

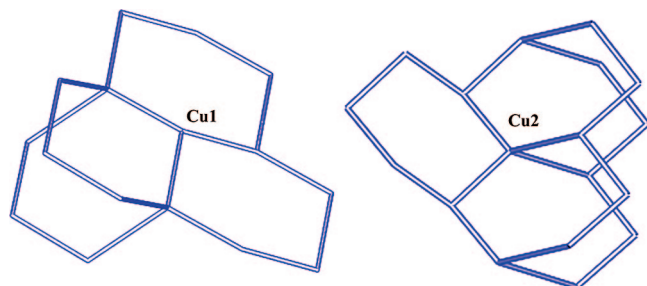


Figure 1. View of the coordination environment of the Cu1(a) and Cu2(b) center in **1**, showing the 6⁴ and 6⁵ connection modes, respectively.

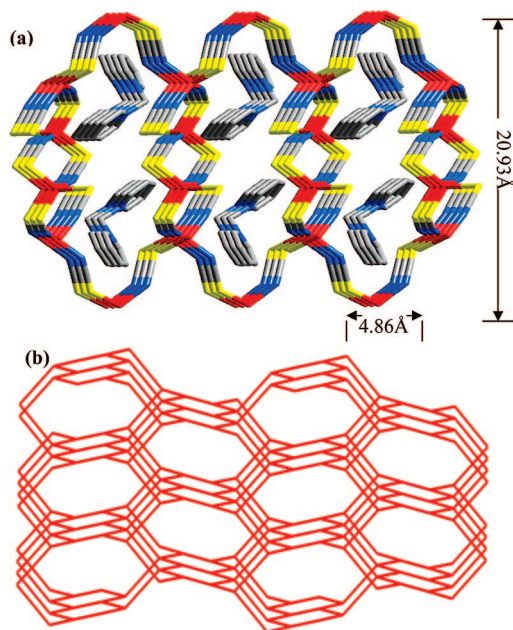


Figure 2. Perspective views showing the 3D open framework containing large tunnel (a) and the schematic representation of (6,3)/(6,4) joint topology (b) in **1**.

could not obtain a good crystal for **4**, which shows a weak directing ability for bpbt. All solid compounds were stable in air.

Description of Crystal Structures. Structure of {(bpm)-[Cu(NCS)₄]}_n **1.** Complex **1** assembled in a DMF–methanol system, crystallizes in a monoclinic space group *P*2(1)/*c* and possesses a 3D network with the porous topology. The polymeric anion comprises pairs of crystallographically independent copper atoms Cu(1,2) linked by four thiocyanate groups. Both copper atoms are four-coordinate, Cu1 having an environment of one nitrogen atom [Cu–N, 1.834(3) Å] and three sulfur atoms [Cu–S, 2.565(1), 2.600(1), and 2.431(1) Å], while Cu2 is coordinated by one sulfur atom [Cu–S, 2.441(1) Å] and three nitrogen atoms [Cu–N, 1.724(4), 1.980(4), and 2.356(4) Å]. Two Cu1 and two μ -N,S NCS form a Cu₂(NCS)₂ dimer, and the separation of the adjacent Cu(I)⋯Cu(I) is 4.77 Å; in the dimer each Cu1 serves as a three-connecting node and there exist four Cu₆ metal rings around it (Figure 1); while Cu2 serves as a four-connecting node, around it there exist five Cu₆ rings. Thus in this manner, a 3D porous (6,3)/(6,4) joint topology forms (Figure 2a), indicative of distinctive difference from widely encountered 3D (6,3) and (6,4) frameworks.¹⁵

The most fascinating feature of **1** is the occurrence of many three-dimensional channels viewing from the *a* direction; these

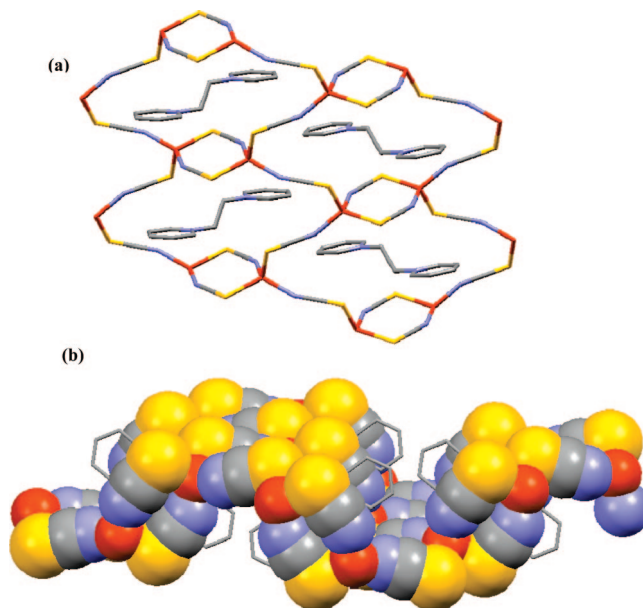


Figure 3. (a) 2D network of macrocycles of **2** viewing along a direction, showing the bpe filled porous framework. (b) The perpendicular directing mode of bpe in the undulating polymeric structure. Cation is shown as capped stick mode, anion as space-filled.

channels possess an inner cavity with size of 20.93 × 4.86 Å, in which bpm bipyridinium counterions were accommodated (Figure 2b).

