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Synthesis, structure and optical limiting effect of a novel inorganic–organic hybrid polymer containing mixed chains of copper(I)/iodine

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Abstract

In this paper, treatment of *N*-ethyl-benzo[f]quinolium (ebq) iodide and CuI with excess KI afforded an unusual coordination polymer $[(\text{ebq})_2(\text{Cu}_3\text{I}_4)(\text{CuI}_2)]_n$ (**1**). **1** crystallizes in tetragonal system, space group $P4(2)bc$ with cell parameters of $a = 23.2040(6)$ Å, $c = 6.7393(3)$ Å, $V = 3628.6(2)$ Å^3, $Z = 8$, $D_c = 2.622\,\text{g/c}^3$, $R_1 = 0.0447$ and $\text{w}R_2 = 0.0974$. A highly interesting feature of **1** is its presence of mixed types of chains $[(\text{Cu}_3\text{I}_4)_n^-$ and $(\text{CuI}_2)_n^-$ chain] in one crystal lattice based on supramolecular self-assembly directed by cations. The infinite chains $(\text{Cu}_3\text{I}_4)_n^-$ and $(\text{CuI}_2)_n^-$ in **1** could be described as the edge-sharing arrangement of CuI_4 tetrahedron. Furthermore, IR, EA, UV–Vis, thermal analysis and optical limiting measurements were adopted to characterize polymer **1**. The optical limiting experiment shows that the present polymer exhibits a large optical limiting capacity.

Keywords: Coordination polymers; organic–inorganic hybrid; copper(I) iodide; optical limiting effect

1. Introduction

Research into the chemistry of supramolecular coordination polymers has rapidly grown in recent years due to an increased demand for functional materials with tunable properties [1]. Particularly, as materials in the fields of absorption, molecular recognition, catalysis, separation, optics, and electromagnetism manifest themselves as different networks, it is vital to be able to generate various polymeric systems with both novel structural topologies and functional properties [2]. In recent years, considerable interests have been focused on the design and synthesis of inorganic functional materials with a hybrid approach [3]. Among the various families of hybrid functional materials, the family of metal halides is an important one. As a branch of the metal halides, copper iodides occupy an important position. A variety of copper(I) iodides exhibiting varying dimensionality through influence of versatile size, shape and charge distribution of the associated organic components have been synthesized [4]. In summary, the basic copper(I) iodides (CuI) skeletons of these compounds generally exhibit several structural motifs: square (rhomboid) dimers, cubane tetramers, zigzag chains, double-stranded ladders, and hexagonal grid chains. All of the reported works are polymers with single type of inorganic moiety, but compounds containing multiple types of chains in one crystalline lattice, to the best of our knowledge, have not been reported so far.

Optical limiting material is a kind of substance whose transmission is high when it is illuminated by low-intensity light but low when exposed to intense laser radiation.

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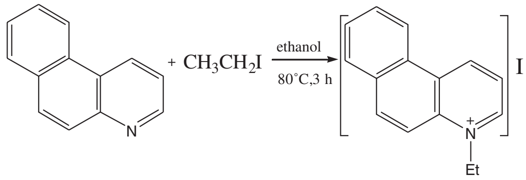
Because of their potential applications in the protection of optical sensors from high-intensity laser beams, the search for better optical limiting materials has become increasingly intensive. The most frequently reported materials are fullerenes (C_{60}) and phthalocyanine complexes, which are generally regarded as the best compounds for optical limiting [5,6]. Recently, large nonlinear optical effects have also been observed in inorganic clusters and their polymers [7]. On the basis of previous experimental facts, we focus our attention on iodometalate polymeric clusters. Here we report an interesting cation-induced coordination polymer $[(\mathrm{ebq})_2(\mathrm{Cu_3I_4})(\mathrm{CuI_2})]_n$, which was obtained from the reaction of copper iodide with of *N*-ethyl-benzo[f]quinolium (ebq) iodide, and find that it shows a large optical limiting property.

