Hydrothermal Syntheses, Supramolecular Structures and the Third-order Non-linear Optical Properties of Three Copper(I) Halide Amine Complexes Connected via Secondary Bonding Interactions

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The hydrothermal reactions of CuI, KI and bidentate amines [1,10-phenanthroline (phen) or ethylenediamine (en)] gave the three copper(I) halide compounds, $Cu_3I_3(phen)_2$ (1), $CuI(phen)_2$ (2) and $[Cu(en)_2][CuI_2]_2$ (3), which were structurally characterized via single-crystal X-ray diffraction studies. Hydrogen bonds and π-π interactions are the most remarkable structural features of the title compounds. All can be described as higher-dimensional supramolecular compounds connected via these secondary bondings. Moreover, the title compounds were characterized by elemental analyses, IR spectra and TGA analyses. The third-order non-linear optical properties of the title compounds were also investigated and all exhibit nicer non-linear absorption and self-focusing performance.

Keywords   copper(I) halide, hydrothermal synthesis, the third-order non-linear optical property, supramolecular structure

Introduction

Secondary bondings such as hydrogen bonds and π-π interactions are important non-covalent intermolecular forces,[1] which contribute to self-assembly processes when extended structures are formed from simple precursors. Recently much attention has been paid to the hydrogen bonds and π-π interactions in the area of metal-ligand

compounds, since some functional properties of compounds have something to do with their supramolecular structures. For example, good carried transport ability and relatively high electroluminescence (EL) efficiency of Gaq_3 molecule are attributed to hydrogen bonds and π-π interactions existing in the Gaq_3 solid.[2] The bridging hydrogen bonds could provide pathways for magnetic exchange interactions in complexes $[C_5H_7N_2][CuBr_3(C_5H_5BrN_2)]$, $[C_5H_7N_2]_2[CuBr_4]_3$, $[Cu_2(dpt)_2Cl_2]Cl_2$ (dpt = dipropylenetriamine),[4] etc.. So it is great interest in the information not only on the covalent metal-ligand bond distances and angles from crystal structure, but also on how the complexes or coordination polymers are packed in the crystal structure through secondary bondings. Herein, we report the supramolecular structures of three copper(I) halide amine complexes obtained by hydrothermal syntheses and their third-order non-linear optical properties.

Experimental

The syntheses were conducted using regent grade

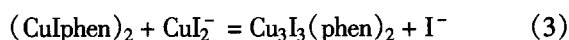CuI, KI, phen·H$_2$O and en from commercial sources without further purification. Infrared spectra of the title compounds were recorded on a Perkin Elmer spectrophotometer in the 400—4000 cm^{-1} region using powdered samples on KBr plates. Elemental analyses were determined using a Perkin-Elmer 2400LS II elemental analyzer.
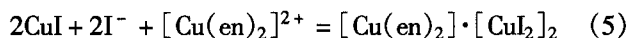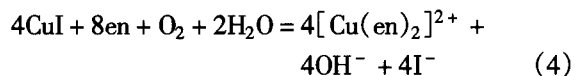
Syntheses of the title compounds

Red rhombic crystals of Cu$_3$I$_3$(phen)$_2$ (**1**) were grown from hydrothermal reactions of CuI (0.30 g), phen·H$_2$O (0.31 g), KI (0.66 g) and H$_2$O in a molar ratio of 1:1:2.5:300 in a 30 mL of Teflon-lined autoclave at 150 ℃ for 5 d. The yield was 25% based on the CuI. IR (KBr) ν: 3455 (b), 1619 (w), 1572 (w), 1508 (m), 1492 (w), 1423 (s), 1221 (w), 1138 (m), 866 (m), 841 (s), 765 (m), 725 (s), 637 (w), 423 (w) cm^{-1}. Anal. calcd for Cu$_{1.5}$I$_{1.5}$C$_{12}$H$_8$N$_2$: C 30.94, H 1.73, N 6.01; found C 30.44, H 1.70, N 6.21. The equations may be written as:

$$\text{CuI} + \text{I}^- = \text{CuI}_2^- \qquad (1)$$

$$2\text{CuI}_2^- + 2\text{phen} = (\text{CuIphen})_2 + 2\text{I}^- \qquad (2)$$

$$(\text{CuIphen})_2 + \text{CuI}_2^- = \text{Cu}_3\text{I}_3(\text{phen})_2 + \text{I}^- \qquad (3)$$

