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Investigation on ultrafast third-order optical nonlinearity of metal(dmit)$_2$/(mnt)$_2$ charge transfer complexes*

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We have investigated the transient third-order optical nonlinearity of the solutions of Metal(dmit)$_2$/(mnt)$_2$ salts in acetone by employing femtosecond optical Kerr gate measurement at 830 nm wavelength. An order of enhancement on the second-order hyperpolarizability is found for the above salts with central atoms of Cu and Ni. We have suggested an explanation for the enhancement based on the extension of electronic conjugation by the centring Cu or Ni atom.

Keywords: third-order optical nonlinearity, organic charge transfer complexes, ultrafast spectroscopy
PACC: 4265, 4280W, 7820, 7855K

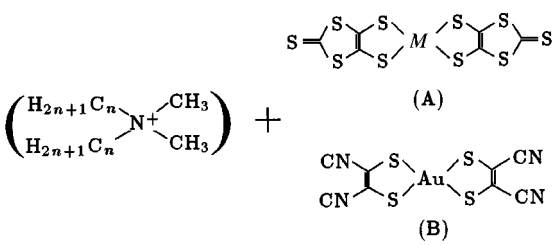
1. Introduction

Nonlinear optical applications, including all-optical switch and optical computing, require instantaneous and large nonlinear optical response without absorption in working wavelength. Organic materials have been proved to have these properties and are relatively easy to be obtained. Their structures and property can be adjusted by chemical methods to fit many requirements. Moreover, the chemical modification can also help to learn the origination of nonlinear optical responses of a series of organic materials. With a chemical modification, organometallic molecules have been widely synthesized and investigated extensively for their structural flexibility and easiness of tailoring. Their optical properties, especially the third-order optical nonlinearity, have recently attracted more and more attention.[1−4] The change of metal atoms within organic molecules may change the conjugation or charge transfer status. The charge transfer occurs between metal and ligands due to the change of electron distributions. At the same time, the d orbital of metal atoms or ions conjugate with the system π conjugation to form a larger electron delocalization length. These properties affect the nonlinear optical response of organic molecules considerably. By adjusting the metal atoms, e.g. through changing oxidation states and configurations of the ligands, the charge transfer process and conjugations can be optimized for better nonlinear response.

Besides metallophthalocyanines (MPCs),[5] metalloporphyrins (M-PP),[6] metal polyynes,[7] metallocenes[8], etc., metal dithiolenes are also very important organic materials for nonlinear optics applications, including third-order nonlinearity[9−13] and optical limiting.[14] Their second-order hyperpolarizability γ was measured to be as large as 10^{-31}esu, using the picosecond degenerate four-wave mixing measurement at the resonant wavelength 1064 nm,[12] and 10^{-32}esu using more recent femtosecond optical Kerr effect (OKE) measurement at 830 nm.[13] In this paper, we conduct a systematical femtosecond OKE investigation on the transient nonlinear optical response of a series of dithiolene complexes, $[(C_nH_{2n+1})_2N(CH_3)_2]$ M(dmit)$_2$/(mnt)$_2$, where n=1, 10, 12, 16,

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18, as shown in Scheme 1 with M=Au, Cu and Ni. The sulphur-rich anion, metal(dmit)$_2$, where dmit = 1, 3 dithiol-2-thione-4, 5-dithiolate, is an intriguing constituent for constructing organic conductors. For instance, several metal(dmit)$_2$ salts, such as TTF[Ni(dmit)$_2$]$_2$ (TTF=tetrathiafulvalene),[15] TTF[Pd(dmit)$_2$]$_2$,[16] [$(CH_3)_4$N] [Ni(dmit)$_2$]$_2$,[17] and [$(CH_3)_4$N] [Pd(dmit)$_2$]$_2$,[18] have been found to undergo superconducting transition. Furthermore, a series of metal-dithiolene complexes have also been found to be a promising class of candidates for fabricating conductive Langmuir–Blodgett (LB) films for electronic device applications.[19] The origination of the conductivity is the conjugation of delocalized π-π and d-π electrons, which is also beneficial to the large and fast third-order optical nonlinearity.