Another particularly salient feature of the polymeric structure is the charge-balanced bpm cation pairs trapped within the channels of the molecule, which serve as the nut⋯bolt of the porous combination (Figure 2a). Each bpm acts as a bent geometry with a N–C–N angle of 101.87°, and the dihedral angle of the two pyridyl rings of 71.18°. The distance between the two parallel pyridyl rings of the bpm pairs is 6.65 Å, which shows no apparent π – π interactions. However, it is unlikely that an empty 3D framework is preformed for the encapsulation of the cation pairs; instead, the formation of the polymeric motif can be best described as a bpm ion pair-induced self-assembly of the Cu with NCS ligands. In addition, although there are many examples for CuNCS 3D self-assembly induced or controlled by an organic cation (such as [C₅H₆N]⁺ **1a**,⁷ [Me₂CNMe₂]⁺ **1b**,^{9a} Me₃N⁺ **1c**,^{9c}), complex **1** represents the first product of assembly induced by coexistent 1, ω -cation pairs. In compounds **1a** and **1c**, the fundamental building unit is Cu₂S₂ and metal cycles Cu₄ (for **1a**), Cu₃ (for **1c**) as skeletal units, while in **1** and **1b**, the fundamental building unit is Cu₂(SCN)₂, and metal cycles Cu₄ (for **1**), Cu₆ (for **1b**) as skeletal units. This reflects that the 3D motifs in the compounds described above with the smaller counterions [C₅H₆N]⁺, [Me₃NH]⁺ are somewhat more closely packed (Cu–Cu distance 2.801 Å and 2.975 Å) than those of compounds with the more spacious bpm²⁺, [Me₂CNMe₂]⁺ cations (Cu–Cu distance 4.773 Å and 5.307 Å, respectively).

Structure of {(bpe)[Cu₂(NCS)₄]}_n **2.** The X-ray single-crystal structural analysis showed that compound **2** crystallizes in the monoclinic system with space group *P*2(1)/*c*. A portion of the polymer is shown in Figure 3. The structure of **2** is made up of organic bpe cations trapped in the infinite 2D inorganic [Cu₂(NCS)₄]_n^{2n−} nets.

In the polymeric structure, copper atoms are in distorted tetrahedral sites, covalently coordinated to two N atoms and two S atoms from distinguished NCS[−] groups with the bond

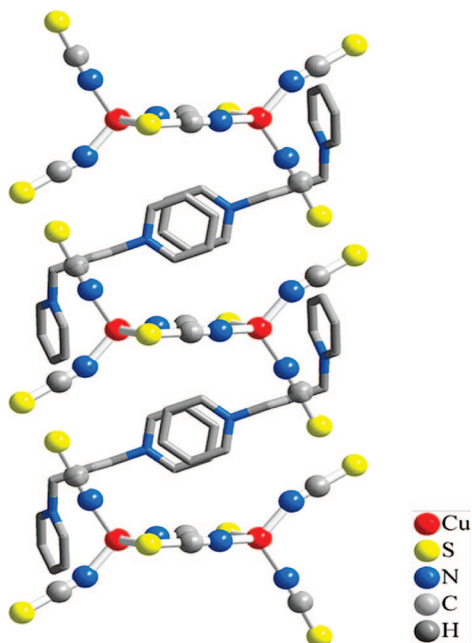


Figure 4. Molecular structure of **3**. Cation is shown as capped stick mode, anion as ball stick.

angles ranging from 97.56(4) to 121.65(9)°. They compare well with those found in its pyridinium analogue {[pyH⁺]-[Cu₂(SCN)₃][−]}_n (103.7(1)–122.1(4)°).⁷ The Cu–N distances vary from 1.981(3) and to 2.013(3) Å, comparable with those found in the pyridinium analogue (1.93–1.95 Å) and [(CuBr)₃(C₁₀H₇N₃)] (2.004(2) Å).⁶

Each inorganic polymeric net is composed of large hexagonal rings, which is formed by sharing four μ -N,S NCS[−] groups and two [Cu₂(NCS)₂] rectangular units and further binds with six adjacent hexagonal rings. In these hexagonal rings there exist three types of opposite furthest Cu–Cu dimensions: 13.99, 8.41 and 9.14 Å (Figure 3a). However, the Cu···Cu separations through the single μ -NCS bridge have one distance of 5.93 Å; the Cu–Cu distance in the [Cu₂(NCS)₂] rectangular unit is 5.19 Å. Topologically, the network can be identified as a 2D (6,3) net where two bridging NSC[−] anions in the [Cu₂(NCS)₂] rectangular units only act as a connector, slightly different from the regular one, [Cu^{II}(DMF)₄].⁸

The bpe dication acts as a classical anti-conformation with two parallel pyridyl rings. Along the *b*-direction, the 2D net undulates with threadlike bpe cations penetrating it (Figure 3b). Interestingly the bpe exhibit two types of perpendicular directing modes. This is not by accident. This perpendicular penetrating mode should be responsible for the undulating polymeric structure. There have been reported pseudorotaxane of bis(benzimidazole) dication acting as template for threading through dibenzo-24-crown-8.¹⁶ However, polyrotaxane architecture consisting of a 2D inorganic network perforated with organic molecules was little reported. An only closely related example is bis[4-(*N*-benzylpyridinium)] piperazine dication-templated Cd(SCN)₃]_{2n}^{2n−} polymeric framework,¹⁷ and from this point of view, compound **2** can be regarded as the first representative example of polypseudorotaxane from bis(pyridinium)dication.

