

# Cluster-cracking Reaction, a New Method to Synthesize Unsymmetrical Dithiolate Complexes for the Study of Third-Order Nonlinear Optical Properties

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A new cluster-cracking method to synthesize dithiolate metal complexes was reported and four unsymmetric complexes with formula  $(Me_4N)_2[M(Ln)(SPh)_2]$  ( $M = Cd$  and  $Zn$ ,  $L1 = dmit = 1,3$ -dithiole-2-thione-4,5-dithiolate,  $L2 = dmid = 1,3$ -dithiole-2-one-4,5-dithiolate,  $SPh = thiophenolate$ ) (1—4) were characterized by elemental analysis, IR, UV NMR spectra and so on. The advantages of this method are summarized in two aspects: (1) the preparation is very convenient; (2) the reaction usually completed giving the product with high purity. The crystal structure of 1 showed that the bond distances of Cd(II) to the sulfur of the thiophenolate group are shorter than those of Cd(II) to the sulfur of dmit, so that the thiophenolate group does not be replaced in the reaction and the mixed ligand complexes are the dominant products. The dmit complexes showed well third-order NLO properties, but not of the dmid complexes, although dmid is an analogue to dmit.

**Keywords** synthetic method, dmit complexes, dithiolate, NLO properties

## Introduction

Sulfur-rich compounds based on TTF (tetrathiafulvalene or 2-(1,3-dithiole-2-ylidene)-1,3-dithiole) and dithiolene systems, such as dmit (1,3-dithiole-2-thione-4,5-dithiolate), have been interested for a long time owing to their unusual electrical conductive properties.<sup>1</sup> Over the past decades, numerous derivatives of TTF and metal-dmit complexes have been designed and synthesized as the precursors for conductive materials. Lately, a number of TTF derivatives and metal dmit complexes were also found to exhibit unusual magnetic behaviors<sup>2</sup> and optical properties.<sup>3,7</sup> Some metal dithiolene complexes are known to be very stable to intense irradiation in near-infrared region and have been used as Q-switch dyes for Nd-YAG laser.<sup>4</sup> Meanwhile, a series of symmetrical dmit complexes with third-order optical non-linearity were re-

ported and considered to be promising candidates for all-optical signal-processing device.<sup>5</sup> More recently, good values of third-order non-linear susceptibility  $\chi^{(3)}$ <sup>6</sup> as well as negative molecular first hyperpolarizability ( $\beta$ ) (second-order non-linearity)<sup>7</sup> were observed for some unsymmetrical dithiolene-metal complexes. It is therefore attractive to explore the synthesis of dithiolate complexes, especially unsymmetrical complexes, and to study their non-linear optical (NLO) properties.

This paper describes a synthetic method for the preparation of new dithiolate complexes. Thiophenolate clusters  $(Me_4N)_2[M_4(SPh)_{10}]$  ( $M = Zn$  or  $Cd$ ) were used as precursors, which were attacked by dithiolate ligands: dmit, dmid. By using this cluster-cracking reaction, four unsymmetrical dithiolene-thiophenolate complexes were isolated,  $(Me_4N)_2[M(Ln)(SPh)_2]$  ( $M = Cd$  and  $Zn$ ,  $L1 = dmit = 1,3$ -dithiole-2-thione-4,5-dithiolate,  $L2 = dmid = 1,3$ -dithiole-2-one-4,5-dithiolate,  $SPh = thiophenolate$ ) (1—4). The synthetic method and third order NLO properties for these complexes are discussed. Part of this work has been published as a primary communication.<sup>8</sup>

## Experimental

### General procedures

The metal clusters of  $(Me_4N)_2[M_4(SPh)_{10}]$  ( $M = Zn$  or  $Cd$ ),<sup>9</sup> the precursory compounds 4,5-bis(benzoylthio)-1,3-dithiole-2-thione<sup>10</sup> and 4,5-bis(cyanoethylthio)-1,3-dithiole-2-one<sup>10</sup> were prepared according to the reported method. Preparation of the complexes was performed by using Schlenk technique. Solvents were dried and distilled by standard methods before use.

