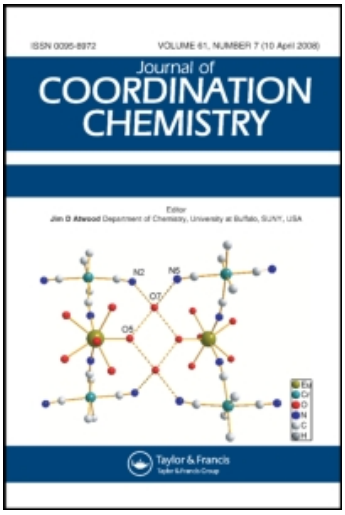

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, Crystal Structure and Nonlinear Optical Properties of Heterobimetallic Cluster Compound [WOS 3 Cu 3 I(2-Mepy) 3]

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Online publication date: 15 September 2010

To cite this Article Zhang, Chi , Song, Ying-Lin , Jin, Guo-Cheng , Wang, Yu-Xiao , Pan, Tao and Xin, Xin-Quan(2002) 'Synthesis, Crystal Structure and Nonlinear Optical Properties of Heterobimetallic Cluster Compound [WOS 3 Cu 3 I(2-Mepy) 3]', Journal of Coordination Chemistry, 55: 1, 33 — 42
To link to this Article: DOI: 10.1080/00958970211873
URL: http://dx.doi.org/10.1080/00958970211873

J. Coord. Chem., 2002, Vol. 55(1), pp. 33–42

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SYNTHESIS, CRYSTAL STRUCTURE AND NONLINEAR OPTICAL PROPERTIES OF HETEROBIMETALLIC CLUSTER COMPOUND [$WOS_3Cu_3I(2\text{-}Mepy)_3$]

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(Received 18 April 2000; In final form 14 October 2000)

The heterobimetallic cluster compound [$WOS_3Cu_3I(2\text{-}Mepy)_3$] was synthesized and characterized by elemental analysis, IR and electronic spectroscopy. Its structure has been crystallographically determined. The nonlinear optical properties of the cluster were measured by using Z-scan technique. The comparison of the optical limiting performance of this cluster with fullerene C_{60} has demonstrated the cluster to be superior to the fullerene C_{60}.

Keywords: Synthesis; Crystal structure; Nonlinear optical properties; Heterobimetallic cluster compound

INTRODUCTION

During the last two decades, the chemistry of Mo(W)/S/Cu(Ag) cluster compounds have been studied extensively because it plays special roles in catalysis reaction and biological processes [1–6]. Recently, the heterobimetallic cluster compounds attracted considerable attention since they have very interesting nonlinear optical (NLO) properties [7–10]. Unlike traditional NLO materials, due to the characteristic and diversity of their

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ISSN: 0095-8972 DOI: 10.1080/00958970290000632

molecular structures [11, 12], these clusters exhibit various NLO behaviors [13 – 19]. In order to further develop this active field and also as a part of our search for better NLO materials, herein we report the synthesis and crystal structure of the cluster $[WOS_3Cu_3I(2\text{-Mepy})_3]$. The results of Z-scan measurements show that this cluster possesses strong NLO absorption and effective self-focusing effect. In comparison with fullerene C_{60}, the optical limiting (OL) ability of this cluster is superior to the fullerene C_{60}.

EXPERIMENTAL

The starting material $(NH_4)_2WOS_3$ was prepared according to the literature [20]. Other chemicals were of reagent grade. Infrared spectra (KBr pellets) were recorded on a Nicolet FT-170SX spectrophotometer. Carbon, nitrogen and hydrogen analyses were performed on a Perkin-Elmer 240C instrument. Electronic spectra were measured on a Shimazu UV-3100 spectrophotometer.

Preparation of Cluster Compound $[WOS_3Cu_3I(2\text{-Mepy})_3]$

Method A

CuI (3 mmol, 0.57 g) was added to 20 mL 2-Mepy and the solution was stirred for *ca.* 5 min. at room temperature. Then $(NH_4)_2WOS_3$ (1 mmol, 0.332 g) was added. The solution immediately turned deep-red and was stirred for an additional 10 min. The resulting solution was subsequently filtered to afford a deep-red filtrate. Red crystals (0.556 g) (Yield: 62.3%) were obtained after several days by laying the filtrate with i-PrOH. Anal. Calcd. for $WOS_3Cu_3IC_{18}H_{21}N_3$ (%): C, 24.2; H, 2.4; N, 4.7. Found: C, 24.1; H, 2.3; N, 4.8. IR spectra: ν(W-O_t), 917 cm^{-1} (vs); ν(W-μ_3-S), 437 cm^{-1} (vs).