Structure of {(bppp)[Cu(NCS)₃]}_n **3.** The host structure of **3** is a [Cu₂(NCS)₆] dimer with Cu–Cu distances of 5.19 Å (Figure 4). Each copper is coordinated by three N atoms and one S atom from four NCS groups. Between the dimers there also exist pairs of bppp bipyridinium counterions. Each bppp

behaves as a gauche-anti conformation. The distance between the two parallel pyridyl rings of the bppp pairs is 4.06 Å. Since the Cu–Cu distances of 5.19 Å is the same as that in **2**, compound **3** can be regarded as an excision product from **2**. So bppp plays a different role in the formation of **3** with that of bpe in **2**.

Structure of {(bpbt)[Cu(NCS)₄]}_n **4.** The polyanionic structure of **4** exists as a two-dimensional network which can be regarded as sheets of [Cu(SCN)₄]_n lying essentially parallel to the (101) plane (Figure 5a). Within the sheets each copper(I) center is coordinated by three (two μ -S and one μ -N) μ_3 -S,S,N thiocyanato ligands (Scheme 1d), which leads to the formation of ten-membered (Cu–S–Cu–NCS–Cu–SCN–) rings. Each of the rings is fused to six other rings to give a distorted honeycomb pattern. The fourth ligand points out of the plane of sheet as a terminal mode.

The bpbt cations are located in large cavities among the sheets (Figure 5b) in the polymer with no unusually short contacts to it, as evidenced by their considerable flexibility for maneuvering. In consequence, cation geometries are imprecise as well as being somewhat uncertain in their assignment.

Structure of {(bppt)[Cu₂(NCS)₄]}_n **5.** The X-ray single-crystal structural analysis showed that compound **5** crystallizes in the monoclinic system with space group *P*2(1)/*c*. A portion of the polymer is shown in Figure 6. The structure of **5** has also an interlocked geometry between bppt cations and the infinite [Cu₂(NCS)₄]_n nets similar to that of **2**.

In the polymeric structure, copper atoms are in distorted tetrahedral geometry, covalently coordinated to two N atoms and two S atoms from distinguished NCS[−] groups with the bond angles ranging from 103.90(7) to 119.02(7)°. They compare well with those found in its pyridinium analogue {[pyH⁺]-[Cu₂(SCN)₃][−]}_n (103.7(1)–122.1(4)°).⁷ The Cu–N distances vary from 1.964(2) to 1.997(2) Å, comparable with those found in pyridinium analogue (1.93–1.95 Å) and [(CuBr)₃(C₁₀H₇N₃)] (2.004(2) Å).⁶

Each inorganic polymeric planar net is composed of large hexagonal rings formed by sharing four NCS[−] and two [Cu₂(NCS)₂] rectangular units with six adjacent hexagonal rings. In these hexagonal rings there also exist three types of opposite furthest Cu–Cu dimensions: 12.4, 10.7 and 10.2 Å (Figure 2). Correspondingly the Cu···Cu separations through the μ -NCS single bridge have two distances of 5.8 and 5.9 Å; the Cu–Cu distance in the [Cu₂(NCS)₂] rectangular unit is 5.10 Å.

The bppt dication threads exhibit a similar templating effect with that of bpp in **2**. The crystal packing is dominated by noncovalent supramolecular interaction. Perhaps that is why **2** and **5** possess similar framework. However the difference from the Cu···Cu separations through the μ -NCS single bridge in **2** and **5** shows that **5** has a less compact anion packing structure than **2**, which is consistent with the effects of the cation size.⁹ Another closely related example is the 2D tetrathiafulvalene (TTF)–thiocyanate complex, (TTF)Cu(SCN)₂ **5a**,^{6d} which possesses the same space group *P*2(1)/*c* and topological (6,3) net with that of **2** and **5**.

However, in **2** the anion sheet exhibits apparent undulation (Figure 3b), which indicates the influence of the template effects of bpe²⁺ on the crystal structure is greater than bppt²⁺ and TTF⁺.