No. of sample	n	l	M	(A) or (B)
1	10	1	Au	(A)
2	12	1	Au	(A)
3	16	1	Au	(A)
4	18	1	Au	(A)
5	18	1	Au	(B)
6	18	2	Cu	(A)
7	1	1	Ni	(B)

Scheme 1. metal(dmit)$_2$/(mnt)$_2$.

2.Samples and experimental method

The absorption spectra of the sample solutions are shown in Fig.1(a) and (b). We used acetone as the solvent for all the materials for good solubility. The obvious peak shifts were noticed. The materials were synthesized following the procedure reported by Steimecke *et al.*[20] For each sample, we prepared a series of concentrations to verify its square dependence on OKE signals, which was predicted theoretically. This phenomenon is a reliable proof for ruling out other non-molecular contributions, including aggregations. The relationship between the OKE signal and the laser intensity was also studied and the cubic intensity dependence was demonstrated.

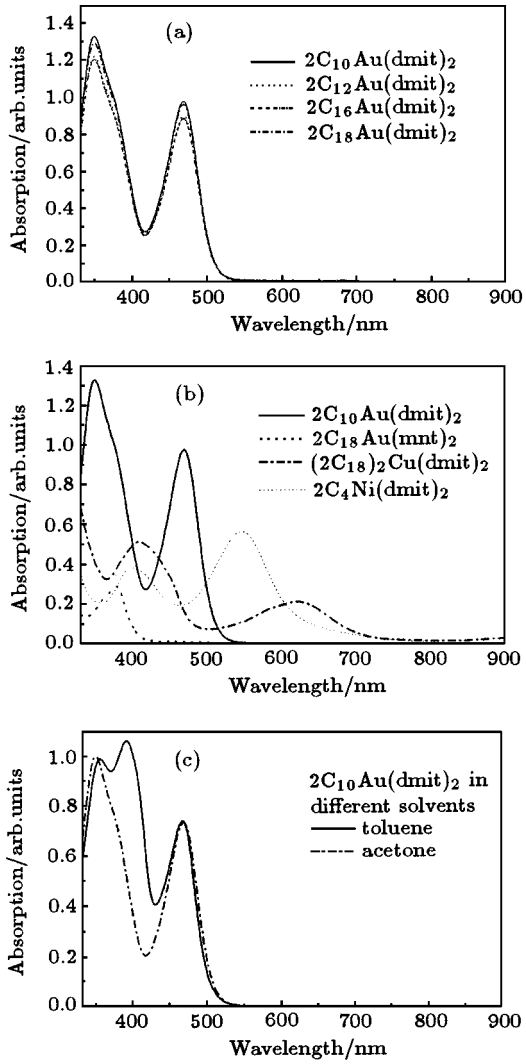


Fig.1. Absorption spectra of samples. (a) Samples 1–4 with different alkyl group lengths. (b) Different central atoms of Au, Cu and Ni, while Au complex with (mnt)$_2$ group is also shown. (c) 2C$_{10}$Au(dmit)$_2$ in toluene and acetone.

The ultrafast OKE response of solutions of samples in acetone was measured with a Ti:sapphire laser system (Mira900F, Coherent Co. Ltd., USA). It was operated at a repetition rate of 76MHz. The laser wavelength was centred at 830 nm. The laser beam from Mira 900F was divided into two parts: a pump beam and a probe beam. The polarization of the probe beam was rotated 45° with respect to the linear polarization of the pump beam. The intensity ratio of the pump beam to the probe beam was about 8:1. The pump beam passed through a delay line driven by a step motor so that the optical length difference between the pump beam and the probe beam could be changed during the measurement. And then the two

beams were adjusted parallel and focused by a single convex lens and overlapped at the focus, located in the sample cell of 1mm in thickness. The cell was filled with sample solution. An analyser (polarizer) was inserted into the optical path of the probe beam behind the cell, with its transmission axis perpendicular to the original polarization of the probe beam. Thus, only the generated orthogonal signal, i.e. the OKE signal, could be detected by the photodiode positioned behind the analyser. In order to increase the signal-to-noise ratio, we used a mechanical chopper to chop both the pump and the probe beams with different frequencies and a lock-in amplifier to pick up the sum frequency signal from the detector. The signal was A/D transmitted to a computer. All the measurements were proceeded under the control of a computer program. We replaced the sample cell with a BBO crystal (0.2mm thickness) to determine the zero-delay point and the autocorrelation signal of the laser beam. The pulse duration was then determined to be 120 fs. More detailed apparatus configuration was reported in our previous papers.[21−23]