Method B

A well-ground mixture of $(NH_4)_2WOS_3$ (1 mmol, 0.332 g), CuI (3 mmol, 0.57 g) and Et_4NI (1 mmol, 0.257 g) was put into a reaction tube and heated to 90°C for 8 hours under a nitrogen atmosphere. After extracting the resultant black solid with a mixture of (20 mL) of 2-Mepy and DMF (V : V = 3 : 2), the extract was filtered to afford a purple-red filtrate. Single crystals (0.185 g) (Yield: 20.7%) were achieved after several days by laying the filtrate with i-PrOH.

Crystal Structure Determination

A well-developed single crystal of the cluster with suitable dimensions was mounted on a glass fiber. The data were collected using a Siemens P4 four-circle diffractometer with graphite monochromated MoKα ($\lambda = 0.71073$ Å) radiation using ω/θ scan mode with a variable scan speed $4.0-40.0^\circ\,\mathrm{min}^{-1}$ in ω at 293(2) K. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Hydrogen atoms were placed in their calculated positions, assigned fixed isotropic thermal parameters and allowed to ride, on their respective parent atoms. The Flack parameter of the cluster is $-0.003(13)$. All computations were carried out on a PC-586 computer using the SHELXTL PC Program Package. Details of data collection and structure refinement are summarized in Table I. Atomic coordinates and isotropic thermal parameters of the cluster are given in Table II.

Optical Measurements

A DMF solution of the cluster was placed in a 5 mm-quartz cuvette for NLO optical property measurements. The laser pulse was from a

TABLE I Crystal data and details of intensity measurements and structure refinement

Formula	$C_{18}H_{21}N_3IOS_3Cu_3W$
Formula weight	892.93
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a(Å)	11.968(5)
b(Å)	19.102(4)
c(Å)	11.209(2)
α(°)	90.00
β(°)	90.00
γ(°)	90.00
V(Å^3)	2562.3(13)
Z	4
T(K)	293(2)
D_c(g·cm^{-1})	2.315
F(000)	1680
μ(MoKα)(cm^{-1})	8.395
λ(Å)	0.71069 (graphite monochromated)
Collection range (°)	$2.01 < \theta < 25.00$
Index ranges	$-1 \le h < 14, -1 \le k \le 22, -1 \le l \le 13$
Number of total reflection	3116
Number of observed	2771
R($I > 2\sigma(I)$)	0.0365
wR	0.0933
Flack parameter	$-0.003(13)$
Goodness-of-fit	1.098
Largest diff. peak and hole(e/Å^3)	0.738 and -1.117

TABLE II Atomic coordinates and isotropic thermal parameters ($Å^2$) for $[WOS_3Cu_3I(2\text{-}Mepy)_3]$

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
W(1)	0.53551(4)	0.85315(2)	0.52387(4)	0.06165(14)
I(1)	0.59835(9)	0.94434(5)	0.18991(8)	0.0796(3)
Cu(1)	0.71622(12)	0.90530(8)	0.4149(2)	0.0775(4)
Cu(2)	0.5171(2)	0.81076(9)	0.29441(15)	0.0803(4)
Cu(3)	0.45499(15)	0.96482(8)	0.4062(2)	0.0824(4)
S(1)	0.6632(2)	0.7900(2)	0.4222(3)	0.0683(7)
S(2)	0.5990(3)	0.96399(15)	0.5413(3)	0.0671(7)
S(3)	0.3764(2)	0.8550(2)	0.4156(3)	0.0722(7)
O(1)	0.5123(8)	0.8156(5)	0.6669(7)	0.080(2)
N(1)	0.8775(8)	0.9218(5)	0.3895(9)	0.064(2)
N(2)	0.4857(9)	0.7521(5)	0.1512(9)	0.072(3)
N(3)	0.3646(9)	1.0493(5)	0.3657(11)	0.077(3)

Continuum Np70 ns/ps Nd : YAG laser system with a pulse width of 8 ns at 532 nm and a near-Gaussian transverse mode. The laser pulse was divided into two beams, one was used to monitor the incident laser energy and the other was focused into the sample cell. The input and the output energies of beams were measured with energy meters (Laser Precision Corporation Rjp-735), while the incident energies were varied with an attenuator. The experimental data have been collected utilizing a single shot at a rate of 1 pulse per minute to avoid the influence of thermal and long-term effects.