Structure of {(bph)[Cu₂(NCS)₄]}_n **6.** An ORTEP drawing with the atom numbering scheme of **6** is shown in Figure 7. Each Cu^I atom is tricoordinated by two μ -N,S NCS[−] groups and one terminal NCS[−] group with Cu–N (*t*-NCS), Cu–N (μ -NCS), and Cu–S distances of 1.908(3), 1.936(2) and

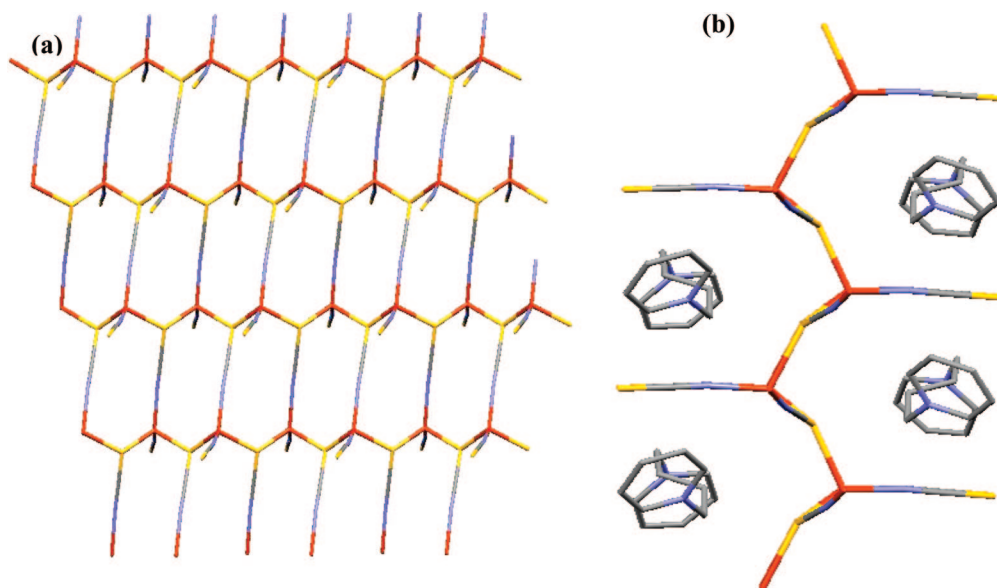


Figure 5. (a) Top view of a 2D “open” 10-membered ring based (6,3) network motif in **4** showing the coordination environment of Cu.

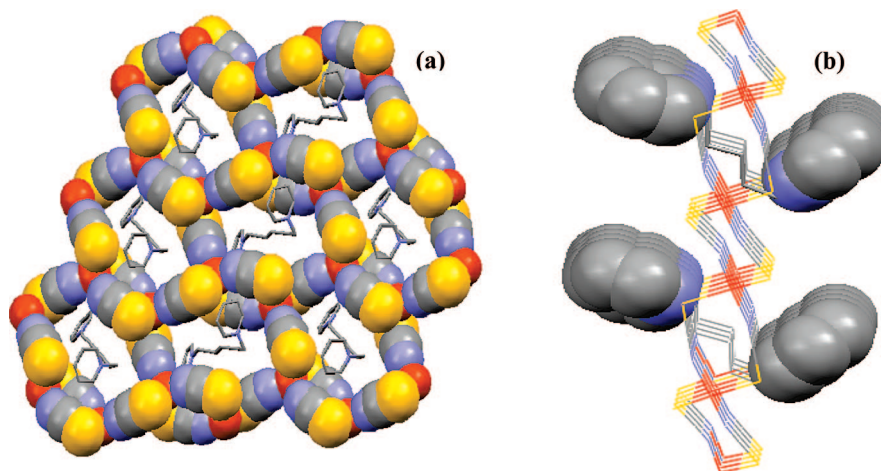


Figure 6. (a) Top view of a 2D “open” motif in **5**. Cation is shown as capped stick style, anion as space-filled style. (b) Solid state of **5** showing the threading mode of bis(pyridinium) dication.

2.3006(9) Å, respectively. Each polymeric anion structure comprises the $(\text{CuNCS})_n$ “folding ruler-shaped” inorganic chains extend along the *a*-direction. It is particularly interesting that there exist complementary chain-pairs in the anion. Two nearest chains were drawn in through $\text{S} \cdots \text{Cu}$ interactions (2.90 Å) to form a new 1D hanging ladder-shaped chain. In this chain the nearest $\text{Cu} \cdots \text{Cu}$ interaction is 3.63 Å; the distance is shorter than that in the $[\text{Cu}_2(\text{NCS})_2]$ rectangular unit of compound **1** (4.77 Å), compounds **2** and **3** (5.19 Å) and compound **5** (5.10 Å), which shows that the cooperative interaction plays an important role in forming these complementary chains. It is interesting to compare compound **6** with other 1D anion salts based on the Ph_4P^+ ,^{9b} the electron donor molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF)⁺ and its isomers.^{6e-i} In all the latter compounds the anion array is organized in infinite zigzag chains of $\text{Cu}(\text{SCN})_2$, so this 1D hanging ladder-shaped chain in **6** with complementary $\text{S} \cdots \text{Cu}$ interactions can be regarded as a novel $\text{Cu}(\text{SCN})$ assembly motif. In the *bc* plane these chains show two packing modes along the *b*-direction and the bph^{2+} cations are located in the separations among the chains with no short contacts to them.