Microanalytical data were obtained on an EA1110 ele-

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ment analyser. Infrared spectra were taken on a 550 FT-IR spectrometer as KBr discs and electronic spectra were recorded on a Shimadzu UV 240 spectrophotometer.  $^1\text{H}$  NMR spectra were measured by a UNITYNOVA-400 spectrophotometer.

#### Synthesis of the complexes

##### $(\text{Me}_4\text{N})_2[\text{Cd}(\text{L}1)(\text{SPh})_2]$ (1)

4,5-Bis(benzoylthio)-1,3-dithiole-2-thione (1.62 g, 4 mmol) was suspended in ethanol (10 mL) under argon. Sodium (0.183 g, 8 mmol) dissolved in ethanol (3.0 mL) was added dropwise to the suspension and then an intense wine-red color appeared. To this solution metal cluster  $(\text{Me}_4\text{N})_2[\text{Cd}_4(\text{SPh})_{10}]$  (1.73 g, 1 mmol) was added in one portion. The mixture was stirred for 50 min at room temperature under argon atmosphere. A red precipitate was formed which was washed with ethanol and dried *in vacuo* (yield 62%, m. p. 162–165 °C). Single brick crystals suitable for X-ray analysis were grown by slow evaporation of the filtrate of the reaction mixture.  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$ : 3.33 (s, 24H), 6.66 (t,  $J = 7.2$  Hz, 2H), 6.82 (t,  $J = 7.6$  Hz, 4H), 7.51 (d,  $J = 7.2$  Hz, 4H). Anal. calcd for  $\text{C}_{23}\text{H}_{34}\text{N}_2\text{S}_7\text{Cd}$ : C 40.90, H 5.07, N 4.15; found C 40.49, H 4.97, N 4.06.

##### $(\text{Me}_4\text{N})_2[\text{Zn}(\text{L}1)(\text{SPh})_2]$ (2)

Following the above procedure, 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (0.406 g, 1 mmol) was de-protected in methanol (7 mL) in a methanol solution (5.0 mL) of sodium (0.047 g, 2 mmol). To this solution, metal cluster  $(\text{Me}_4\text{N})_2[\text{Zn}_4(\text{SPh})_{10}]$  (0.38 g, 0.25 mmol) was added. The mixture was stirred for 1 h at room temperature under argon atmosphere. Red microcrystals were isolated from the filtrate after concentration (yield 57%, m. p. 182–184 °C).  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$ : 3.35 (s, 24H), 6.68 (t,  $J = 7.6$  Hz, 2H), 6.84 (t,  $J = 7.2$  Hz, 4H), 7.51 (d,  $J = 7.2$  Hz, 4H). Anal. calcd for  $\text{C}_{23}\text{H}_{34}\text{N}_2\text{S}_7\text{Zn}$ : C 43.96, H 5.45, N 4.46; found C 43.51, H 5.23, N 4.19.

##### $(\text{Me}_4\text{N})_2[\text{Cd}(\text{L}2)(\text{SPh})_2]$ (3)

4,5-Bis(cyanoethylthio)-1,3-dithiole-2-one (0.144 g, 0.5 mmol) was suspended in ethanol (2 mL) under argon. Methanol solution of tetramethylammonium hydroxide in 25wt% concentration was added to the suspension and then a brown color appeared. To this solution metal cluster  $(\text{Me}_4\text{N})_2[\text{Cd}_4(\text{SPh})_{10}]$  (0.21 g, 0.125 mmol) in acetonitrile (4 mL) was added in one portion. The mixture was stirred for 4 h at room temperature under argon atmosphere and turned to pale yellow. A pale yellow precipitate was formed, which was washed with ethanol and dried *in vacuo* (yield 45%, d. p. 130 °C).  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$ : 3.37 (s, 24H), 6.65 (t,  $J = 7.2$  Hz, 2H), 6.81 (t,  $J = 7.6$  Hz, 4H), 7.53 (d,  $J = 7.2$  Hz, 4H). Anal. calcd for  $\text{C}_{23}\text{H}_{34}\text{N}_2\text{S}_6\text{OCd}$ : C

41.94, H 5.17, N 4.26; found C 41.71, H 5.03, N 4.24.