RESULTS AND DISCUSSION

Crystal Structure of $[WOS_3Cu_3I(2\text{-}Mepy)_3]$

The crystal structure of $[WOS_3Cu_3I(2\text{-}Mepy)_3]$ is shown in Figure 1. Selected bond lengths and angles are listed in Table III. Consisting of a (WCu_3) tetrahedron interlocked with an (IS_3) tetrahedron, the skeleton of the neutral cluster can be described as a slightly distorted cube, in which the four corners are occupied by one I atom and three Cu atoms, respectively, with a 2-Mepy ligand bonding to each Cu atom. Three Cu(2-Mepy) groups are coordinated to the $[WOS_3]^{2-}$ unit across three S–S edges. The W atom has basically retained the C_{3v} geometry of the free $[WOS_3]^{2-}$ anion with S–W–S(O) angles ranging from 107.92(12)° to 111.0(3)°. The W(1)–O(1) bond length is 1.778(8) Å while the three W–S bond lengths are similar to each other (2.256(3) Å ~ 2.258(3) Å), consistent with an expected arrangement of one W=O double bond and three W–S single bonds.

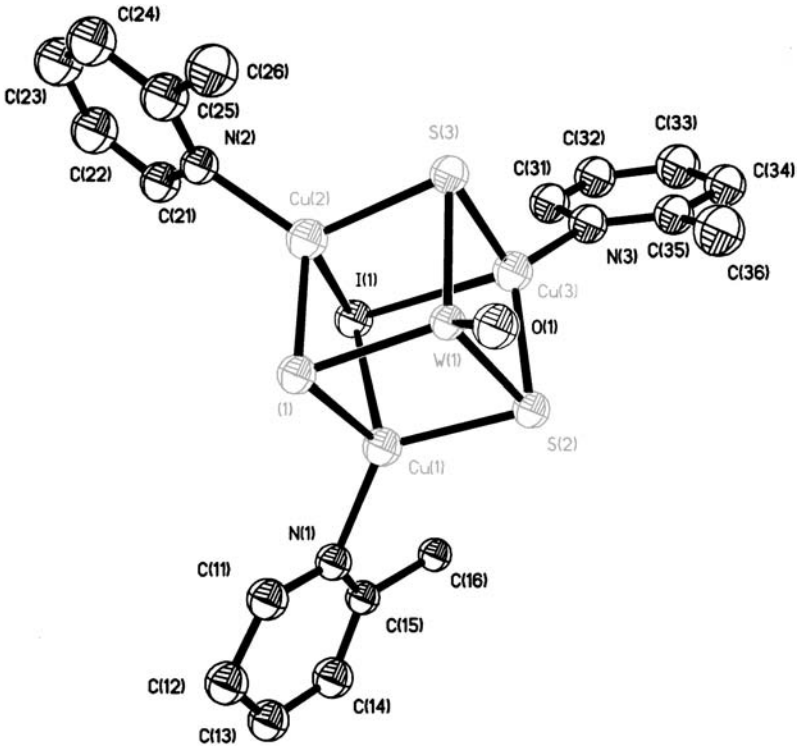

FIGURE 1 A perspective view of the structure of the neutral cluster $[WOS_3Cu_3I(2\text{-Mepy})_3]$.

The three Cu atoms are almost equivalent, each coordinated with two μ_3-S atoms, one μ_3-I atom and one 2-Mepy ligand, forming three reverse distorted tetrahedran. The bond angles of these three Cu atoms are $96.37(10)^\circ \sim 127.6(3)^\circ$ in Cu(1), $98.35(10)^\circ \sim 123.3(3)^\circ$ in Cu(2), and $95.93(11)^\circ \sim 124.3(3)^\circ$ in Cu(3). The W–Cu lengths ranging from 2.676(2) Å to 2.705(2) Å resemble those in $[Et_4N]_3[WOS_3(CuI)_3(\mu_2\text{-I})]$ (2.663(6) Å ~ 2.693(4) Å) [21]. The Cu–S distances varying from 2.288(4) Å to 2.322(4) Å are comparable to these found in $[WOS_3Cu_3Cl(PPh_3)_3]$ (2.287(5) ~ 2.362(5) Å) [22]. The distances of Cu(2)–N(2) (1.994(9) Å) and Cu(3)–N(3) (1.995(11) Å) are slightly longer than that of Cu(1)–N(1) (1.977(9) Å), while the three Cu–I bond lengths are almost the same. From the bond distances of Cu–S and Cu–N, we also conclude that coordination between the Cu(1) atom with an S(1)–S(2) edge and N(1) atom is stronger than that of Cu(2) with an S(1)–S(3) edge and N(2) atom as well as Cu(3) with an S(2)–S(3) edge and N(3) atom, although three Cu atoms have the same coordination mode $CuS_2I(2\text{-Mepy})$.