Crystal growth of CuI(phen)$_2$ (**2**) was carried out under identical reaction conditions as for **1** except that the amount of the phen·H$_2$O used was doubled [CuI (0.30 g), phen·H$_2$O (0.62 g), KI (0.66 g) and H$_2$O in a molar ratio of 1:2:2.5:300]. The dark-red columnar crystals of **2** were obtained in 30% yield. IR (KBr) ν: 3448 (b), 1619 (w), 1504 (m), 1491 (w), 1421 (s), 1409 (m), 1218 (w), 1135 (w), 838 (s), 762 (m), 722 (s), 425 (w) cm^{-1}. Anal. calcd for Cu$_{0.5}$I$_{0.5}$C$_{12}$H$_8$N$_2$: C 52.36, H 2.93, N 10.18; found C 52.60, H 2.75, N 9.97. The difference of stoichiometry has an effect on the Eq. (2). So it should be revised by CuI$_2^-$ + 2phen = CuI(phen)$_2$ + I$^-$.

Reactions of CuI (0.30 g), en (0.095 g), KI (0.66 g) and H$_2$O in a molar ratio of 1:1:2.5:300 in a 30 mL of Teflon-lined autoclave at 150 ℃ for 5 d resulted in the brown-red needle crystals of [Cu(en)$_2$]·[CuI$_2$]$_2$ (**3**). The yield was *ca* 30% based on the CuI. IR (KBr) ν: 3444 (b), 3299 (s), 3248 (s), 3221 (s), 2928 (m), 2870 (m), 1582 (s), 1564 (s), 1456

(m), 1361 (w), 1275 (w), 1168 (w), 1119 (w), 1037 (s), 1009 (s), 966 (m), 789 (w), 690 (m), 565 (m), 530 (m) cm^{-1}. Anal. calcd for Cu$_{1.5}$I$_2$C$_2$H$_8$N$_2$: C 5.87, H 1.97, N 6.85; found C 5.63, H 2.03, N 7.08. We can write the equations as:

$$4\text{CuI} + 8\text{en} + \text{O}_2 + 2\text{H}_2\text{O} = 4[\text{Cu(en)}_2]^{2+} +$$
$$4\text{OH}^- + 4\text{I}^- \qquad (4)$$

$$2\text{CuI} + 2\text{I}^- + [\text{Cu(en)}_2]^{2+} = [\text{Cu(en)}_2]·[\text{CuI}_2]_2 \qquad (5)$$

X-Ray crystal structure determination

Crystal data and structure refinement for the title compounds are given in Table 1. Selected bond lengths and angles are given in Table 2. Data were collected with Mo Kα radiation (λ = 0.071073 nm) using a Siemens SMART CCD diffractometer. The structures were solved using direct methods with SHELXTL program and refined by full-matrix least-squares techniques. The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. The hydrogen atoms were treated using a riding model. The structure was then refined on F^2 using SHELXL-97.

Thermal analysis

Thermogravimetric analyses were performed on a Perkin-Elmer TGA-7 instrument, with a heating rate of 20 ℃·min^{-1} in air.