3. Results and discussions

During the experiments, the sample solution in the 1mm cell was found to be almost transparent at 830 nm. A small heating effect which changed the pump profile was found at a very high laser intensity or high concentration. We then lowered the concentration or reduced the incident laser power to a certain level, at which the heating effect could be ignored. Since the sample was prepared as a solution, the measured third-order nonlinear optical susceptibility, $\chi^{(3)}$, is the combination of contributions from both the sample solute and solvent. Following the standard reference measurement,[24] we use the following equation to calculate the total third-order nonlinear optical susceptibility of the solution at different concentrations:

$$\chi_S^{(3)} = \chi_R^{(3)} \left(\frac{I_S}{I_R}\right)^{\frac{1}{2}} \left(\frac{n_S}{n_R}\right)^2. \qquad (1)$$

The subscripts, S and R, are the parameters of the sample solution and the reference sample CS_2. I denotes the intensity of OKE, n is the refractive index. The concentration of the sample is very dilute in the solution, so we take the refractive index of acetone (n=1.36) as that of the solution. The index n of CS_2 is 1.62. The third-order nonlinear susceptibility of CS_2 was estimated as 1×10^{-13}esu in femtosecond time scale.[25] Using Eq.(1), we can obtain $\chi^{(3)}$ directly by measuring the OKE signal intensity for both the sample and the reference under the same conditions.

The OKE signals of the sample solutions of different concentrations have been measured. The typical response is demonstrated in Fig.2, in which the contribution from the solvent is shown to be very small. With Eq.(1) and the measured signal for CS_2 under identical conditions, the magnitudes of $\chi^{(3)}$ for the sample solutions can be deduced, as listed in Table 1. The square dependence of the signal on the solution concentration can be fitted excellently. The experimental results in Fig.3 show a linear increase of $\chi^{(3)}$ with increasing sample concentration. The second-order hyperpolarizability of the sample molecule can then be estimated using the following equation:[26]

$$\gamma = \chi^{(3)}/(NL), \qquad (2)$$

where N is the concentration of the solution and L is the local field correction factor, $L=[(n^2+2)/3]^4$ (n is the refractive index of the solution). The calculated magnitudes of γ, shown in Table 1, lie within the large off-resonant values of the second-order hyperpolarizability. More importantly, the electronic contribution to the organometallic complex can be found, though the obtained γ cannot be directly compared with those in other reports due to the different experimental conditions. Compared with the reported highest γ, 3×10^{-32} esu, obtained by third-harmonic generation (THG) for an organometallic complex under resonant enhancement[27] and 2.3×10^{-31}esu measured by picosecond degenerate four-wave mixing (DFWM) at the resonant wavelength 1064 nm,[12] our samples 6 and 7 exhibit a larger and even instantaneous magnitude of γ.

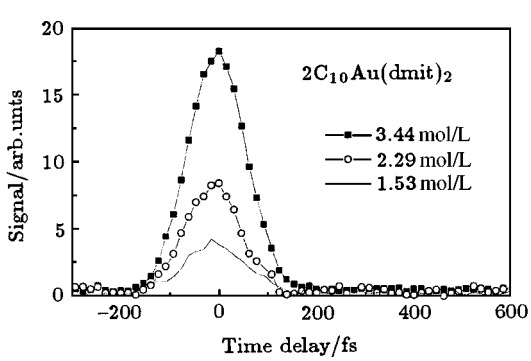


Fig.2. Ultrafast nonlinear response signal of $2C_{10}Au(dmit)_2$.

Table 1. Transient optical nonlinearity of sample materials.