TABLE III Selected bond lengths (Å) and angles (°) for $[WOS_3Cu_3I(2\text{-Mepy})_3]$

W(1)–O(1)	1.778(8)	Cu(1)–N(1)	1.977(9)
W(1)–S(1)	2.256(3)	Cu(1)–S(2)	2.288(4)
W(1)–S(2)	2.258(3)	Cu(1)–S(1)	2.293(3)
W(1)–S(3)	2.258(3)	Cu(2)–N(2)	1.994(10)
W(1)–Cu(1)	2.676(2)	Cu(2)–S(1)	2.294(4)
W(1)–Cu(3)	2.687(2)	Cu(2)–S(3)	2.322(4)
W(1)–Cu(2)	2.705(2)	Cu(3)–N(3)	1.995(11)
I(1)–Cu(2)	2.971(2)	Cu(3)–S(2)	2.294(4)
I(1)–Cu(1)	2.985(2)	Cu(3)–S(3)	2.302(4)
I(1)–Cu(3)	2.996(2)		
O(1)–W(1)–S(1)	110.2(3)	N(2)–Cu(2)–I(1)	103.1(3)
O(1)–W(1)–S(2)	110.7(3)	S(1)–Cu(2)–I(1)	98.35(10)
S(1)–W(1)–S(2)	108.51(11)	S(3)–Cu(2)–I(1)	98.94(10)
O(1)–W(1)–S(3)	111.0(3)	N(3)–Cu(3)–S(2)	124.3(3)
S(1)–W(1)–S(3)	107.92(12)	N(3)–Cu(3)–S(3)	121.8(3)
S(2)–W(1)–S(3)	108.41(12)	S(2)–Cu(3)–S(3)	105.68(12)
Cu(2)–I(1)–Cu(1)	66.85(5)	N(3)–Cu(3)–I(1)	103.4(4)
Cu(2)–I(1)–Cu(3)	66.78(5)	S(2)–Cu(3)–I(1)	95.93(11)
Cu(1)–I(1)–Cu(3)	67.63(5)	S(3)–Cu(3)–I(1)	98.73(10)
N(1)–Cu(1)–S(2)	127.6(3)	W(1)–S(1)–Cu(1)	72.06(10)
N(1)–Cu(1)–S(1)	115.4(3)	W(1)–S(1)–Cu(2)	72.97(10)
S(2)–Cu(1)–S(1)	106.19(13)	Cu(1)–S(1)–Cu(2)	91.31(12)
N(1)–Cu(1)–I(1)	107.4(3)	W(1)–S(2)–Cu(1)	72.13(10)
S(2)–Cu(1)–I(1)	96.37(10)	W(1)–S(2)–Cu(3)	72.35(10)
S(1)–Cu(1)–1(1)	97.99(10)	Cu(1)–S(2)–Cu(3)	93.17(13)
N(2)–Cu(2)–S(1)	123.3(3)	W(1)–S(3)–Cu(3)	72.19(9)
N(2)–Cu(2)–S(3)	122.6(3)	W(1)–S(3)–Cu(2)	72.40(10)
S(1)–Cu(2)–S(3)	104.48(13)	Cu(3)–S(3)–Cu(2)	90.50(12)

Nonlinear Optical Properties

The electronic spectrum of $[WOS_3Cu_3I(2\text{-Mepy})_3]$ in DMF solution is depicted in Figure 2, with the first absorption peak located at 426 nm. The cluster has relatively low linear absorption in the visible and near-IR region. A broad transparent range is an important criterion for NLO applications such as optical limiters.

The experimental results of OL effects for the cluster in DMF solution and fullerene C_{60} in toluene solution are shown in Figure 3 demonstrating that at very low fluence, they respond linearly to the incident fluence obeying Beer's law. The light transmittance starts to deviate from Beer's law when the input light fluence rises to certain values with respect to each compound, and the solution becomes increasingly less transparent. It also manifests that comparing with C_{60}, the OL of the cluster (with $Eth = 0.1\,J/cm^2$) in DMF solution is obviously superior to that of fullerene C_{60} in toluene solution [23] with linear transmission of about 76%.