Template Effect in Directing the Crystal Structures. By changing the templates 1, ω -bis(pyridinium)alkane from $\omega = 1$ to 6, with the same bridging ligand and metal salt, we have succeeded in synthesizing four types of copper(I)–NCS complexes: compound **1** has a 3D porous (6,3)/(6,4) joint topology structure, compounds **2** and **5** have two-dimensional polypseudorotaxane structures, compound **3** has a dimeric structure, compound **4** has a two-dimensional honeycomb structure, and compound **6** exhibits an interesting 1D hanging ladder-shaped complementary chain structure. In compounds **1–3**, and **5**, there exists an analogous building unit of $\text{Cu}_2(\text{NCS})_6$ dimer. In the dimer **3**, two NCS group bridges the two Cu atoms in a N,S-mode. The remaining four NCS in the dimer, which could be accordingly viewed as a potential bidentate “ligand”, coordinate to the Cu atoms in the neighboring dimer units, thus forming two-dimensional layered structures of **2** and **5**. When another Cu knot appeared between these $\text{Cu}_2(\text{NCS})_6$ units, a three-dimensional compound **1** was formed. The development of such a layer is blocked in **3**, which shows the dimeric structure with the coordination of the Cu atom terminated by bppp cation cutter.

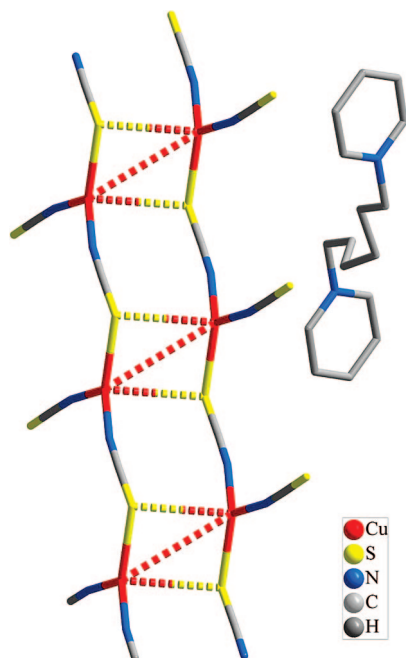


Figure 7. View of the 1D hanging ladder chain containing complementary S...Cu interactions.

In compounds **1–3** and **5**, NCS acts as the classical μ -N,S-coordinate mode, while in **4** and **6**, NCS behaves as terminal-mode and μ_3 -S,S,N mode (or pseudo- μ_3 -S,S,N mode) and no above dimeric unit exists. The pronounced structural differences in **1–6** have revealed that the dication templates play a key role in directing the structures of them because the preparations of the six compounds were conducted under similar experimental conditions. Actually, these templates serve as the charge-compensating counterions of the polymeric anions in **1–6**. The cations of $\omega = 2, 4, 5, 6$ with larger size favor packing with a one- to two-dimensional anionic layer, whereas the cation of $\omega = 1$ with a smaller size directs the formation of a three-dimensional anionic network. In the case of **3**, the steric factor and the weak flexibility of bppp may exert a cooperative effect in the template-assisted formation of this dimer.

These results demonstrate that zero-, one-, two-, and three-dimensional metal extended motifs of NCS are reachable by a suitable choice of organic blocks. The title compounds are mainly based on the coordination mode of SCN^- or NCS^- linkers. There are existing complexes of $\text{Cu}(\text{SCN})_2$ in the presence of metal sulfide ligands such as $[\text{ReS}_4]^{-18}$ and $[\text{WS}_4]^{2-}$.¹⁹ Because the $[\text{MS}_4]^{n-}$ ($\text{M} = \text{Re}, \text{W}, n = 1-2$) tetrahedron can bind directly M^+ successively with its six S–S edges,^{11c} these diverse binding types means that new structural types could be expected through the introduction of matched cation templates or an appropriate anion linker or knot, which may further bring interesting physical properties.

Third-Order NLO Properties of 3. The study about inorganic–organic hybrid polymers is greatly focused on novel structures and properties. Recently we found that many hybrid polymers exhibit interesting third order nonlinearities in DMF solution. Determination of the molecular weight of these polymers in DMF solution showed that the number-average molecular weights (M_n) and the weight-average molecular weights (M_w) are relatively larger, which indicated that polymers are intact (or partly intact) in DMF solution.²⁰

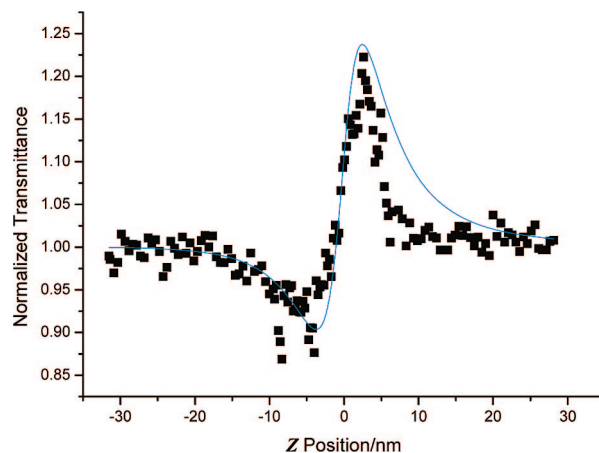


Figure 8. Z-Scan experiments of polymer **3** in $1.25 \times 10^{-4} \text{ mol dm}^{-3}$ DMF solution at 532 nm. The data were obtained by dividing the normalized Z-scan data obtained under a closed aperture configuration by the normalized Z-scan data of open aperture configuration. The black dots are the experimental data, and the solid curve is the theoretical fit.

