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A novel optical limiting coordination polymer with ladder-like framework

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ABSTRACT The optical limiting (OL) properties of a novel coordination polymer $\{[Et_4N][Ag_2I_3]\}_n$ with a ladder-like framework were investigated using 532-nm nanosecond laser pulses. The coordination polymer in dimethylformamide solution exhibits better OL performance than C_{60} in toluene. The results were discussed using a phenomenological model based on excited-state nonlinear absorption.

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1 Introduction

Coordination polymers have attracted increasing attention because of their interesting structure, novel topologies, unusual physicochemical properties and potential applications as functional materials. Remarkable progress has been made in the field of coordination polymers of various dimensionality with different structural motifs [1–7]. Up to now, however, most of the research concerned has been largely focused on the synthesis, structures and magnetic properties, and relatively less effort has been expended on their nonlinear optical properties [5–7]. To our knowledge, no research has been conducted on optical limiting (OL) in a ladder-like coordination polymer.

In the present paper, OL performance in such a novel coordination polymer was investigated experimentally with nanosecond laser pulses at 532-nm wavelength and a strong OL effect was observed. The result was basically analyzed by using a phenomenological model of excited-state nonlinear absorption.

2 Materials and experiments

The coordination polymer was synthesized by the reaction of Et_4I with AgI in dichloromethane and acetonitrile. The resulting deep-red solution was stirred for 10 h at room temperature. By laying the filtrate with i-PrOH for several days, single crystals were obtained. An ORTEP (Oak Ridge Thermal Ellipsoid Plot) drawing of $\{[Et_4N][Ag_2I_3]\}_n$
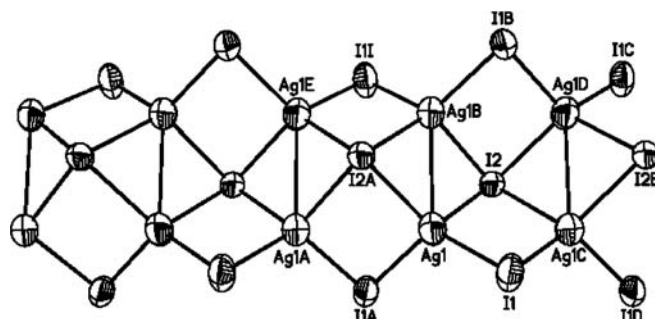

FIGURE 1 ORTEP diagram of a section of the crystal structure of $\{[Et_4N][Ag_2I_3]\}_n$

is shown in Fig. 1. As shown in Fig. 1, the polymeric anion is a hanging ladder-like polymeric anion. The linear absorption spectrum of the sample in dimethylformamide (DMF) is shown in Fig. 2, where only a sharp peak can been seen around 425 nm, and absorption around 532 nm is relatively weaker.

The investigation of the OL properties of the coordination polymer was conducted by measuring output fluence and nonlinear fluence transmittance change with input fluence at the wavelength of 532 nm. The laser pulses used in the experiments were supplied by a frequency-doubled, Q-switched,
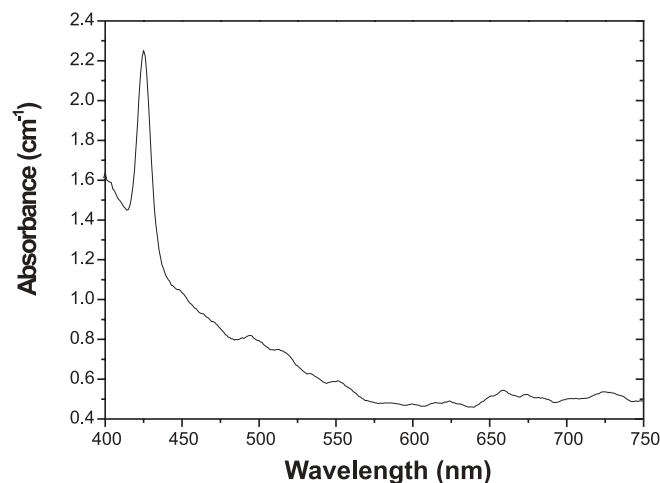

FIGURE 2 Linear absorption spectrum of coordination polymer $\{[Et_4N][Ag_2I_3]\}_n$ in DMF

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mode-locked Continuum ns/ps Nd:YAG laser system, which provides linearly polarized 8-ns (FWHM) pulses at 532 nm with a repetition rate of 1 Hz. The transverse mode of the laser pulses is nearly Gaussian. The experimental setup for OL measurement is same as that used in our previous work [8]. The input laser pulses adjusted by an attenuator were split into two beams. One was employed as a reference to monitor the incident laser energy, and the other was focused onto the sample cell positioned at the focus by using a lens with 30-cm focal length. The beam profile at the sample surface was measured to have a $1/e^2$ diameter of 110 μm. Incident and transmitted laser pulses were monitored by utilizing two energy detectors. The coordination polymer was dissolved in DMF with a no-saturation concentration of 1 mg/ml and housed in a quartz cell with a path 5-mm long. The linear transmission of the solution is 87% at 532 nm. For comparison, C_{60} in toluene with the same linear transmission was measured under the same experimental conditions.