The nonlinear absorptive performance of the cluster solution was measured by the Z-scan technique [24] under an open-aperture configuration with

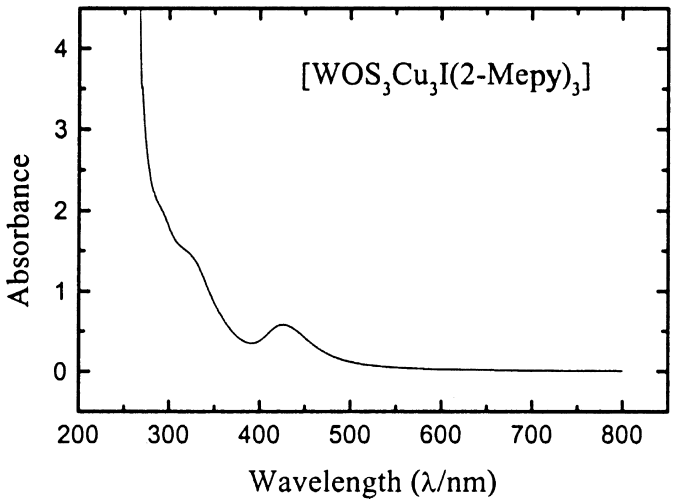

FIGURE 2 Electronic spectra of $[WOS_3Cu_3I(2\text{-Mepy})_3]$ in DMF solution with a 1 cm optical path. The concentration of $[WOS_3Cu_3I(2\text{-Mepy})_3]$ is 1.0×10^{-4} m.

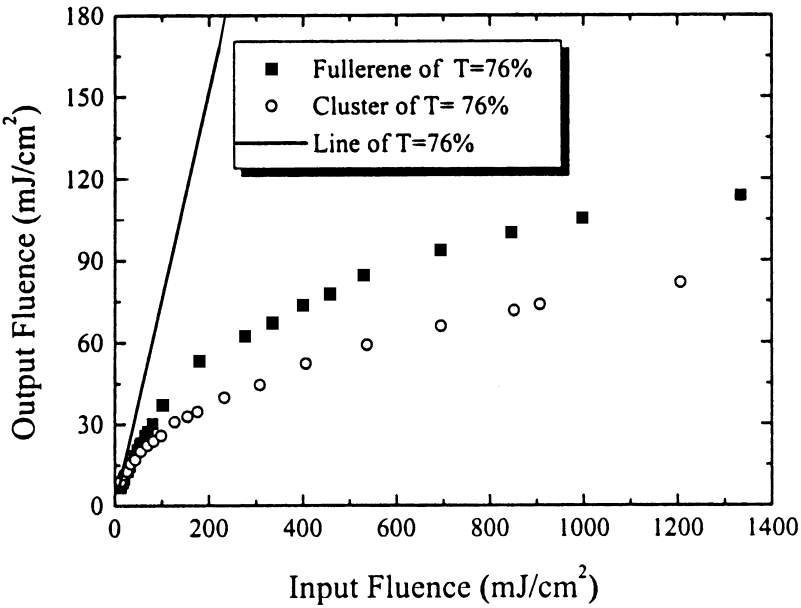

FIGURE 3 Optical limiting effects of the cluster $[WOS_3Cu_3I(2\text{-Mepy})_3]$ (in 7.3×10^{-4}m DMF solution) and fullerene C_{60} (in toluene solution).