A preliminary study of the third-order NLO properties of **3** was carried out by the Z-scan method in a $1.33 \times 10^{-4} \text{ mol L}^{-1}$ DMF solution. The results illustrate that the absorption is weak and the nonlinear optical properties are dominated by nonlinear refraction. The Z-scan data of the compound are given in Figure 8. The filled boxes are the experimental data measured under an open aperture. The nonlinear refractive components of the compound were assessed by dividing the normalized Z-scan data obtained in an open-aperture configuration. An effective third-order nonlinear refractive index, n_2 , can be derived from the difference between normalized transmittance values at valley and peak positions (ΔT_{V-P}) by using eq 1, where ΔT_{V-P} is the difference between normalized transmittance values at valley and peak positions, α_0 is the linear coefficient, L is the sample thickness, I is the peak irradiation intensity at focus, and λ is the wavelength of the laser. The effective third-order NLO refractive index was calculated to be $3.03 \times 10^{-11} \text{ esu}$. The data show that the cluster has a positive sign for refractive nonlinearity, and the valley–peak pattern of the normalized transmitted curve obtained in the closed-aperture configuration shows the characteristic self-focusing behavior of propagating light in the sample.

$$n_2^{\text{eff}} = \frac{\lambda \alpha_0}{0.812\pi I(1 - e^{-\alpha_0 L})} \Delta T_{V-P} \quad (1)$$

The good optical data for **3** implies an overall balance effect on NLO from the dimer skeleton and the organic dication structure. In addition, although the concentration of the dimer in solution is apparently limited by their poor solubility, larger nonlinear index values may be expected if higher concentrations are attained.

The Fluorescence Properties. The study of luminescent properties of 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.²¹ The fluorescence spectra of **1–6** in solid state were recorded using a HITACHI-F-4500 (fluorescence spectrophotometer) in a 1 cm quartz cell. The excitation and emission bandwidths were set at 5 nm. The solid spectra of complexes **1–3** at room temperature are illustrated in Figure 9. Excitation of the solid samples at 397

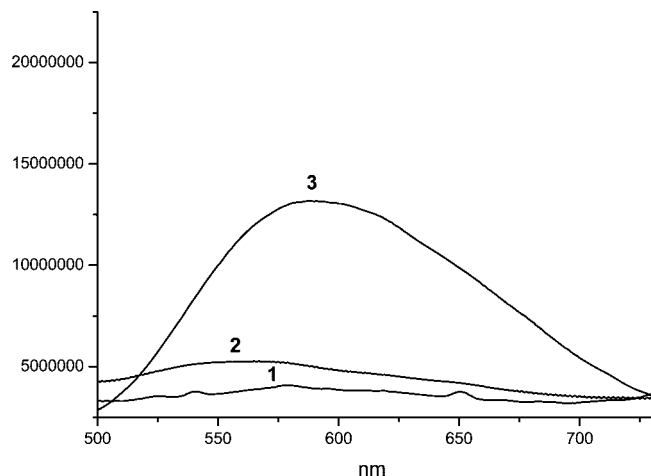


Figure 9. Solid-state emission spectra of **1–3** at room temperature.

nm (for **1**), 397 nm (for **2**) and 413 nm (for **3**) produces emissions with peak maximum at 579 nm (for **1**), 567 nm (for **2**) and 591 nm (for **3**). Polymers **1** and **2** possess weaker luminescence emission than **3**, but no photoluminescence was observed for **4–6**. On the basis of the photoluminescence of other CuSCN compound such as $[\text{Cu}_2(\text{bppz})(\text{SCN})]_n$ ²² type complexes, the emissions of the three compounds are tentatively ascribed to a ligand-to-metal charge transfer ($\text{S} \rightarrow \text{Cu}$).

Conclusions

In summary, we developed a convenient way to fabricate encapsulation assemblies by changing 1, ω -bis(pyridinium)alkane cations. This presentation summarizes the most important results on the use of 1, ω -bis(pyridinium)alkane cations as directing agents for the syntheses of a wide range of metal halide/ pseudohalide assemblies (such as monomeric, oligomeric, and polymeric extended structures). The excess NCS^- facilitates the preassembly of Cu^+ atom, yielding new CuNCS complexes, and this may be a general route to constructing novel CuNCS frameworks, which may not be obtained directly by other methods. The present work has shown that 0–3D organic–inorganic hybrid frameworks can be constructed from CuNCS and the 1, ω -(dipyridino-1-yl)alkane cations ($\omega = 1–6$). It is noteworthy that the striking structural difference among compounds **1–6** is simply caused by a subtle difference in the flexible organic dications' structure, i.e., the presence of different polymethylene moieties in them, which are mainly attributed to the template effects during the reactions. These templates, acting as charge-compensating counterions, play an important role in the crystal packing with the polymeric anionic layers or networks. It is hoped that this will stimulate a closer look into this emerging area of supramolecular chemistry and provide an avenue for preparing new metal halide/pseudohalide functional materials. Further work is in progress to extend this facile method to other metal pseudohalides, to evaluate the influences of cation structure modifications and different anions on the resulting supramolecular structures as well to elucidate the mechanism of inorganic polymeric framework formation, to further probe their structure/properties relationship with potential applications in functional materials.