Results and discussion

The molecular structure of compound **1** is displayed in Fig. 1(a). Though large number of copper(I) halide frameworks including from mononuclear species to tetranuclear discrete clusters as well as polymeric structures have been observed, trinuclear species having similar framework as compound **1** are very rare so far.[5] As far as the molecular structure of **1** is concerned, there are two crystallographically independent monovalent copper ions. The Cu(1) atom in the tetrahedral site is coordinated to two bridging iodide ions and two N atoms from a phen ligand. The Cu(2) atom with a slightly distorted triangular planar geometry is coordinated to two bridging and one terminal iodide ions. In Cu$_3$I$_3$ core, the Cu(1)—Cu(2) separation (0.2549 nm) is even shorter than the Cu(1)—

Table 1 Crystal data and structure refinement for the title compounds

	1	2	3
Chemical formula	$Cu_{1.5}I_{1.5}C_{12}H_8N_2$	$Cu_{0.5}I_{0.5}C_{12}H_8N_2$	$Cu_{1.5}I_2C_2N_2H_8$
M_r	465.86	275.25	409.23
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2/n$	$C2/m$
a (nm)	1.00495(8)	0.75723(9)	1.0411(2)
b (nm)	1.50351(12)	0.96325(11)	1.3411(3)
c (nm)	1.68237(12)	1.44102(16)	0.65825(13)
β (°)	94.105(2)	90.015(3)	117.49(3)
V (nm³)	2.5355(3)	1.0511(2)	0.8153(3)
Z	8	4	2
Crystal size (mm)	$0.14 \times 0.14 \times 0.08$	$0.40 \times 0.16 \times 0.04$	$0.30 \times 0.08 \times 0.08$
λ (nm)	0.071073	0.071073	0.071073
T (K)	293(2)	293(2)	293(2)
$D_c(g \cdot cm^{-3})$	2.441	3.320	3.543
μ (mm⁻¹)	6.168	11.109	12.699
R_1 $[I > 2\sigma(I)]$	0.0440	0.0514	0.0432
wR_2 (all data)	0.0948	0.2434	0.1108

Table 2 Selected bond lengths (nm) and angles (°) for the title compounds

1[a]			
I(1)—Cu(1)	0.2591(13)	Cu(1)—N(2)	0.2050(8)
I(1)—Cu(2)	0.2696(12)	Cu(1)—N(1)	0.2069(7)
I(1)—Cu(1) #1	0.2738(15)	Cu(1)—Cu(2)	0.2548(18)
I(2)—Cu(2)	0.2434(19)		
Cu(1)-I(1)-Cu(2)	57.59(3)	N(2)-Cu(1)-Cu(2)	174.8(2)
Cu(1)-I(1)-Cu(1) #1	76.40(4)	N(1)-Cu(1)-Cu(2)	102.2(2)
Cu(2)-I(1)-Cu(1) #1	55.93(3)	N(2)-Cu(1)-I(1)	111.64(19)
N(2)-Cu(1)-N(1)	82.2(3)	N(1)-Cu(1)-I(1)	135.9(2)
Cu(2)-Cu(1)-I(1)	63.26(3)	Cu(1) #1-Cu(2)-Cu(1)	80.64(8)
N(2)-Cu(1)-I(1) #1	120.6(2)	Cu(1)-Cu(2)-I(1) #1	62.89(5)
N(1)-Cu(1)-I(1) #1	105.0(2)	I(2)-Cu(2)-I(1)	129.44(3)
Cu(2)-Cu(1)-I(1) #1	61.19(3)	Cu(1)-Cu(2)-I(1)	59.14(4)
I(1)-Cu(1)-I(1) #1	102.72(4)	I(1) #1-Cu(2)-I(1)	101.13(6)
I(2)-Cu(2)-Cu(1)	139.68(4)		

2[b]			
Cu—N(2)	0.2040(7)	Cu—N(1)	0.2057(7)
N(2)-Cu-N(2) #1	105.9(4)	N(2)-Cu-N(1)	82.7(3)
N(2)-Cu-N(1) #1	147.2(3)	N(1) #1-Cu-N(1)	107.3(4)

3			
Cu(1)—I(1)	0.2710(13)	Cu(1)—I(2)	0.2691(2)
Cu(2)—N(1)	0.2014(7)		

[a] Symmetry transformations used to generate equivalent atoms for **1**: #1 $-x$, y, $-z + 1/2$; [b] symmetry transformations used to generate equivalent atoms for **2**: #1 $-x + 1/2$, y, $-z - 1/2$.