##### $(\text{Me}_4\text{N})_2[\text{Zn}(\text{L}2)(\text{SPh})_2]$ (4)

Following the above procedure, 4,5-bis(cyanoethylthio)-1,3-dithiole-2-one (0.144 g, 0.5 mmol) was de-protected in ethanol (3 mL) by tetramethylammonium hydroxide. To this solution, metal cluster  $(\text{Me}_4\text{N})_2[\text{Zn}_4(\text{SPh})_{10}]$  (0.19 g, 0.125 mmol) in acetonitrile (3 mL) was added. The mixture was stirred for 6 h at room temperature. The filtrate liquid was sealed in glass tube. The product pale greenish-yellow crystals were isolated some days later (yield 37%, d. p. 135 °C).  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$ : 3.38 (s, 24H), 6.65 (t,  $J = 7.2$  Hz, 2H), 6.80 (t,  $J = 7.6$  Hz, 4H), 7.55 (d,  $J = 7.2$  Hz, 4H). Anal. calcd for  $\text{C}_{23}\text{H}_{34}\text{N}_2\text{S}_6\text{OZn}$ : C 45.17, H 5.56, N 4.58; found C 45.09, H 5.72, N 4.81.

#### X-Ray structure determination

The single-crystal X-ray diffraction data for complex 1 were collected on a Rigaku AFC-7R diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.071069$  nm) and a rotating anode generator. Unit cell parameters were obtained from least-squares refinement using the 25 reflections in the range  $26.90^\circ < 2\theta < 33.38^\circ$ . The data were collected at a temperature of  $(23 \pm 1)$  °C using the  $\omega$ - $2\theta$  scan technique to a maximum  $2\theta$  value of  $55.0^\circ$ . Of 3917 reflections collected, 3705 were unique. The intensities of three representative reflections were measured after every 150 reflections. The linear absorption coefficient ( $\mu$ ) is  $12.1 \text{ cm}^{-1}$ . An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.90 to 1.00. The structure was solved by direct method (SAPI91)<sup>11</sup> and expanded using Fourier techniques (DIRD94).<sup>12</sup> The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3705 observed reflections [ $I > 2.0\sigma(I)$ ] and 299 variable parameters, giving  $R$  and  $wR$  factors 0.038 and 0.088 respectively. Crystallographic computations were performed by using the TEXSAN program system.<sup>13</sup>

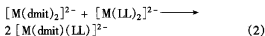
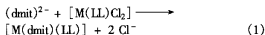
#### Non-linear optical measurements

The third-order optical non-linearities of the complexes were measured by phase conjugate forward three-dimensional degenerate four-wave mixing (3D DFWM) technique.<sup>14</sup> After passing through a quarter wavelength plate, the pulse laser beam (wavelength 532 nm) from a frequency-doubled picosecond pulse mode-locked Nd:YAG laser is split into three beams  $k_1$ ,  $k_2$  and  $k_3$  with the same energy by use of reflecting beam splitters, then temporally and spatially overlapped in the sample with a 205 mm focal-length lens. In the experiment, the intensity  $I_4$  of the phase conjugate beam  $k_4$  was detected by PIN photodiode.

## Results and discussion

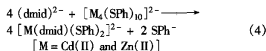
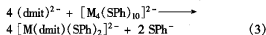
### Synthesis of new dithiolate complexes by cluster-cracking reaction

Up to now, there have been two useful methods for the synthesis of mixed ligand complexes with 1,3-dithiole-2-thione-4,5-dithiolate. One is a conventional metathesis reaction of the dmit dianion with the corresponding dichloro-metal complexes, method (1) [Eq. (1)]. The other is a ligand exchange reaction between two symmetrical metal complexes with dmit and the other chelate ligand, method (2) [Eq. (2)].