2. Experimental

2.1. Synthesis of $[(\mathrm{ebq})_2(\mathrm{Cu_3I_4})(\mathrm{CuI_2})]_n$ (**1**)

ebq · I was prepared as reported in literature [8]:



1 was synthesized by self-assembling reaction of CuI, KI and ebq · I in DMF solvent. ebq · I (0. 335 g, 1.0 mmol) and CuI (0.076 g, 0.4 mmol) were dissolved in 7 mL DMF, and then KI (0.132 g, 0.8 mmol) was added into the above solution with the pH being adjusted to 6.0 by the addition of 10% $\mathrm{HNO_3}$/DMF solution. The mixed solution was stirred for 30 min at 50 °C and then filtered. The filtrate was kept at room temperature for 5 days to obtain orange block single crystals (0.129 g, yield 46.3% based on Cu). Calcd. for $C_{15}H_{14}NCu_2I_3$ (716.07)(%): calcd. C 25.16, H 1.97, N 1.96; found C 25.20, H 1.95, N 1.99. IR (cm^{-1}): 3452 (s), 3060 (m), 2942 (s), 2865 (m), 1598 (m), 1575 (m), 1510 (m), 1450 (m), 1385 (w), 812 (s), 760 (s).

2.2. Characterization

All chemicals except ebq · I were of reagent grade quality obtained from commercial sources and used without further purification. C, H, N analyses were carried out with a Vario EL III element analyzer. IR spectra were recorded on a Nicolet Co. Magna-IR 750 spectrometer with KBr pellets in the 4000–400 cm^{-1} regions. UV–Vis spectra were performed on a Perkin-Elmer Lambda 900 spectrometer. Thermal stability (TG-DTA) study from room temperature to 800 °C in nitrogen atmosphere with a heating rate of 10 °C min^{-1} were executed on a Perkin-Elmer TGA 7 instrument.

Optical limiting behavior of **1** was investigated by fluence-dependence transmittance measurement. Radiation of 532 nm wavelength provided by a Qswitched Nd:YAG laser with the pulse duration of 8 ns was used. The spatial distribution of the pulses was nearly Gaussian after passing through a spatial filter. Laser was operated at single shots so that the response of the sample to each pulse was monitored and the effect of thermal defects was avoided. Average energy value of five pulses was adopted to minimize the fluctuation. Input pulse energy was varied from 10 to 180 mJ by using a waveplate–polarizer combination. The pulse was divided into two parts by a beam splitter. Reflected part was taken as a reference representing the incident light energy and the transmitted beam was focused through the sample. The incident and transmitted pulse energy were measured simultaneously by two energy detectors (P&E 2000B, Chinese Measure Science Institute). The sample was fixed at the focus.

2.3. X-ray structure determination

A suitable orange block single crystal of as-synthesized compounds with the dimensions of $0.15 \times 0.12 \times 0.10\,\mathrm{mm}^3$ was carefully selected under an optical microscope and glued to a thin glass fiber with epoxy resin. Crystal structure determination by X-ray diffraction was carried out on a Siemens SMART CCD diffractometer with graphite-monochromated Mo-$K\alpha$ ($\lambda = 0.71073$ Å) radiation at room temperature. An empirical absorption correction was applied using the SDAABS program [9]. The structure was solved by the direct method and refined on F^2 by full-matrix least squares using SHELXTL97 [10]. The hydrogen atoms were placed geometrically and refined using a riding model. All non-hydrogen atoms were refined anisotropically. Experimental details for the structure determination are presented in Table 1. Selected bond lengths and angles are listed in Table 2.