Acknowledgment. This research was funded by the SFDYS in Henan Province (Grant Nos. 0612002800, 6410002800) and

the NSFC (Grant No. 20671083). We thank Dr. Meng Xiang-Gao, Huazhong Normal University, and professor Li Hua, Wuhan University, for structural data collection.

References

- (1) Escamilla, G. H.; Newkome, G. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1937–1940.
- (2) (a) Fuhrhop, J.-H.; Koning, J. In *Membranes and Molecular Assemblies: the Synkinetic Approach*; Stoddart, J. F., Ed.; Monographs in Supramolecular Chemistry; The Royal Society of Chemistry: Cambridge, U.K., 1994. (b) Neve, F.; Crispini, A. *Cryst. Growth Des.* **2001**, *1* (5), 387–393.
- (3) Xiao, X.; Tao, Z.; Ge, J.-Y.; Ma, P.-H.; Xue, S.-F.; Zhu, Q.-J. *Acta Chim. Sin.* **2006**, *64* (2), 131–138.
- (4) Li, H.-H.; Chen, Z.-R.; Li, J.-Q.; Huang, C.-C.; Zhang, Y.-F.; Jia, G.-X. *Eur. J. Inorg. Chem.* **2006**, 2447–2453.
- (5) (a) Rath, N. P.; Holt, E. M.; Tanimura, K. *Inorg. Chem.* **1985**, *24*, 3934–3938, and references therein. (b) Hardt, H. D.; Pierre, A. *Inorg. Chim. Acta* **1977**, *25*, L59–L60.
- (6) (a) Deluzet, A.; Perruchas, S.; Bengel, H.; Batail, P.; Molas, S.; Fraxedas, J. *Adv. Funct. Mater.* **2002**, *12* (2), 123–128. (b) Beno, M. A.; Wang, H. H.; Kini, A. M.; Carlson, K. D.; Geiser, U.; Kwok, W. K.; Thompson, J. E.; Williams, J. M.; Ren, J. Q.; Whangbo, M.-H. *Inorg. Chem.* **1990**, *29*, 1599–1601. (c) Geiser, U.; Beno, M. A.; Kini, A. M.; Wang, H. H.; Schultz, A. J.; Gates, B. D.; Cariss, C. S.; Carlson, K. D.; Williams, J. M. *Synth. Met.* **1988**, *27*, A235–A241. (d) Pyrk, G. J.; Fernando, Q.; Inoue, M. B.; Inoue, M. *Inorg. Chim. Acta* **1989**, *156*, 257–264. (e) Schultz, A. J.; Beno, M. A.; Geiser, U.; Hau Wang, H.; Kini, A. M.; Williams, J. M.; Whangbo, M. H. *J. Solid State Chem.* **1991**, *94*, 352–361. (f) Urayama, H.; Yamochi, H.; Saito, G.; Nozawa, K.; Sugano, T.; Kinoshita, M.; Sato, S.; Oshima, K.; Kawamoto, A.; Tanaka, J. *Chem. Lett.* **1988**, *55*, 58. (g) Urayama, H.; Yamochi, H.; Saito, G.; Sato, S.; Kawamoto, A.; Tanaka, J.; Mori, T.; Maruyama, Y.; Inokuchi, H. *Chem. Lett.* **1988**, *463*, 466. (h) Moustarder, S. L.; Hudhomme, P.; Durand, C.; Mercier, N.; Azcondo, M. T.; Delhaes, P.; Riou, A.; Gorgues, A. *J. Mater. Chem.* **2000**, *10*, 617–623. (i) Rahal, M.; Chasseau, D.; Gaultier, J.; Ducasse, L.; Kurmoo, M.; Day, P. *Acta Crystallogr.* **1997**, *B53*, 159–167.
- (7) Raston, C. L.; Walter, B.; White, A. H. *Aust. J. Chem.* **1979**, *32*, 2757–2761.
- (8) Kovbasyuk, L. A.; Babich, O. A.; Kokozay, V. N. *Polyhedron* **1997**, *16* (1), 161–163.
- (9) (a) Hehl, R.; Thiele, G. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2167–2172. (b) Thiele, G.; Hehl, R. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1736–1740. (c) Babich, O. A.; Kokozay, V. N.; Pavlenko, V. A. *Polyhedron* **1996**, *15*, 2727–2731. (d) Wilk, A.; Massa, W.; Friebel, C.; Reinen, D. *Z. Anorg. Allg. Chem.* **1992**, *608*, 88–99.
- (10) (a) Jagner, S.; Helgesson, G. *Adv. Inorg. Chem.* **1991**, *37*, 1–41. (b) Domasevitch, K. V.; Rusanova, J. A.; Vassilyeva, O. Y.; Kokozay, V. N.; Squattrito, P. J.; Sieler, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1999**, 3087–3093. (c) Rusanova, J. A.; Domasevitch, K. V.; Vassilyeva, O. Y.; Kokozay, V. N.; Rusanov, E. B.; Nedelko, S. G.; Chukova, O. V.; Ahrens, B.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **2000**, 2175–2182.
- (11) (a) Neman, A. A. *Chemistry and Biochemistry of Thiocyanic Acid and Derivatives*; Academic Press: New York, 1975. (b) Golub, A. M.; Kohler, H.; Skopenko, V. V. *Chemistry of Pseudohalides*; Elsevier: Amsterdam, 1986. (c) Niu, Y. Y.; Zheng, H. G.; Hou, H. W.; Xin, X. Q. *Coord. Chem. Rev.* **2004**, *248*, 169–183.
- (12) (a) Almarzogi, B.; George, A. V.; Isaacs, N. S. *Tetrahedron.* **1986**, *42* (2), 601–607. (b) Loeb, S. J.; Tiburcio, J.; Vella, S. J.; Wisner, A. J. *Org. Biomol. Chem.* **2006**, *4* (4), 667–680. (c) Neve, F.; Crispini, A. *Cryst. Growth Des.* **2001**, *1* (5), 387–393. (d) Ikegami, Y.; Muramatsu, T.; Hanaya, K. *J. Am. Chem. Soc.* **1989**, *111* (15), 5782–5787.
- (13) (a) Sheik-bahae, M.; Said, A. A.; Wei, T. H.; Hagan, D. J.; Van Stryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760–769. (b) Sheik-bahae, M.; Said, A. A.; Van Stryland, E. W. *Opt. Lett.* **1989**, *14*, 955–957.
- (14) Sheldrick, G. M. *SHELXL93*; University of Göttingen: Göttingen, Germany, 1993.
- (15) (a) Shin, D. M.; Lee, I. S.; Chung, Y. K. *Inorg. Chem.* **2003**, *42*, 8838–8846. (b) Pschirer, N. G.; Ciurtin, D. M.; Smith, M. D.; Bunz, U. H. F.; Loye, H. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 583–585. (c) Yaghi, O. M.; Li, H. L.; Gory, T. L. *Inorg. Chem.* **1997**, *36*, 4292–4203. (d) Tian, Y.-Q.; Cai, C.-X.; Ren, X.-M.; Duan, C.-Y.; Xu, Y.; Gao, S.; You, X.-Z. *Chem. Eur. J.* **2003**, *9* (22), 5673–5685. (e) Carrillo-