The direct method (1) is very conventional in the synthesis of neutral complexes from neutral dichloro-compounds. For instance,  $[\text{Pt}(\text{phen})(\text{dmit})]$  has been prepared from  $[\text{Pt}(\text{phen})\text{Cl}_2]^{15}$  and  $[\text{W}(\text{Cp})_2(\text{dmit})]$  has been prepared from  $[\text{W}(\text{Cp})_2\text{Cl}_2]^{16}$  (phen = 1,10-phenanthroline, Cp =  $\eta\text{-C}_5\text{H}_5$ ). However, mixed ligand anions with dichloride are not always easy to prepare. For these dmit mixed complexes, the most efficient method is a ligand exchange reaction (2). For example,  $[\text{Zn}(\text{dmit})(\text{Et}_2\text{dtc})]^-$  was prepared by reaction of  $[\text{Zn}(\text{dmit})_2]^{2-}$  with  $[\text{Zn}(\text{Et}_2\text{dtc})_2]^{2-}$ ,<sup>17</sup> and  $[\text{Ni}(\text{dsit})(i\text{-mnt})]^{2-}$  has been prepared from  $[\text{Ni}(\text{dsit})_2]^{2-}$  and  $[\text{Ni}(i\text{-mnt})_2]^{2-}$ <sup>18</sup> ( $\text{Et}_2\text{dtc}$  = diethyl-dithiocarbamate,  $i\text{-mnt}$  = 1,1-dicyanoethene-2,2-dithiolate,  $\text{C}_4\text{N}_2\text{S}_2^{2-}$ , and  $\text{dsit}$  = 2-thione-1,3-dithiole-4,5-diselenolate,  $\text{C}_3\text{Se}_2\text{S}_2^{2-}$ ). During our work on the syntheses of mixed ligand complexes, however, it was found in some cases that the ligand exchange reaction was not always completed and separation of the product was not easy. Kato's group has successfully isolated a number of mixed ligand dithiolate complexes using a technic of reversed phase HPLC.<sup>19</sup> Other methods for synthesizing mixed cyclopentadienyl/dithiolene organometallic compounds were summarized by Fournig e.<sup>20</sup>

The method used to synthesize unsymmetrical dithiolene metal complexes 1-4 was called as cluster-cracking reaction [Eqs. (3) and (4)].



Since dmit and dmid are strong chelate ligands, they attack the M4 cluster and break the metal-thiophenolate bonds.

Unlike chloride, which is easily displaced in the reaction (1), the thiophenolate group also coordinates strongly to the metal center (see discussion of the structure) and resists displacement. Thus the mixed ligand complexes are the predominant products, even though in excess of the dmit. The dmit complexes are very stable in ambient condition, but the dmid complexes are unstable except that they are sealed in glass-tub under Ar atmosphere. In that condition they can be preserved for months.

Thiophenolate coordinated or bridged complexes are very common for transition metals and numerous metal dithiolene complexes were studied, but based on our knowledge, no thiophenolate/dmit mixed complexes have been reported yet. Wu and Sheng<sup>21</sup> have reported the synthesis and structure of some mixed ligand dmit complexes with dithiol, but their challenge on synthesis of heteroleptic complexes of thiophenolate failed. By the cluster-cracking method, the mixed complexes can be prepared with high purity and need not further purification, which is the most extrusive advantage for this method.