Cu(1A) one (0.3298 nm). The fragment of the packing diagram for compound **1** is given in Fig. 1(b). The crystal structure contains two types of hydrogen bonds, namely, each bridging iodine atom [I(1C)] links two different kinds of hydrogen atoms attached to carbon atoms [C(9) and C(5D)] of adjacent phen ligands, which come from other two trinuclear units. Indications for the presence of hydrogen bonds are the angles [C(5D)-H···I(1C) = 134.9°, C(9)-H···I(1C) = 167.9°], which are within the accepted range of angles (119.3°—169.2°) for this type of interaction,[6] and the distances [C(5D)···I(1C) = 0.3950, C(9)···I(1C) = 0.4143 nm], which are shorter than the corresponding van der Waals separation (this is also the standard that we judge the presence of hydrogen bonds[7]). Moreover, It can be found the extensive array of π-π stacking among the phen rings. The π-π distance is ~0.342 nm, indicating the existence of spatial π-π interactions. Since strong interactions are around 0.330 nm and weaker interactions lie above 0.360 nm with 0.380 nm being approximately the maximum contact for which π-π interactions are accepted.[8] So all the discrete trinuclear molecules are connected via these hydro-
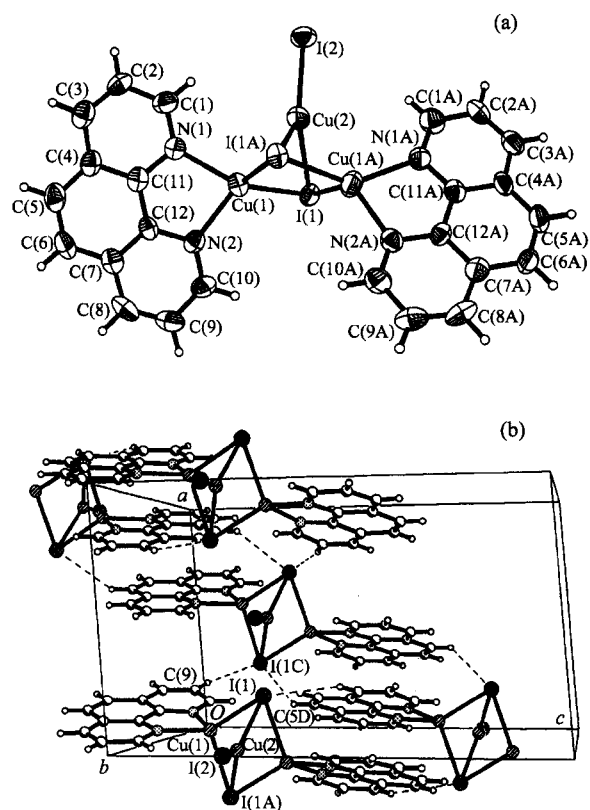
gen bonds and π-π interactions to form a three-dimensional supramolecule network.