3. Results and discussion

3.1. Description of the structure

According to structural analysis, the crystal structure of **1** presents a one-dimensional arrangement constructed from mixed chains $(\mathrm{Cu_3I_4})_n^-$, $(\mathrm{CuI_2})_n^-$ and ebq$^+$ fragments in combination with each other by static attracting force. The organic moiety ebq$^+$ units are discrete, but the inorganic moieties, i.e., $(\mathrm{Cu_3I_4})_n^-$ and $(\mathrm{CuI_2})_n^-$ chains, are polymeric and exist in the crystal as extended chains along *c*-axis. In other words, this structure is mixed one-dimensional infinite polymeric anions accompanied by discrete cations. Compared with the reported works possessing only single type of inorganic moiety in the lattice, the highly interesting feature of compound **1** is with multiple types of chains combined in one crystalline lattice. Both types of iodocuprate(I) chains are known, the novelty

Table 1
Crystal data and structure refinement summary for complex **1**

Formula	$C_{15}H_{14}Cu_2I_3N$
Formula weight	716.07
Crystal system	Tetragonal
Space group	$P4(2)bc$
a (Å)	23.2040(6)
c (Å)	6.7393(3)
V (Å^3)	3628.6(2)
Z	8
Calculated density (mg/m^3)	2.622
Absorption coefficient (mm^{-1})	7.441
F (000)	2624
T (K)	293(2)
λ (Å)	0.71073
θ range for data collection (deg.)	3.17–27.48
Limiting indices	$-30 \leqslant h \leqslant 30$, $-29 \leqslant k \leqslant 29$, $-8 \leqslant l \leqslant 8$
Reflections collected	17781
Independent reflections	4114 [R(int) = 0.0440]
Reflections observed	3600
Completeness to $\theta = 27.48$	99.7%
Goodness-of-fit on F^2	1.110
Data/restraints/parameters	4114/1/191
Final R indices ($I > 2\sigma(I)$)^a	$R_1 = 0.0447$, w$R_2 = 0.0974$
R indices (all data)	$R_1 = 0.0535$, w$R_2 = 0.1020$
$(\Delta\rho)_{max}$ (e/Å^3)	1.152
$(\Delta\rho)_{min}$ (e/Å^3)	−1.003

$^a R_1 = \|F_o| - |F_c\|/|F_o|$, w$R_2 = [w(F_o^2 F_c^2)^2/[w(F_o^2)^2]]^{1/2}$.

Table 2
Selected bond lengths (Å) and bond angles (deg.) for complex **1**

Cu(1)–I(1)	2.671(6)	Cu(1)–I(1)#4	2.670(5)
Cu(1)–I(1)#5	2.670(5)	Cu(1)–I(1)#6	2.671(6)
Cu(2)–I(1)	2.758(2)	Cu(2)–I(1)#5	2.815(2)
Cu(2)–I(2)	2.595(3)	Cu(2)–I(2)#5	2.590(1)
Cu(3)–I(3)	2.656(1)	Cu(3)–I(3)#7	2.656(1)
Cu(3)–I(3)#8	2.662(6)	Cu(3)–I(3)#9	2.662(6)
Cu(1)–Cu(2)	2.966(2)		
Cu(1)#1–I(1)–Cu(1)	78.21(4)	Cu(1)–I(1)–Cu(2)	66.21(5)
Cu(1)–I(1)–Cu(2)#2	111.17(4)	Cu(1)#1–I(1)–Cu(2)	110.14(4)
Cu(1)#1–I(1)–Cu(2)#2	65.40(4)	Cu(2)–I(1)–Cu(2)#2	74.40(3)
Cu(2)#2–I(2)–Cu(2)	81.06(3)	Cu(3)–I(3)–Cu(3)#3	78.62(3)
I(1)–Cu(2)–I(1)#5	110.44(5)	I(1)–Cu(1)–I(1)#6	101.76(8)
I(1)#4–Cu(1)–I(1)	109.09(9)	I(1)#4–Cu(1)–I(1)#5	101.81(8)
I(1)#4–Cu(1)–I(1)#6	117.94(2)	I(1)#5–Cu(1)–I(1)	117.94(2)
I(1)#5–Cu(1)–I(1)#6	109.09(9)	I(2)#5–Cu(2)–I(1)	109.06(7)
I(2)–Cu(2)–I(1)	102.74(7)	I(2)–Cu(2)–I(1)#5	110.34(7)
I(2)#5–Cu(2)–I(1)#5	101.31(7)	I(3)–Cu(3)–I(3)#7	101.55(8)
I(3)–Cu(3)–I(3)#8	113.66(4)	I(3)#7–Cu(3)–I(3)#8	113.66(4)
I(3)–Cu(3)–I(3)#9	113.66(4)	I(3)#7–Cu(3)–I(3)#9	113.66(4)
I(3)#8–Cu(3)–I(3)#9	101.21(8)		