### X-Ray structure determination of 1

Experimental and crystal data of complex 1 are summarized in Table 1 and important bond lengths and bond angles for 1 are listed in Table 2. Final atomic coordinates and de-

Table 1 Crystallographic data of complex 1

Formula	C <sub>23</sub> H <sub>14</sub> CdN <sub>2</sub> S <sub>7</sub>
<i>M<sub>r</sub></i>	675.37
Crystal color, habit	red, brick
Crystal size (mm)	0.20 × 0.20 × 0.25
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub>
<i>a</i> (nm)	0.9534(3)
<i>b</i> (nm)	1.0626(2)
<i>c</i> (nm)	1.5079(3)
$\beta$ (°)	91.75(2)
<i>V</i> (nm <sup>3</sup> )	1.5269(5)
<i>Z</i>	2
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.469
<i>F</i> (000)	692.00
Diffractometer	Rigaku AFC7R
Radiation	Mo K $\alpha$ ( $\lambda$ = 0.071069 nm)
$\mu$ (cm <sup>-1</sup> )	12.10
Scan type	$\omega$ -2 $\theta$
Scan rate [(°)/min]	16.0 (in $\omega$ )
2 $\theta$ range (°)	6-55
No. of reflns measd	3917
No. of obed data ( <i>I</i> > 2.00 $\sigma$ ( <i>I</i> ))	3705
No. of params	299
<i>R</i> <sup>a</sup>	0.029
<i>wR</i> <sup>b</sup>	0.088
Goodness of fit	0.97

<sup>a</sup>  $R = \sum (F_o - F_c) / \sum F_o$ . <sup>b</sup>  $wR = \{ \sum w (F_o - F_c)^2 / \sum w (F_o)^2 \}^{1/2}$ ,  $w = 1 / [\sigma^2(F_o)]$ .

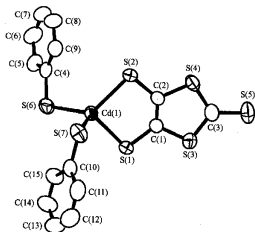
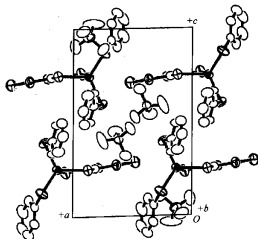
**Table 2** Selected bond lengths (nm) and angles ( $^{\circ}$ ) of complex **1**

Gd(1)—S(1)	0.2566(2)	Gd(1)—S(2)	0.2530(2)
Gd(1)—S(6)	0.2519(2)	Gd(1)—S(7)	0.2507(1)
S(1)—C(1)	0.1738(5)	S(2)—C(2)	0.1742(5)
S(3)—C(1)	0.1755(5)	S(3)—C(3)	0.1704(7)
S(4)—C(2)	0.1755(5)	S(4)—C(3)	0.1733(6)
S(5)—C(3)	0.1669(5)	S(6)—C(4)	0.1757(6)
S(7)—C(10)	0.1755(6)	C(1)—C(2)	0.1355(7)
S(1)—Cd(1)—S(2)	88.72(5)	S(1)—Cd(1)—S(6)	110.69(6)
S(1)—Cd(1)—S(7)	108.26(5)	S(2)—Cd(1)—S(6)	118.59(6)
S(2)—Cd(1)—S(7)	117.10(6)	S(6)—Cd(1)—S(7)	110.77(6)
Gd(1)—S(1)—C(1)	95.3(2)	Gd(1)—S(2)—C(2)	95.8(2)
C(1)—S(3)—C(3)	99.6(3)	C(2)—S(4)—C(3)	98.9(3)
Gd(1)—S(6)—C(4)	107.5(2)	Gd(1)—S(7)—C(10)	102.2(2)
S(1)—C(1)—S(3)	116.0(3)	S(1)—C(1)—C(2)	129.0(4)
S(3)—C(1)—C(2)	115.0(4)	S(2)—C(2)—S(4)	115.2(3)
S(2)—C(2)—C(1)	129.8(4)	S(4)—C(2)—C(1)	115.1(4)
S(3)—C(3)—S(4)	111.4(3)	S(3)—C(3)—S(5)	124.6(4)
S(4)—C(3)—S(5)	123.9(4)		