Compound **2** is a new example containing [CuN$_4$]$^+$ core [Fig. 2(a)]. In general, the [CuN$_4$]$^+$ species should approach its ideal *mm* or 222 symmetry (interligand N-Cu-N angles varying between 114.3°—132.4°[9]) such as complex [Cu(tmen)$_2$]$^+$ (tmen = *N*, *N*, *N'*, *N'*-tetramethylethylenediamine)[10] and [Cu(phen)$_2$]-ClO$_4$[11]. But as for the [CuN$_4$]$^+$ core geometries of compound **2**, the tetrahedrally coordinated copper is highly distorted, since the range of interligand angles is 105.9(4)°—147.2(3)°. Moreover, The Cu—N distances are normal, ranging from 0.2040(7) to 0.2057(7) nm, the intraligand N-Cu-N angle is 82.7(3)°, and the dihedral angle between the ligand planes is 43.2°. The fragment of packing diagram for compound **2** can be found in Fig. 2(b). Hydrogen bonds and π-π interactions are the most remarkable structural features of CuI(phen)$_2$ solid. Though the anion I$^-$ does not interact with the copper atom of the cation, it is the hydrogen bonds that link the anion and the cation coming from two different molecule units and being adjacent each other. Perfect crystal packing determines that there is only one type of hydrogen bond, since all the C—I distances and C-H···I angles
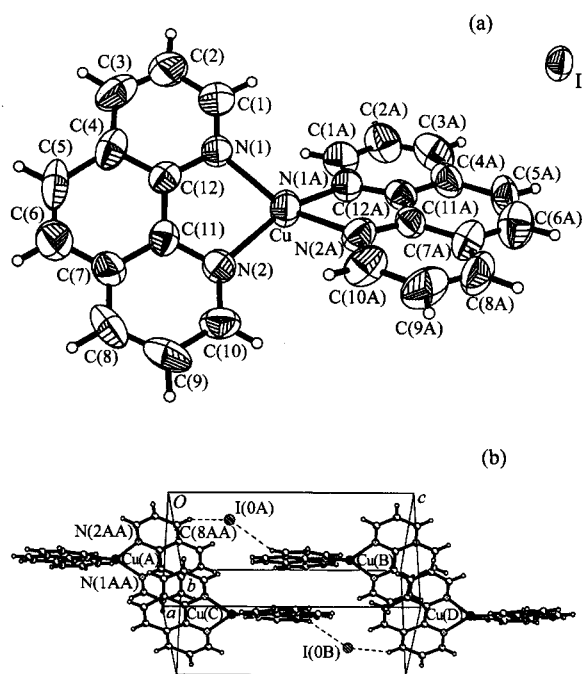

(a)

(b)

Fig. 1 Molecular structure (a) and fragment of the packing diagram (b) for **1**.

(a)

(b)

Fig. 2 Molecular structure (a) and fragment of the packing diagram (b) for **2**.

[C(8AA)—I(0A) = 0.4046 nm, C(8AA)-H···I(0A) = 152.8°] are equal, respectively. There exist π-π interactions in two different directions because two phen ligands binding to the copper atom have a certain angle (the distances are ~ 0.350 and ~ 0.354 nm, respectively).

Though the structure of compound **3** had been determined previously, complete structural information, especially secondary bonding interactions, was not given in details.[12] Complex **3** consists of one-dimensional [CuI₂]⁻ chains and planar [Cu(en)₂]²⁺ units [Fig. 3 (a)]. As to the [CuI₂]²⁻ unit, the monovalent copper ion is in the distorted tetrahedral site, the adjacent Cu₂I₂ cores are perpendicular each other, and the distorted CuI₄ tetrahedra share edge via μ₂-I to form an extended one-dimensional chain along the c-axis. The most important is that the [Cu(en)]²⁺ cation interacts with the an-

(a)

ion [CuI₂]⁻ chain not only via two self-coordinate Cu—I bonds [Cu(2A)—I(2AB) and Cu(2A)—I(2C)] at 0.3408 nm (also one of secondary bondings¹), but also via numerous hydrogen bonds from the N atoms or the C atoms of the en to the I atoms of the anion [CuI₂]⁻ chains. They are N—H···I hydrogen bonds [N(1A)—I (1A) = 0.3630 nm, N(1A)-H···I(1A) = 153.7°] or C—H··· I ones [C(1A)—I(1AE) = 0.3759 nm, C (1A)-H···I(1AE) = 135.8°]. So the structure of compound **3** can be described as a three-dimensional supramolecular network via these secondary bondings [Fig. 3(b)].