Symmetry transformations used to generate equivalent atoms: #1 $-y+1/2$, $-x+1/2$, $z+1/2$; #2 $y+1/2$, $x-1/2$, $z+1/2$; #3 $-y+1$, $x-1$, $z+1/2$; #4 $-y+1/2$, $-x+1/2$, $z-1/2$; #5 $y+1/2$, $x-1/2$, $z-1/2$; #6 $-x+1$, $-y$, z; #7 $-x+2$, $-y$, z; #8 $y+1$, $-x+1$, $z-1/2$; #9 $-y+1$, $x-1$, $z-1/2$.

of this compound lies significantly in their incorporation in the same structure.

In one-dimensional $(Cu_3I_4)_n^-$ chain (chain 1), each copper atom has an I_4 donor set and tetrahedral geometry when the Cu–Cu interactions are not taken into account. It could be discussed as a tri-$(CuI_2)_n^-$ chains based on edge-sharing CuI_4 tetrahedra running parallel to the c-axis (Fig. 1). As a result, two distinct types of iodine atoms are found: peripheral iodine atoms which are two-coordinate make up the edges of the polymeric string, and four-coordinate central iodine atoms lie on a mirror plane which is normal to the polymeric axis. Because the iodine atoms are of a bridging nature, coordination environments of two crystallographic independent copper atoms are distorted from perfect tetrahedron. But the distorted extent is different. Cu(1)I_4 tetrahedron, which locates in the center of the tri-chain, only has slight distortion with Cu–I varying from 2.670(5) to 2.671(6) Å. But Cu(2)I_4 occupying the two side ridges of the tri-chain, has much greater distortion with bond distances ranging from 2.590(1) to 2.815(2) Å. The Cu–Cu distance is 2.966(2) Å (Cu(1)–Cu(2)), which are longer than that of metallic copper (2.566 Å) and the van der Waals radius (1.4 Å) sum of Cu(I). So it could not be described as chemical bonds and just exists as weak metal–metal interaction. The Cu–Cu interactions have been found in many copper complexes. The attraction between d^{10}–d^{10} closed-shell metals promotes the aggregation of copper(I) centers, which has been supported by spectroscopic and structural evidence.

The polymeric $(Cu_3I_4)_n^-$ chain could be compared with $(Cu_2I_3)_n^-$ polyanion chain, which has been subject of previous independent determination [4a]. $(Cu_3I_4)_n^-$ chain of this work presents tri-$(CuI_2)_n^-$ chains running parallel to the c-axis constructed from edge-sharing CuI_4 tetrahedra, but the $(Cu_2I_3)_n^-$ chain only takes on double $(CuI_2)_n^-$ chains extending parallel to a certain axis. In addition, in present structure of parallel tri-chain, the metal atoms are four-coordinate and the iodine atoms two- and four-coordinate, but in $[(Hquild)_2H]^+[Cu_2I_3]^- \cdot$(H-Quild)$\cdot H_2O$ [4b], which also has a $(Cu_2I_3)_n^-$ polyanion, the copper atoms are three- and four-coordinate with coordination polyhedrons of tetrahedron and planar trigon, and the iodine atoms are two- and three-coordinate.

It's worth mentioning that $[(Pr_4N)(Cu_3I_4)]_n$ [4a], $[(C_3H_8NO)(Cu_3I_4) \cdot DMF]_n$ [4c] and $\{[(C_6H_5)_4P](Cu_3I_4)\}_n$ [4d] also have the same composition form of Cu_3I_4. But their real structures differ greatly from present work in linkage modes. For example, $(Cu_3I_4)_n^-$ chain of $\{[(C_6H_5)_4P](Cu_3I_4)\}_n$ presents a helix arrangement constructed from face-sharing of CuI_4 tetrahedra, furthermore, the individual $(Cu_3I_4)_n^-$ chains are chiral, in the crystal the chains are separated by the tetraphenylphosphonium ions and arranged in a rod packing parallel to [100] direction. Similarly, $[(Pr_4N)(Cu_3I_4)]_n$ also possesses $(Cu_3I_4)_n^-$ inorganic chains based on face-sharing CuI_4 tetrahedra. But the $(Cu_3I_4)_n^-$ chain of present work is built upon edge sharing.