tails of crystal data in CIF format are available via the Internet.<sup>8</sup> X-Ray structure determination reveals that the cadmium(II) center of **1** involves a CdS<sub>4</sub> tetrahedral coordination environment. The structure is illustrated by ORTEP view in Fig. 1. The bond distances of Cd(II) to the sulfur of the thiophenolate group, Cd(1)—S(6) 0.2519(2) nm and Cd(1)—S(7) 0.2507(1) nm, are shorter than those of Cd(II) to the sulfur of dmit, Cd(1)—S(1) 0.2566(2) nm and Cd(1)—S(2) 0.2530(2) nm. That is the reason why the thiophenolate is not easy replaced during the synthesis, and the mixed ligand complexes formed dominantly. The longer Cd—S distances of the dmit chelate can be explained by the results from PM3 calculation. The negative charge on the mercapto-sulfur of thiophenolate ( $-0.6766$ ) is larger than that of dmit

( $-0.5927$ ). On the other hand, the rigid structure of dmit might be another reason, because the S(1)—Cd(1)—S(2) angle of 88.72(5) $^{\circ}$  deviates significantly from the 109 $^{\circ}$  of a tetrahedron. While the mono-dentate ligand thiophenolate coordinates to the metal without any bond strain; the S(6)—Cd(1)—S(7) angle is just 110.77(6) $^{\circ}$ .

The complex **1** is monoclinic with space group of  $P2_1$ . Fig. 2 shows the molecular packing and single crystal cell along  $b$ -axis that is also the 2<sub>1</sub> screw axis. The structure has no symmetry center, either as individual molecules or in crystalline form. This character might be important in potential second order NLO properties of the complex. All of the dmit planes are approximately perpendicular to the  $c$ -axis, but no any intermolecular S $\cdots$ S contact or  $\pi$ - $\pi$  stacking was found.

**Fig. 1** ORTEP view of the complex **1** with the atom labeling scheme. Ellipsoids represent 50% probability.**Fig. 2** Molecular packing and crystal cell of **1** look along the  $b$ -axis.

## Spectroscopic studies

The selected IR spectra of the complexes 1–4 are listed in Table 3 together with the data of corresponding bis(dmit) complexes. By comparing the data of dmit complexes 1 and 2 with those of the dmid complexes 3 and 4, the stretching frequency of C=S of dmit and those of C=O of dmid are easily characterized. The stretching peak of C=O locates at the rather lower energy (about  $1590\text{ cm}^{-1}$ ) for their conjugation with the heterocycle. The C=C frequency of dmit in 3 and 4 has about  $35\text{ cm}^{-1}$  blue shift comparing with that of dmit in 1 and 2. The C=C and C=S stretching of dmit ligand shows no significant changes in both symmetrical and unsymmetrical complexes. In contrast to the symmetric bis(dmit) complexes, the C—S vibration mode of 1 and 2, around  $890\text{ cm}^{-1}$  disappears and the C—S vibration mode of around  $945\text{ cm}^{-1}$  gets stronger.<sup>22(a)</sup> Characteristic frequencies of thiophenolate for 1–4 are also listed in the Table 3.<sup>22(b)</sup>

<sup>1</sup>H NMR spectra of the complexes were measured in acetone-*d*<sub>6</sub>. The data were given in experiment section. For complex 1, the chemical shifts of thiophenolate are at  $\delta$  6.66 (t, 2H), 6.82 (t, 4H) and 7.51 (d, 4H) and the shift at 3.33 (s, 24H) is assigned to tetramethylammonium. The chemical shifts for complexes 2–4 are almost the same as those of 1, considering the experiment deviation.