The thermal behaviors of the title compounds were studied from 30 to 700 ℃. The TGA curve of [Cu₃I₃-(phen)₂] indicated two steps of weight-loss. Compound **1** was thermally stable up to around 240 ℃, and then began to decompose till about 430 ℃, which is the first and attributed to the loss of terminal I⁻. The observed weight-loss (15.02%) is comparable with the calculated result (13.60%). The second occurred from ~ 450 to ~ 630 ℃, due to the release of two bridging I ions and two phen molecules. After decomposition of **1** at high temperature, the residue was copper, since the weight of the residue (21.61%) is in agreement with the calculated value (20.50%). The TGA curves of **2** and **3** indicated multistep stages of weight-loss. **2** and **3** were thermally stable up to around 220 and 190 ℃, respectively, and then began to decompose. Both the residues were copper oxides (observed values: 13.86% for **2** and 29.27% for **3**, respectively; calculated values: 14.44% for **2** and 29.16% for **3**, respectively).

The third-order nonlinear optical (NLO) properties of the title compounds were investigated at 532 nm with 8 ns pulses produced by a Q-switched frequency-doubled Nd:YAG laser in 8.00×10^{-4}, 9.10×10^{-4} and 6.70×10^{-4} mol·dm⁻³ DMF solutions for **1**, **2** and **3**, respectively, and revealed by using a Z-scan technique. The cell being selected to place the samples is 1-mm-thick quartz one. The open and filled circles depict their nonlinear absorptive and refractive properties. The solid curve was obtained after a reasonably good fit between the experimental data and theoretical curve (Figs. 4, 5 and 6).

In accordance with the observed α_2 and n_2 (α_2 and n_2 are effective third-order NLO absorptive and refractive coefficients, respectively), the modulus of the effective third-order susceptibility $\chi^{(3)}$ can be calculated by Eq. (6).
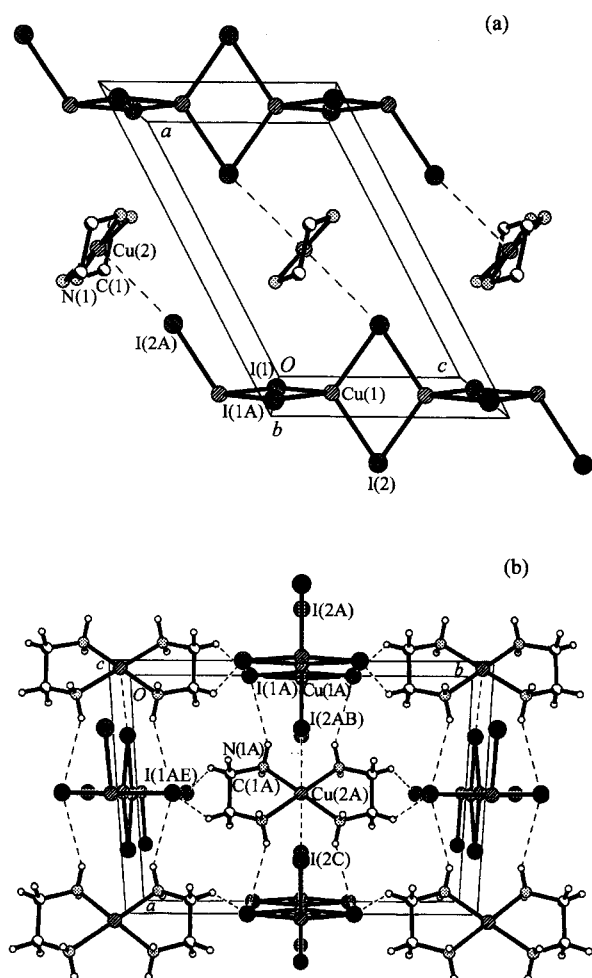