And in the polymeric $(CuI_2)_n^-$ species (chain 2), the copper and iodine atoms constitute chains of edge sharing CuI_4 tetrahedron running parallel to the c axis (Fig. 1). This chain has been previously observed [4e,f] and is common in copper/iodine polymer. In Cu(3)I_4 tetrahedron,

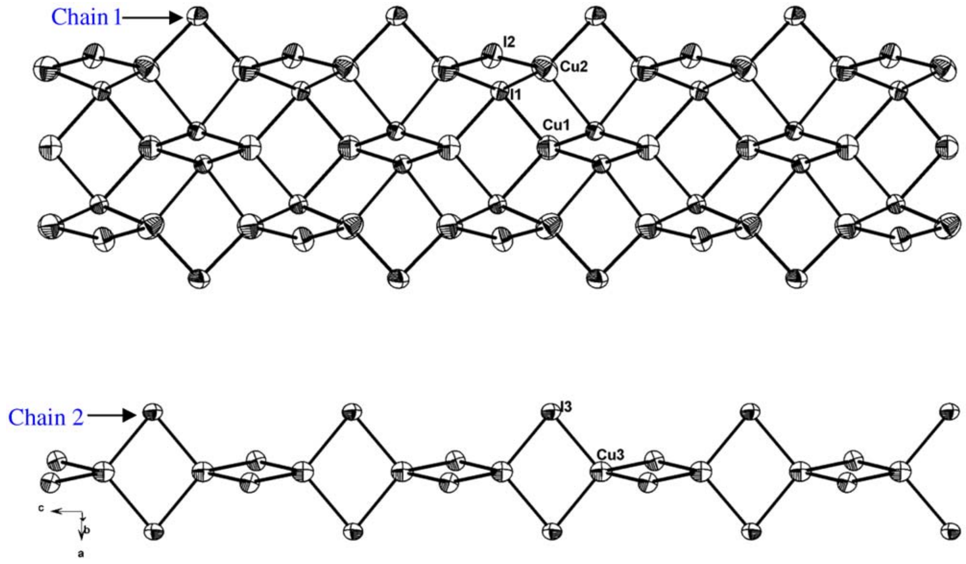


Fig. 1. Structure of mixed chains of $(Cu_3I_4)_n^-$ and $(CuI_2)_n^-$ in one crystal lattice, showing the atom-labeling scheme and 50% thermal ellipsoids.

Cu–I distances vary from 2.656(1) to 2.662(6) Å (Table 2), indicating a slight distortion of CuI_4 tetrahedron. These bond lengths are much longer than those reported (2.394(2) and 2.383(1) Å) in the previously described linear CuI_2^- species [4g], but closely corresponds to the distances observed in CuI complexes in which Cu is bound to two iodine atoms in the dimeric Cu_2I_2 units, for example, $[CuI(quinoline)_2]_2$ (2.686 Å) [4h], $\{CuI(3\text{-Me-pyridine})_2\}_2$ (2.655 Å) [4i]. The Cu–Cu distance is 3.370 Å, suggesting no existence of metal–metal interaction. The structure of the present $(CuI_2)_n^-$ species is very similar to that found in the structure of (paraquat)(Cu_2I_4) [4e], except that the four Cu–I bond lengths are comparable to each other (from 2.629(6) to 2.644(6) Å) and the angles (103.7(3)°, 76.7(1)°) are much smaller than those in the present specie.