The electronic spectra of the complex 1 in acetone show one strong band at 512 nm in the 400–700 nm regions (Fig. 3a). This band is assigned to  $n\text{-}\pi^*$  transition of the  $\text{C}_2\text{S}_2$  ligand by comparison with the spectra of  $\text{Na}_2\text{dmit}$  and  $(\text{Bu}_4\text{N})_2[\text{Zn}(\text{dmit})_2]$ , 514 nm in MeOH, and 530 nm in MeCN respectively.<sup>22(c)</sup> Contrast to 1, there is not obviously absorption of complex 3 in that region (Fig. 3b). Therefore the intense absorption of dmit complexes in visible region is clearly brought from C=S group and that is important for NLO properties. Complexes 2 and 4 also exhibited quite similar spectral behavior as 1 and 3, respectively.

## Third-order non-linear optical properties of the complexes

The third-order non-linear optical properties of 1 and 2 were measured by three-dimensional degenerate four-wave mixing (3D DFWM) technique,<sup>14</sup> using the pulse laser beam (wavelength 532 nm) from a frequency-doubled pico-second

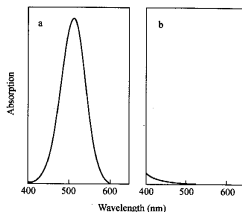


Fig. 3 UV-Vis spectra of 1 (a) and 3 (b).

pulse mode-locked Nd:YAG laser. According to the following formulae, the third-order nonlinear optical susceptibility  $\chi^{(3)}$  was obtained by comparing the measured signals for the acetone solution of the complexes with that for carbon disulfide as a reference, under the same experimental conditions.

$$\chi^{(3)} = (I_4/I_0)^{1/2} (L_r/L) (n/n_0)^2 [aL \exp(aL/2) / (1 - \exp(-aL))] \cdot \chi_r^{(3)} \quad (1)$$

$$\langle \gamma \rangle = \chi^{(3)} / (L^4 N) \quad (L^4 = [(n_0^2 + 2)/3]^4) \quad (2)$$

Where the tensor element  $\chi_r^{(3)}$  is  $6.8 \times 10^{-13}$  esu for  $\text{CS}_2$ <sup>23</sup> and the subscript (*r*) refers to carbon disulfide. The symbol  $\alpha$  is absorption coefficient of the solution and *L* is the thickness of the sample. The letter *I*,  $n_0$  and *N* refer to intensity of light, the refractive index of the solvent and molecular density respectively. The results are summarized in Tables 4 and 5. No third-order NLO response was found for the pure acetone solvent in the experiment conditions. The values of third-order non-linear susceptibility  $\chi^{(3)}$  are in the range of  $10^{-13}$ – $10^{-11}$  esu corresponding to different concentration. The larger  $\alpha$  gave the larger  $\chi^{(3)}$  values. However, the largest second-order hyperpolarizability  $\gamma$  is calculated as  $2.61 \times 10^{-30}$  esu at the concentration of  $2.57 \times 10^{-3}$  mol  $\cdot$  cm<sup>-3</sup> for 1 and  $2.86 \times 10^{-30}$  esu at the concentration of  $2.05 \times 10^{-3}$  mol  $\cdot$  cm<sup>-3</sup> for 2.

Table 3 Selected IR spectra data of the dmit complex ( $\text{cm}^{-1}$ )

Complexes	$\nu$ (Ph-H)	$\nu$ (C=O)	$\nu$ (C=C)Ph	$\nu$ (C=C)	$\nu$ (C=S)	$\nu$ (C-S)	$\nu$ (Ph-H)	$\nu$ (Ph-H)
$(\text{Me}_4\text{N})_2[\text{Cd}(\text{L1})(\text{SPh})_2]$ (1)	3056		1574	1412	1038	945	733	691
$(\text{Me}_4\text{N})_2[\text{Zn}(\text{L1})(\text{SPh})_2]$ (2)	3056		1574	1416	1038	945	737	694
$(\text{Me}_4\text{N})_2[\text{Cd}(\text{L2})(\text{SPh})_2]$ (3)	3063	1590	1574	1448		948	731	688
$(\text{Me}_4\text{N})_2[\text{Zn}(\text{L2})(\text{SPh})_2]$ (4)	3058	1594	1574	1454		949	732	692
$(\text{Et}_4\text{N})_2[\text{Cd}(\text{L1})_2]$				1412	1038	898		
$(\text{Bu}_4\text{N})_2[\text{Zn}(\text{L1})_2]$				1414	1032	891		

L1 = dmit, L2 = dmid.