- Cabrera, W.; Caroca-Canales, N.; Peters, K.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1993**, 619 (9), 1556–1563. (f) Bi, M. H.; Li, G. H.; Hua, J.; Liu, X. M.; Hu, Y. W.; Shi, Z.; Feng, S. H. *CrystEngComm* **2007**, 9, 984–986.
- (16) Li, L. W.; Clarkson, G. J. *Org. Lett.* **2007**, 9 (3), 497–500.
- (17) Lai, L. L.; Wu, C. H.; Lu, K. L.; Wen, Y. S.; Liu, Y. H.; Wang, Y.; Cheng, K. L.; Soldatov, D. V.; Yu, Z.; Yu, K. *CrystEngComm* **2007**, 9, 345–349.
- (18) Muller, A.; Hildebrand, A.; Krickemeyer, E.; Khan, M. I.; Penk, M.; Bogge, H.; Secheresse, F. *Chem. Eur. J.* **1998**, 4, 1932–1937.
- (19) (a) Manoli, J. M.; Potvin, C.; Secheresse, F.; Marzak, S. *Chem. Commun.* **1986**, 1557–1558. (b) Potvin, C.; Manoli, J. M.; Secheresse, F.; Marzak, S. *Inorg. Chem.* **1987**, 26, 4370–4374. (c) Manoli, J. M.; Potvin, C.; Secheresse, F.; Marzak, S. *Inorg. Chim. Acta* **1988**, 150, 257–268.
- (20) (a) Niu, Y. Y.; Song, Y. L.; Hou, H. W.; Zhu, Y. *Inorg. Chem.* **2005**, 44, 2553–2559. (b) Hou, H. W.; Li, L. K.; Zhu, Y.; Fan, Y. T.; Qiao, Y. Q. *Inorg. Chem.* **2004**, 43, 4767–4774. (c) Zhang, Q. F.; Niu, Y. Y.; Leung, W. H.; Song, Y. L.; Williams, I. D.; Xin, X. Q. *Chem. Commun.* **2001**, 1126–1127.
- (21) (a) Rensmo, H.; Lunell, S.; Siegbahn, H. *J. Photochem. Photobiol. A* **1998**, 114, 117–124. (b) Ren, C. X.; Ye, B. H.; He, F.; Cheng, L.; Chen, X. M. *CrystEngComm* **2004**, 6, 200–206. (c) Wu, D. Y.; Hayashi, M.; Shiu, Y. J.; Liang, K. K.; Chang, C. H.; Yeh, Y. L.; Lin, S. H. *J. Phys. Chem. A* **2003**, 107, 9658–9667.
- (22) Zhan, S.-Z.; Li, D.; Zhou, X.-P.; Zhou, X.-H. *Inorg. Chem.* **2006**, 45, 9163–9165.

CG701241V