FIGURE 4   Fluence-dependent transmission of $\{[Et_4N][Ag_2I_3]\}_n$ and C_{60} at 532 nm

3   Results and discussion

The OL results, namely output-fluence changes with input fluence, are shown in Fig. 3. It is clearly found that the sample in DMF provides a lower output fluence at a given input fluence than C_{60} in toluene with the same linear transmission of 87%. For example, when the incident fluence reaches 1800 mJ/cm², the output fluences for the coordination polymer and C_{60} are about 230 mJ/cm² and 360 mJ/cm², respectively. The former value is about 1.5 times lower than the latter, indicating that the coordination polymer DMF solution has stronger OL capacity than C_{60} in toluene. Figure 4 demonstrates the changes of transmission as a function of input fluence. As shown, when the input fluence increases to 1800 mJ/cm², the transmissions decrease from 87% to around 12% and 20% for the coordination polymer and C_{60}, respectively. It is also found that the OL threshold, defined here as the input fluence at which the transmission decreases to 50% of the linear transmission, is about 235 mJ/cm² for the coordination polymer and 675 mJ/cm² for C_{60}, which proves further
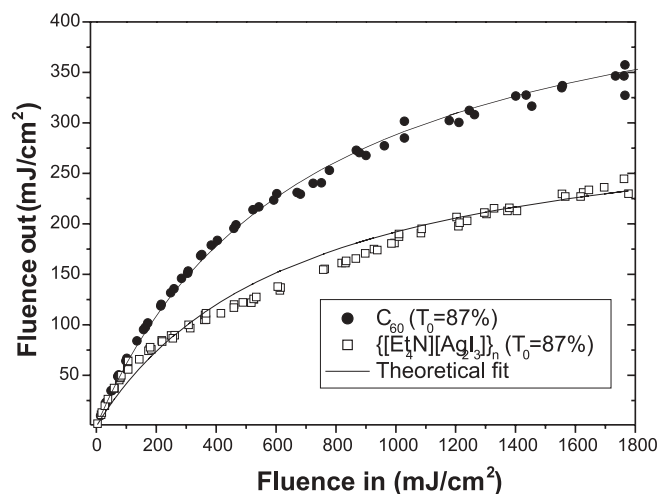

FIGURE 3   OL results for $\{[Et_4N][Ag_2I_3]\}_n$ in DMF and C_{60} in toluene at 532 nm

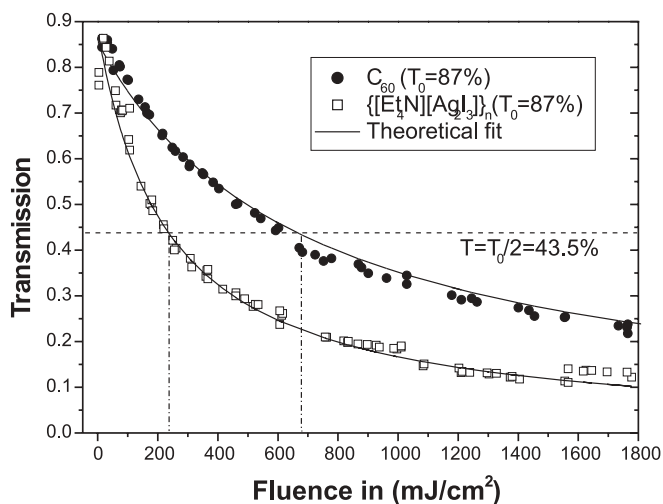that, compared with C_{60}, the metal cluster displays better OL effects.

It has been extensively accepted that the OL of metal clusters under nanosecond laser pulses arises mainly from excited-state absorption [9–12]. Similarly, we assume that the mechanism responsible for the OL in the coordination polymer is mainly excited-state absorption. Thus, we can use a phenomenological model of Golovlev et al. [13] based on nonlinear absorption to fit the OL experimental results for the coordination polymer in DMF and C_{60} in toluene. In this model, the absorption cross section σ is assumed to be a function of the laser fluence φ. Then, $\sigma(\varphi)$ can be written in the form of a series expansion in powers of φ:

$$\sigma(\varphi) = \sigma_0 + \mu_1\varphi + \mu_2\varphi^2 + \dots, \tag{1}$$

where σ_0 is the ground state absorption cross section. Taking the first two terms into Beer's law and integrating temporally, we can obtain the equation for the energy fluence of a laser beam passing through a nonlinear absorbing medium:

$$d\varphi/dz = -\sigma_0\varphi N_0 - \mu_1\varphi^2 N_0. \tag{2}$$

Then, by integrating (2) again, we can easily obtain the equation for the dependence of the output fluence φ_{out} on the input fluence φ_{in} as follows:

$$\varphi_{out} = T_0\varphi_{in}/[1 + (1 - T_0)\varphi_{in}/\varphi_{nl}]. \tag{3}$$

