Synthesis and molecular second hyperpolarizability determination of ET$_2$Hg(SCN)$_2$Cl

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Donor molecule bis(ethylenedithio)tetrathiofulvalene (BEDT-TTF, or short for ET, see Scheme 1) constitutes a member of an important class of molecular organic conductors. Using the electrochemical method, we have successfully synthesized ET$_2$Hg(SCN)$_2$Cl. The compound was characterized by x-ray powder diffraction and IR spectrum methods. The linear refractive index of its acetonitrile solution in the concentration of 5.357×10$^{-5}$ mol/L was measured at 20 °C using V-prism refractometer at four different wavelengths, and the results were fitted with the three-term Sellmeier dispersion function. The molecular second hyperpolarizability γ of ET$_2$Hg(SCN)$_2$Cl was determined by z-scan technique. A value of be 6.64×10$^{-32}$ esu was obtained.

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1. Introduction

ET series compounds are well-known charge transfer compounds. Up to now over hundreds of ET compounds have been synthesized. As an organic optical material, high nonlinear coefficients have been found to be associated with strongly donor and acceptor substituents on molecules. To our knowledge little attention has been paid to the nonlinear optical property of ET series compound. Based on this point, we synthesized ET$_2$Hg(SCN)$_2$Cl using electrochemical method and have characterized it by powder X-ray diffraction and IR spectrum methods. Its nonlinear optical property were reported in this paper. The results show that this kind of material has relative high second hyperpolarizability.

![Scheme 1. Bis(ethylenedithio)tetrathiofulvalene (ET).](image)

2. Experiments

2.1 Synthesis and characterization of ET$_2$Hg(SCN)$_2$Cl

ET was synthesized according to the route of reference [1,2], and recrystallized twice in chlorobenzene. ET$_2$Hg(SCN)$_2$Cl was obtained using electrochemical method [3] and detailed step as follows: according molar ratio of Hg(SCN)$_2$:KCl:18-crown-6 equal 1:1:1 added stoichiometry of ET, Hg(SCN)$_2$, KCl and 18-crown-6 and all the above was dissolved in mixed solvent of 100 mL TCE(1,1,2-trichloroethane) and 20 mL ethanol; then the solution was stirred over 18 hours, and poured into a two room electrolytic cell; then nitrogen was introduced for 5 min. to drive away oxygen, after which the electrolytic cell was obturated immediately with electrodes and the electrodes were joined to the constant-current power supply controlling voltage was 3.5 V. The current was 2 µA. After 18 days bright-black needle like compound ET$_2$Hg(SCN)$_2$Cl was obtained. IR spectrum was recorded from 4000 cm$^{-1}$ to 400 cm$^{-1}$ by KBr pellet technique with a NEXUS700 FT-IR photometer.

2.2 Linear absorption coefficient and linear refractive indices measurements

The linear absorption spectrum of the solution (of ET$_2$Hg(SCN)$_2$Cl in acetonitrile 5.357×10$^{-5}$ mol/L) was recorded in the wavelength range of 350 nm to 1100 nm with a Hitachi U-4100 spectrophotometer. The linear refractive index measurements of the above substance were performed at four different wavelengths at 20 °C using V-prism refractometer (model WZV-1 manufactured by Shanghai Optical Instrument Company). The four different wavelengths used in the measurement were obtained using mercury lamp, sodium lamp, hydrogen lamp and helium lamp with the combination of light filters.
2.3 The molecular second hyperpolarizability measurement

The third order nonlinear optical property measurement was performed using a single beam z-scan technique [4]. The thickness of quartz cuvette was 1 mm. The light source was obtained by double-frequency of a mode-locked Nd-YAG laser (Continuum PY61-10, 30 ps, 1064 nm), the focal-length of the positive lens is f=20 cm, the focused radius was \( r_0=17 \ \mu m \), the Rayleigh range of the beam \( z_0=\frac{\pi r_0^2}{\lambda} = 1.7 \) mm and the transmitted energy was measured with EPM2000 sensitive energy meter in the far field and the on-axis irradiance at focus (i.e. \( z=0 \)) L=89 GW/cm². The effect sample length \( L_0=\frac{1-e^{-\alpha_0 L}}{\alpha_0} \) was obtained: 0.099 cm. The diffraction length inside the sample \( n=2.47 \) mm that is more than two times of the effective sample thickness, so the sample could be regarded as “thin”.

3. Results and discussion

3.1 IR spectrum

Fig. 1 shows IR spectrum of ET₂Hg(SCN)₂Cl, and the assignments analysis was shown in Table 1.

![IR spectrum](image)

**Table 1.** IR spectra data and their assignments for ET₂Hg(SCN)₂Cl in the range of 400-4000 cm⁻¹.

<table>
<thead>
<tr>
<th>IR spectra (cm⁻¹)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3421.01, 2965.91, 2921.80, 2107.67, 2076.56, 1624.04, 1406.95, 1346.09, 1282.45, 1259.31, 1124.33, 1047.17, 1012.46, 919.89, 879.41, 773.33, 678.83, 644.12</td>
<td>νCH, νCN, νC=C, δCH, νC=C, δSCN, δSC, νCS, νHgS</td>
</tr>
</tbody>
</table>

3.2 Linear absorption coefficient, ground state absorption cross-section (\( \sigma_0 \)) and linear refractive indices

At \( \lambda = 532 \) nm the absorbance was \( A = 0.092 \), so the linear absorption coefficient \( \alpha_0 \) was deduced to be 0.212 cm⁻³ with equation \( \alpha_0 = \frac{A}{L} \) where \( L \) is the length of the cuvette. In this case, \( L = 1 \) cm, and the ground state absorption cross-section \( \sigma_0 \) was estimated to be 6.57×10⁻²⁸ cm² according \( \sigma_0 = \frac{\alpha_0}{N_A d_0^{10}} \) where \( N_A \) is the Avogadro number, and \( d_0 \) is the concentration (mol/L).