As shown in Fig. 2, the neighboring $(Cu_3I_4)_n^-$ and $(CuI_2)_n^-$ polyanion chains act as cavities wherein organic cations lie sandwiched between two adjacent chains. Cations do not participate in coordination, they are in combination with inorganic moiety by non-covalent interaction: static attracting force. Moreover, it can be found the extensive array of π–π stacking among the benzo[f]quinoline rings. The π–π distance is about 3.574(1) Å, indicating the existence of spatial π–π interactions. Generally speaking, strong π–π interactions are around 3.30 Å and relatively weaker interactions lie above 3.60 Å; 3.80 Å is approximately the maximum contact for which π–π interactions are accepted [11]. So organic–inorganic hybrid structure is constructed from static attracting force and π–π interaction.

3.2. UV–Vis spectrum

The UV–Vis spectrum of complex **1** in aqueous solution exhibits bands at 276 and 397 nm. Comparably, UV–Vis spectra of free ebq · I displays at 272 and 395 nm. So two adsorption peaks of **1** are induced by ebq^+ cations. In detail, peaks at 276 and 397 nm might be attributed to π–π^* transfer of ebq ring [12].

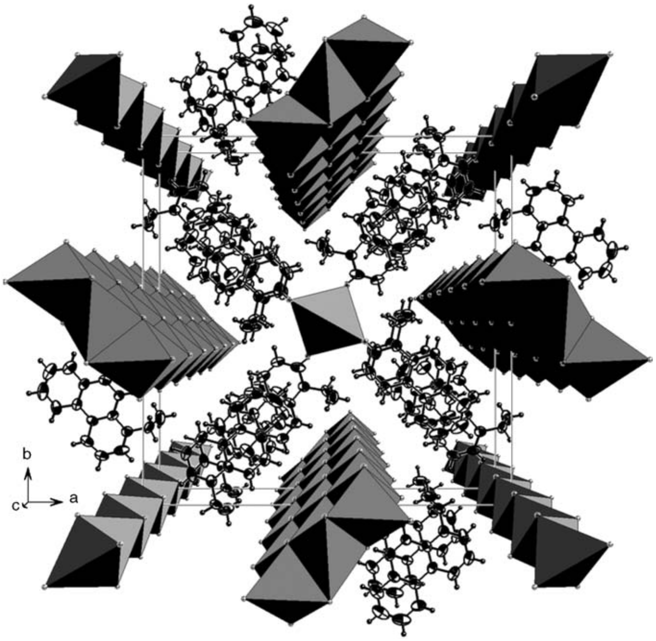


Fig. 2. Unit cell packing diagram of 1.

3.3. Thermal analysis

As shown in Fig. 3, compound **1** has two stages of weight loss: one occurred at 225 °C, the decomposition started at 207 °C and ended at 330 °C. Because isolated ebq^+ molecules take the role of counter-cations, the framework collapses during the removal of organic components. So 45.33% weight loss in this stage could be attributed to the

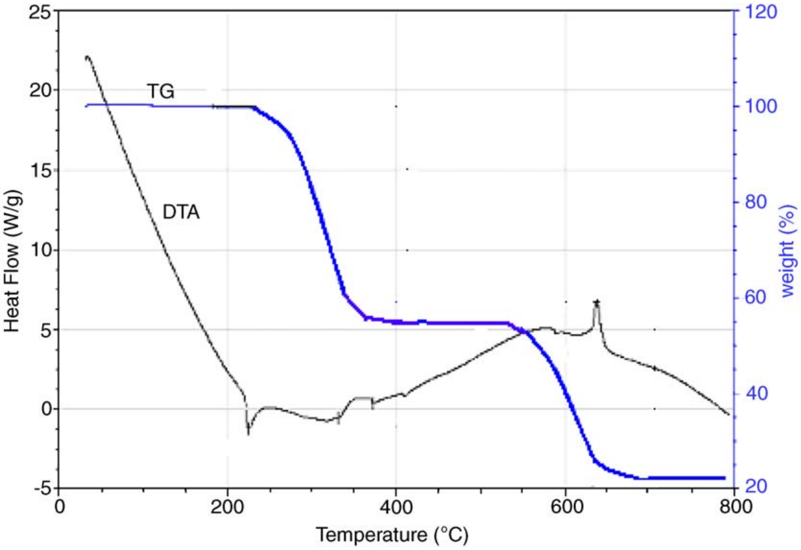


Fig. 3. TG-DTA curve of 1.