(b)

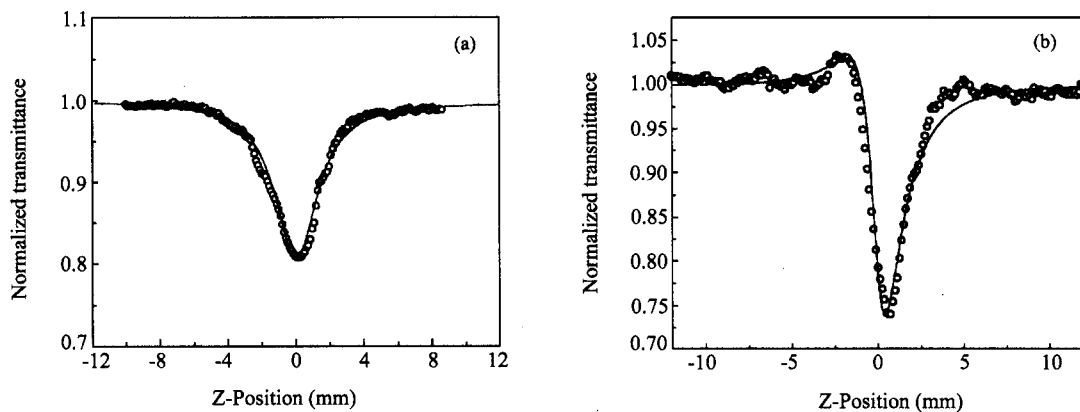**Fig. 3** Two-dimensional sheet (a) and fragment of the packing diagram (b) for **3**.

Fig. 4 Z-scan data of 8.00×10^{-4} mol·dm^{-3} of **1**. (a) Collected under the open apeture configuration showing NLO absorption (the solid curve is a theoretical fit); (b) obtained by dividing the normalized Z-scan data obtained under the closed aperture configuration by the normalized Z-scan data in (a).
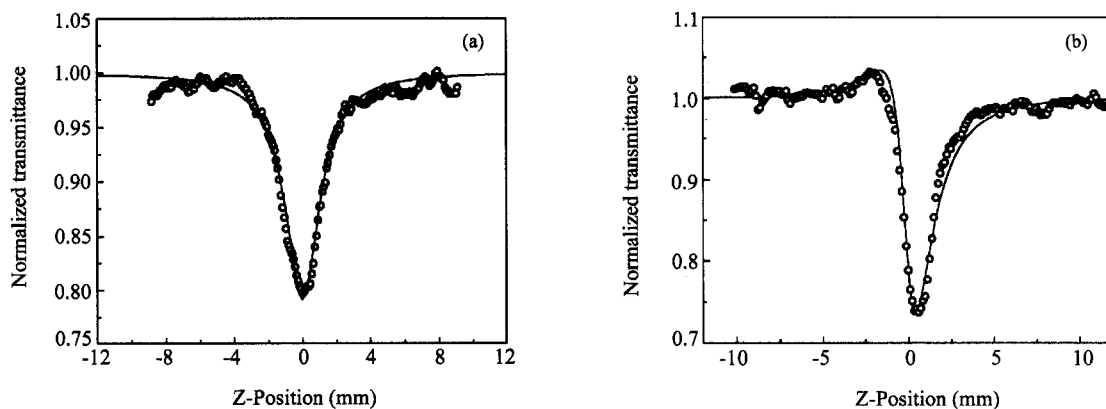

Fig. 5 Z-scan data of 9.10×10^{-4} mol·dm^{-3} of **2**. (a) Collected under the open apeture configuration showing NLO absorption (the solid curve is a theoretical fit); (b) obtained by dividing the normalized Z-scan data obtained under the closed aperture configuration by the normalized Z-scan data in (a).