![Linear absorption spectrum](image)

The respective linear refractive index \( n_0 \) at 20 °C were 1.4548 at \( \lambda = 0.4861 \) μm, 1.4481 at \( \lambda = 0.5893 \) μm, 1.4462 at \( \lambda = 0.6563 \) μm, 1.4460 at \( \lambda = 0.6678 \) μm. It is well known that the three-term Sellmeier dispersion formula [5] is very useful in determining the linear refractive index at a given wavelength. Fitting the three-term Sellmeier dispersion formula [5]

\[ n_0 = A + \left( \frac{B}{\lambda^2} \right) + \left( \frac{C}{\lambda^4} \right) \]  

(1)

(where A, B and C are constant parameters and \( \lambda \) in μm) with the above measured results gave A=1.4442, B=0.000108 and C=0.00085 as shown in Fig. 3, so the linear refractive index \( n_0 \) at \( \lambda = 0.532 \) μm was determined: \( n_0 = 1.4510 \) at 20 °C.
3.3 The molecular second hyperpolarizability $\gamma$

In the same condition of open-aperture measurement no results where got, which could indicate that nonlinear absorption contribution to the third order nonlinear susceptibility $\gamma_{\text{solution}}^{(3)}$ was much less than nonlinear refraction, i.e. $\text{Im}\{\gamma_{\text{solution}}^{(3)}\} \approx \text{Re}\{\gamma_{\text{solution}}^{(3)}\}$. Fig. 4 shows the close aperture result of the $z$-scan measurement. With equation (2) using curve fitting tools one may easily obtain on-axis phase shift at the focus $\Delta \Phi_0 = 0.64$

$$T(\lambda, \Delta \Phi_0) = 1 - \frac{4\Delta \Phi_0 \chi}{(x^2 + 9)(x^2 + 1)}$$

(2)

Where $x = z / z_0$, with equation (3) $\Delta \Phi_0$ was obtained to be $5.5 \times 10^3$

$$\Delta \Phi_0 = k \Delta n_0 L_{\text{eff}}$$

(3)

where $k = 2\pi / \lambda$ is the wave vector, $\lambda$ is the wavelength. Here $\Delta n_0 = \gamma_{\text{solution}} I_0$ with $I_0$ being the on-axis irradiance at focus which is $89 \text{ GW/cm}^2$, so $\gamma_{\text{solution}}$ was obtained to be $6.18 \times 10^{-20} \text{ m}^2/\text{W}$. So the real part of $\gamma_{\text{solution}}^{(3)}$ was obtained to be $3.29 \times 10^{-14} \text{ esu}$ with equation [6].

$$\text{Re}\{\chi^{(3)}\}(\text{esu}) = n_0^2 \gamma (\text{cm}^2\text{W}^{-1}) / 0.0395$$

where $\chi^{(3)} = \sqrt{\chi^{(3)}_{\text{Re}}^2 + \chi^{(3)}_{\text{Im}}^2}$ so $\gamma_{\text{solution}}^{(3)}$ was $3.29 \times 10^{-14} \text{ esu}$. For a solution of noninteracting particles, the effective $\chi^{(3)}$ assuming a pairwise additive model is given by [7]

$$\chi_{\text{solution}}^{(3)} = L^3 (N_{\text{solvent}} \gamma_{\text{solvent}} + N_{\text{solution}} \gamma_{\text{solution}})$$

where $L^3$ is the local field correction factor given by $[/(n_0^2 + 2)]^3$ in this case $L^3 = 3.5$, $N_{\text{solvent}}$ and $N_{\text{solution}}$ are the number densities of molecules per mL of the solute and solvent. For dilute solutions $N_{\text{solution}} = N_{\text{solution}} C$ where $N_A$ is Avogadro number, $M$ is the molecular weight of solute, and $C$ is the concentration of solute in g/mL, in this case $M = 1120 \text{ g/mol}, C = 6.0 \times 10^{-5} \text{ g/mL}$. $5.357 \times 10^{-5} \text{ mol/L})$. We may write

$$\chi_{\text{solution}}^{(3)} = \chi_{\text{solution}}^{(3)} + (L^3 \gamma_{\text{solvent}} N_A / M) C \cdots$$

For acetonitrile $\chi_{\text{solvent}}^{(3)} = 2.54 \times 10^{-14} \text{ esu}$ [8] so $\gamma_{\text{solvent}}$ i.e. values of $\text{ET}_2\text{Hg(SCN)}_2\text{Cl}$'s molecular second hyperpolarizability is $6.64 \times 10^{-32} \text{ esu}$. This is a high value and nearly the same order as lots of reported of metal porphyrin in recent years [9].

4. Conclusion

In conclusion with electrochemical method we have successfully synthesized $\text{ET}_2\text{Hg(SCN)}_2\text{Cl}$. IR spectra measurements and analysis have been performed to provide the structural characteristics. The nonlinear optical properties measurements results show that this is a good
material having high molecular second hyperpolarizability.

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Reference


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