Also, the transmission $T = \varphi_{out}/\varphi_{in}$ can be expressed as

$$T = T_0/[1 + (1 - T_0)\varphi_{in}/\varphi_{nl}], \tag{4}$$

where $T_0 = \exp(-\sigma_0 N_0 L)$ is the linear transmission of the sample, equalling 87% in our experiment, N_0 is the population of the ground state, L is the cell length and $\varphi_{nl} = \sigma_0/\mu_1$ is a parameter characterizing the nonlinear absorption of the materials. It can be seen from (3) that in this model the OL performance of a sample can conveniently be assessed by the value of φ_{nl} only. That is, the smaller the value of φ_{nl}, the stronger the OL capability will be. As shown in Figs. 3 and 4,

the solid lines are obtained through numerical fittings using (3) and (4), respectively. The corresponding values of φ_{nl} for the coordination polymer and C_{60} are 125 and 275 mJ/cm^2, respectively, indicating that the coordination polymer has a stronger OL effect than C_{60}. This is coincident with the conclusion drawn through the comparison of the OL threshold between the coordination polymer and C_{60}. The reasonable fittings of the theory to the experimental results imply that the origin of the OL in the coordination polymer is mainly due to excited-state absorption. But, we also found that the fit for the coordination polymer in DMF is not as good as that for C_{60} in toluene, which indicates that the model used now is not excellent but reasonable to describe the OL for the coordination polymer in DMF; more work concerning this is necessary in the future. In order to evaluate the ageing ability of the coordination polymer in DMF, the OL experiments were repeated in the coordination polymer solution after one month. We did not find that a precipitate had appeared at the bottom of the test tube, nor that the OL characteristics had degraded, which indicates that the coordination polymer DMF solution is stable.

4 Conclusions

In summary, we have investigated the nanosecond OL behavior in a ladder-like coordination polymer at 532-nm wavelength. A stronger OL capability than that in C_{60} was experimentally found, and theoretically discussed by using a phenomenological model based on excited-state absorption. The results indicate that the sample is a promising candidate for OL applications.

REFERENCES

1 H.J. Choi, M.P. Suh: J. Am. Chem. Soc. **120**, 10 622 (1998)
2 S.R. Batten, R. Robson: Angew. Chem. Int. Ed. Engl. **37**, 1460 (1998)
3 P.J. Steel, C.J. Sumby: Inorg. Chem. Commun. **5**, 323 (2002)
4 K.S. Min, M.P. Suh: J. Solid State Chem. **152**, 183 (2000)
5 H.W. Hou, Y.L. Song, Y.T. Fan, L.P. Zhang, C.X. Du, Y. Zhu: Inorg. Chim. Acta **316**, 140 (2001)
6 H.W. Hou, Y.L. Wei, Y.T. Fan, C.X. Du, Y. Zhu, Y.L. Song, Y.Y. Niu, X.Q. Xin: Inorg. Chim. Acta **319**, 212 (2001)
7 C. Janiak, T.G. Scharmann, P. Albrech, F. Marlow, R. Macdonald: J. Am. Chem. Soc. **118**, 6307 (1996)
8 S.L. Qu, Y. Chen, Y.X. Wang, Y.L. Song, S.T. Liu, X.L. Zhao, D.Y. Wang: Mater. Lett. **51**, 534 (2001)
9 H.W. Hou, X.Q. Xin, J. Liu, M.Q. Chen, S. Shu: J. Chem. Soc. Dalton Trans. **22**, 3211 (1994)
10 W. Ji, W. Xie, S.H. Tang, S. Shi: Mater. Chem. Phys. **43**, 45 (1996)
11 M.K.M. Low, H.W. Hou, H.G. Zheng, W.T. Wong, G.X. Jin, X.Q. Xin, W. Ji: Chem. Commun. **4**, 505 (1998)
12 Y.L. Song, C. Zhang, Y.X. Wang, G.Y. Fang, G.C. Jin, S.T. Liu, X.Q. Xin, H.A. Ye: Chem. Phys. Lett. **326**, 341 (2000)
13 V.V. Golovlev, W.R. Garret, C.H. Chen: J. Opt. Soc. Am. B **13**, 2801 (1996)