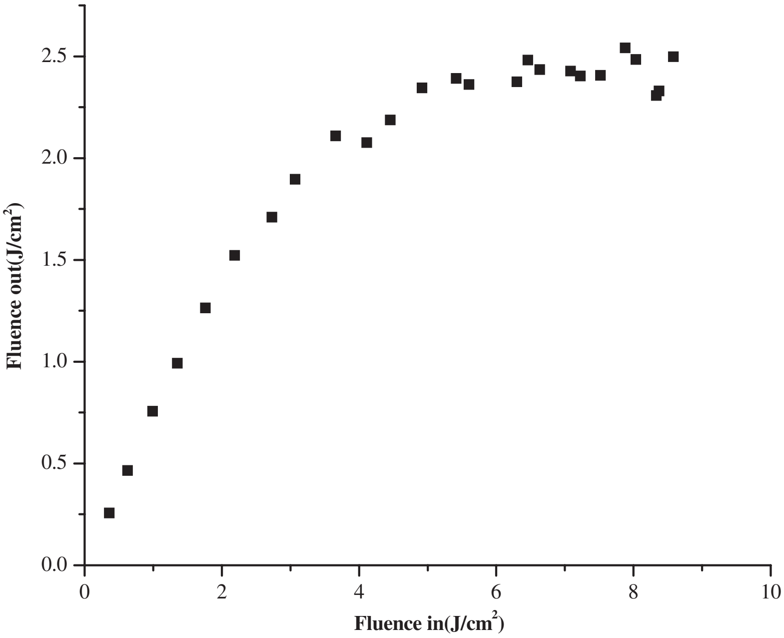


Fig. 4. Optical limiting effect of $[(ebq)_2(Cu_3I_4)(CuI_2)]_n$ (**1**) in a 1.0×10^{-5} mol/dm^3 DMF solution.

loss of quaternary ammonium ebq · I (theoretically calculation value: 46.78%). The other took place at 589.75 °C in the temperature range of 490–650 °C. In this stage, 34.37% weight loss corresponds to the loss of two I^- ions (theoretically calculation value: 35.33%). The thermal analysis is consistent with structural determination.

3.4. *Optical limiting effect*

The optical limiting result of **1** is depicted in Fig. 4. The light energy transmitted begins to deviate from Beer's law as the input light fluence rises to 0.920 J/cm^2, and the solution become increasingly less transparent as the incident fluence strengthens, i.e., a nonlinear relationship is observed between the output and input energy intensity. The limiting threshold, which is defined as the incident fluence at which the actual transmittance falls to 50% of the corresponding linear transmittance, is 0.980 J/cm^2 in DMF solution. It is well known that organic materials with a π-conjugated system show relatively large third-order nonlinear susceptibility and ultrafast response times, which are due to their delocalized π-electrons [13]. In addition, complexes with higher nuclearity or heavy atoms are expected to have favorable NLO properties [7]. So as far as polymers **1** are concerned, the heavier atoms Cu and I together with the polymeric aggregation and π-conjugated ebq$^+$ ligands play a vital role in determining its NLO property.

4. Conclusion

In summary, treatment of *N*-ethyl-benzo[f]quinolium (ebq) iodide and CuI with excess KI afforded an unusual coordination polymer $[(ebq)_2(Cu_3I_4)(CuI_2)]_n$ (**1**). **1** represents a new example containing multiple types of chains in one crystalline lattice based on supramolecular self-assembly directed by cations. IR, EA, UV–Vis, thermal analysis and optical limiting measurements were adopted to characterize polymer **1**. The optical limiting experiment shows that the present polymer exhibits a good optical limiting capacity, which could be potentially used in laser protection.

Supporting information: Additional information including atomic coordinates, thermal parameters and the complete bond lengths and bond angles had been deposited with the Cambridge Crystallographic Data Center (CCDC no. 280601).

Acknowledgments

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