Fig. 6 Z-scan data of 6.70×10^{-4} mol·dm^{-3} of **3**. (a) Collected under the open apeture configuration showing NLO absorption (the solid curve is a theoretical fit); (b) Obtained by dividing the normalized Z-scan data obtained under the closed aperture configuration by the normalized Z-scan data in (a).
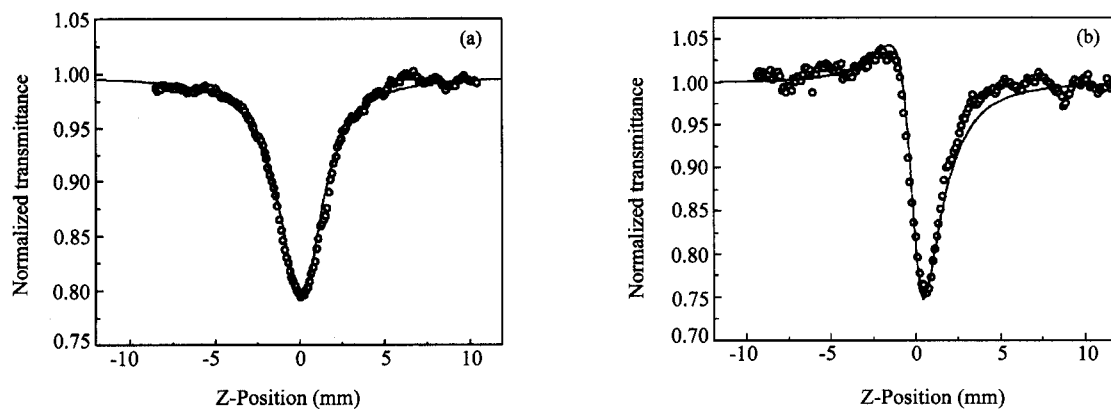
$$|\chi^{(3)}| = [(9 \times 10^8 n_0{}^2 \varepsilon_0 c\lambda a_2/8\pi^2)^2 +$$
$$(n_0 cn_2/80\pi^2)^2]^{1/2} \qquad (6)$$

where λ is wavelengh of the laser light, n_0 is the linear refractive index of the sample (n_0 can be replaced by the one of the solvent if the concentrations of the samples are very small during calculation), ε_0 and c are the permittivity and speed of light $in\ vacuo$, respectively. The corresponding modulus of the hyperpolarizabilities γ was got from $|\gamma| = |\chi^{(3)}|/NF^4$ ($F^4 = [(n^2 + 2)/3]^4$, n is the linear refractive index of the solvent). N is the molecular number density of the compounds in the samples and F^4 is the local Lorents field correction factor. All the calculated results were listed in the Table 3. From the results, It can be stated that the title compounds have similar NLO properties due to the approximative values of $\chi^{(3)}$. Though the supramolecular structures have been disappeared in solution, all exhibit nicer non-linear absorption and self-focusing performance, which can be attributed to the presence of delocalized big π bonds of phen molecules for compound **1** and **2** and of the linear $[CuI_2]^-$ chains for compound **3**.

Table 3   Third-order non-linear optical properties of the title compounds

	a_2 ($m \cdot W^{-1}$)	n_2 ($m^2 \cdot W^{-1}$)	$\chi^{(3)}$ (esu)	$\chi^{(3)}$ (esu$\cdot$mol$^{-1} \cdot$dm^3)	γ (esu)
$Cu_3I_3(phen)_2$	3.41×10^{-11}	3.56×10^{-18}	2.99×10^{-12}	3.74×10^{-9}	1.88×10^{-30}
$CuI(phen)_2$	3.14×10^{-11}	3.47×10^{-18}	2.81×10^{-12}	4.20×10^{-9}	2.11×10^{-30}
$[Cu(en)_2][CuI_2]_2$	3.20×10^{-11}	2.94×10^{-18}	2.52×10^{-12}	3.76×10^{-9}	1.89×10^{-30}

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