Sample No.	Concentration/(mol/L)	$\chi^{(3)}/10^{-14}$esu	$\gamma^{(2)}/10^{-32}$esu
1	2.3	7.3	2.3
2[13]	2.7	10	2.2
5	2	5.2	1.6
6	0.3	11.2	23
7	0.15	3.8	16

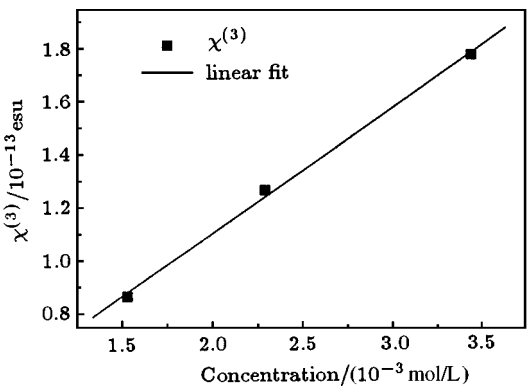


Fig.3. Linear dependence of $\chi^{(3)}$ on the solution concentration. (This is the proof for molecular response).

Within the series of our samples, we have found one order of difference of nonlinear optical response. The magnitude of γ for samples 1–5 is $\sim 10^{-32}$esu. We have carefully tested sample 1 and compared it with the formerly reported sample 2 in Ref.[13]. Samples 3 and 4 are also tested under the same condition. These four samples show nearly the same nonlinear response. Samples 6 and 7 exhibit one order enhancement. To explore the origination of this strong difference, we have analysed the static absorption spectra as shown in Fig.1. Samples 1–4 show nearly the same profile, overlapped absorption spectra for the peak positions located at 350 nm and 469 nm. The optical density (OD) for the peaks are nearly the same. This could explain the same optical response of the four samples. The magnitude of γ is 2.3×10^{-32}esu for both samples 1 and 4, which is also the same as that of sample 2 reported previously.[13] This similarity leads to the result that the length of alkyl groups plays no noticeable effect on the charge transfer or conjugation process. We have also tested the absorption of the samples in various solvents with different polarizations. The spectra for $2C_{10}Au(dmit)_2$ dissolved in acetone and toluene are shown in Fig.1(c). With nearly no shift of the original two peaks, a new peak emerges at 392 nm in the toluene solution. It can be regarded as coming from the weak shoulder located at around 382 nm on the red edge of the 350 nm peak in the acetone solution. This peak is evidently solvent-polarization dependent and it belongs to the $n-\pi^*$ transition. The other two polarization-insensitive peaks corresponds to the $\pi-\pi^*$ transitions. The π conjugation character is believed to be the main contribution of the optical nonlinearity. However, this conjugation can be extended by altering the central metal atom from Au to Cu or Ni as in samples 6 and 7, thus enhancing the optical nonlinearity. As shown in Fig.1(b), the absorption peaks of the latter two samples shift markedly to the visible range. The two peaks are located at 400 nm and 546 nm for sample 6, but at 408 nm and 621 nm for sample 7. This is the evidence for the extension of π conjugation, which is consistent with the strong enhancement of the magnitude of γ. Moreover, as discussed above, the peak of the $n-\pi^*$ transition has been also observed to exhibit a redshift, which is believed to be another important effect for the large γ for samples 6 and 7.

The measured ultrafast nonlinear optical responses of our sample molecules, as presented in Fig.2, are believed to be the contribution from the delocalized electrons as discussed in the following. In the measurements, the transient OKE response of the sample shows the same time scale as the pulse duration measured with an autocorrelator. We have not detected a delayed process. This proves that the response of samples contains mainly an instantaneous process, and the noninstantaneous processes should be ignored. This ensures that the measured large and ultrafast nonlinear optical responses of our samples come mainly from the electronic response. This character has been tested with all the samples at different concentrations.

4. Conclusion

The third-order optical nonlinearity of metal $(dmit)_2$ / $(mnt)_2$ series has been systemically studied by the transient OKE measurement. The response and intensity of OKE signals for the sample solutions in acetone are measured at different concentrations.

Only the instantaneous response is found. Such a kind of fast response is mainly contributed by the electronic part of molecules. Square concentration dependence and cubic laser intensity dependence of the OKE signals are also demonstrated. We have also evaluated the extremely large value of the nonlinear optical susceptibility of the sample with the central metal atom being Cu or Ni, and indicated the potential applications in the future.

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