**Table 4** Third-order non-linear optical properties for complex **1** in different concentration

Entry	$c$ ( $\times 10^{-4}$ mol/L)	$\alpha$ ( $\text{cm}^{-1}$ )	Measurement width	$\chi^{(3)}$ ( $\times 10^{-13}$ esu)	$\langle \gamma \rangle$ ( $\times 10^{-30}$ esu)
1	2.567	2.85	2.08 (100 mV)	2.09	0.50
2	5.133	5.69	4.4 (100 mV)	5.65	0.68
3	7.70	8.55	9.7 (100 mV)	12.7	1.01
4	10.27	11.40	2.26 (50 mV)	22.18	1.33
5	15.40	17.09	8.97 (50 mV)	33.71	1.34
6	20.53	22.79	6.85 (20 mV)	69.25	2.07
7	25.66	28.49	8.82 (20 mV)	109	2.61
8	30.80	34.18	10.36 (5 mV)	125	2.49

**Table 5** Third-order non-linear optical properties for complex **2** in different concentration

Entry	$c$ ( $\times 10^{-4}$ mol/L)	$\alpha$ ( $\text{cm}^{-1}$ )	Measurement width	$\chi^{(3)}$ ( $\times 10^{-13}$ esu)	$\langle \gamma \rangle$ ( $\times 10^{-30}$ esu)
1	2.567	3.56	1.86 (100 mV)	2.26	0.54
2	5.133	7.11	6.04 (100 mV)	7.79	0.93
3	7.70	10.67	9.13 (100 mV)	17.67	1.41
4	10.27	14.2	7.15 (50 mV)	27.8	1.66
5	15.40	21.34	5.70 (20 mV)	52.5	2.09
6	20.53	28.45	13.4 (10 mV)	94.5	2.86
7	25.66	35.5	6.28 (5 mV)	116.1	2.78

Although some of bisdithiolene metal complexes have been examined for their third order NLO properties, good results have only been reported for square  $d^8$  metal complexes.<sup>5</sup> Few of third order NLO properties of unsymmetric tetrahedral dithiolene complexes were reported. The pulse laser beam at 532 nm closes to the  $n-\pi^*$  transition at 512 nm of the complexes **1** and **2**, therefore the relatively large  $\chi^{(3)}$  values observed are dependent on their large absorption coefficient of **1** and **2**. It can be considered that resonance effects enhance the optical non-linearity.<sup>24</sup> Unsymmetric  $d^8$  metal complexes with mixed ligands dmit and thiophenolate are expected to have better third order NLO properties than those of the tetrahedral complexes, but they have not been synthesized for the absence of appropriate precursors.

Third order NLO properties of dmid complexes **3** and **4** were also measured, but no good response was observed. The only difference between **1** and **3**, or **2** and **4**, is the terminal group (C = S being changed to C = O) which significantly affects the  $n-\pi^*$  transition of the ligands (Fig. 3). The results also revealed the importance of resonance effect for the third order NLO properties.

## Conclusion

Suitable precursors (convenient synthetic procedure and good yield), thiophenolate cadmium(II) and zinc(II) clusters, reacted with dithiolate chelate ligands forming a series of new mixed ligand complexes. This kind of reaction is called cluster-cracking reaction and the advantages of this method are summarized in two aspects: (1) the preparation is very convenient; (2) the reaction usually completed giving the prod-

uct with high purity. Up to date, numerous metal clusters have been prepared and characterized. A lot of them are suitable precursors used in cluster-cracking reaction, and novel compounds with mixed ligands are expected to be discovered. However, further exploring the method is necessary to broaden the use as well as to reveal the mechanism.

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