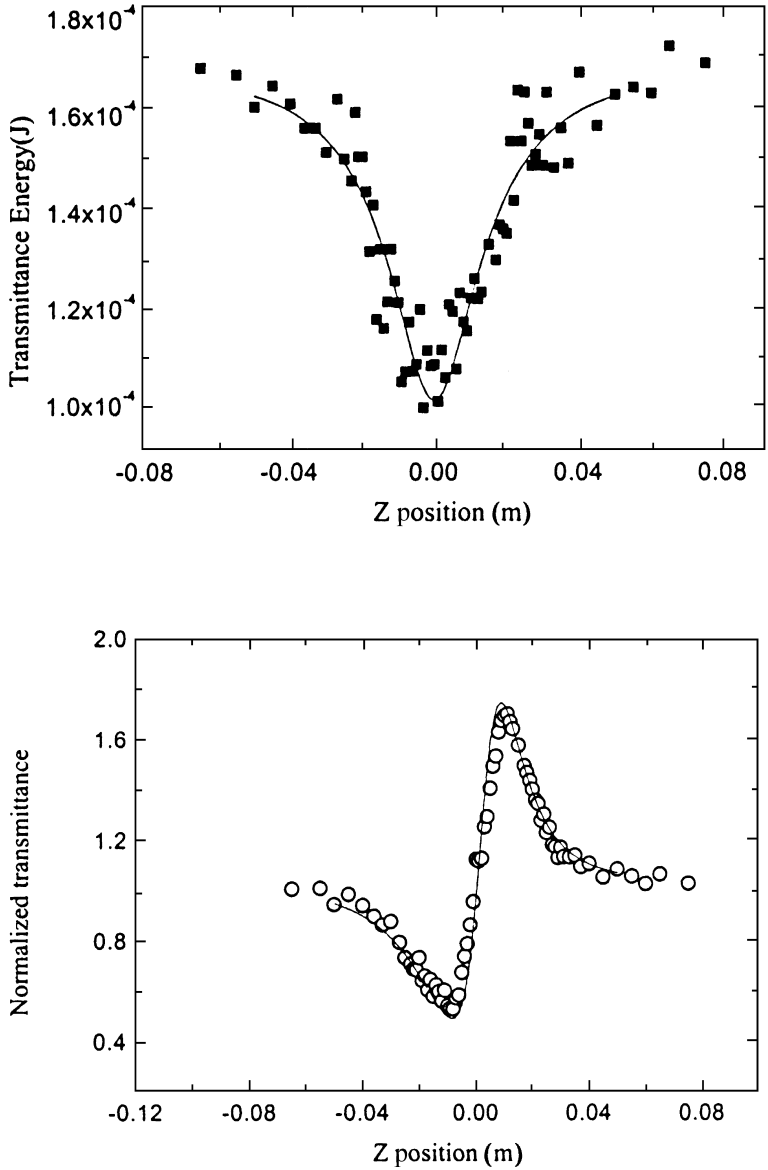

FIGURE 4 Z-scan data of the cluster $[WOS_3Cu_3I(2\text{-Mepy})_3]$ (in 7.1×10^{-4} m DMF solution) at 532 nm with I_0 being 8.2×10^{12} W/cm^2: (a) Collected under the open aperture configuration showing NLO absorption (the solid curve is a theoretical fit); (b) Obtained by dividing the normalized Z-scan data obtained under closed aperture configuration by the normalized Z-scan data in (a) (it shows the self-focusing effect of the cluster).

pulse width of 8 ns at 532 nm and a 1 Hz-repetition rate. The results of NLO absorption are shown in Figure 4a indicating that the laser pulses experience strong excited state absorption in the cluster. The NLO absorption performance of the cluster can be represented by Eqs. (1) and (2):

$$T(z) = \frac{1}{\sqrt{\pi} q(z)} \int_{-\infty}^{\infty} \ln[1 + q(z)] e^{-\tau^2} \, d\tau \tag{1}$$

$$q(z) = \alpha_2 I(z) \frac{1 - e^{-\alpha_0 L}}{\alpha_0} \tag{2}$$

where $T(z)$ represents the transmittance, defined here as the ratio of the transmitted pulse energy and the incident pulse energy at 532 nm; $I(z)$ is the incident light irradiance ($I_0 = 8.2 \times 10^8$ w/cm^2); α_0 and α_2 denote the linear and nonlinear absorption coefficients, respectively; and L is the optical path ($L = 0.5$ cm in the current experiments). The NLO refractive behavior, shown in Figure 4b, was assessed by dividing the normalized Z-scan data obtained under the closed-aperture configuration by the normalized Z-scan data obtained under the open-aperture configuration. The data show that the cluster has a positive sign for refractive nonlinearity, which indicates self-focusing behavior. The effective third-order NLO refractive index n_2 of the cluster is given by Eq. (3):

$$n_2 = \frac{\lambda \alpha_0}{0.812 \pi I (1 - e^{-\alpha_0 L})} \Delta T_{V-P} \tag{3}$$

where ΔT_{V-P} is the difference between normalized transmittance values at valley and peak positions and λ is the wavelength of the laser. A reasonably good fit between the experimental data and theoretical curve was obtained, which suggests that the experimentally obtained NLO effects are effectively third-order in nature. The effective α_2-value of 5.7×10^{-9} W/cm^3 and n_2-value of 1.28×10^{-11} esu were derived for the sample from the theoretical curve. Both excited state population (and absorption) and two-photon absorption can be responsible for the measured NLO effects.

Acknowledgement

This project was supported by the National Science Foundation of China (No. 29631040) and Foundations of HIT.

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