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Synthesis and molecular second hyperpolarizability determination of $ET_2Hg(SCN)_2Cl$

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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 $ET_2Hg(SCN)_2Cl$. 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 as measured at 20 ^oC 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 $ET_2Hg(SCN)_2Cl$ was determined by z-scan technique. A value of be 6.64×10^{-32} esu was obtained.

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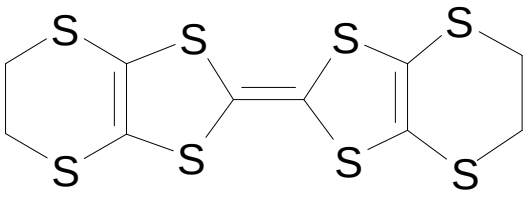
Keywords: Electrochemical method, Z-scan, Nonlinear refractive index, Second hyperpolarizability

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 $ET_2Hg(SCN)_2Cl$ 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).

2. Experiments

2.1 Synthesis and characterization of $ET_2Hg(SCN)_2Cl$

ET was synthesized according to the route of reference [1,2], and recrystallized twice in chlorobenzene. $ET_2Hg(SCN)_2Cl$ 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 $ET_2Hg(SCN)_2Cl$ was obtained. IR spectrum was recorded from 4000 cm^{-1} to 400 cm^{-1} by KBr pellet technique with a $NEXUS_{TM}$ 670·FT-IR photometer.

2.2 Linear absorption coefficient and linear refractive indices measurements

The linear absorption spectrum of the solution (of $ET_2Hg(SCN)_2Cl$ 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 ^oC 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 ω_0=17 μ m, the Rayleigh range of the beam $z_0 = \pi\omega_0^2/\lambda$ = 1.7 mm and the transmitted energy was measured with EPM2000 sensitive energymeter in the far field and the on-axis irradiance at focus (i.e. z = 0) I_0=89 GW/cm^2. The effect sample length $L_{eff} = (1-e^{-\alpha_0 L})/\alpha_0$ was obtained: 0.099 cm. The diffraction length inside the sample $n_0 z_0$ is 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 $ET_2Hg(SCN)_2Cl$, and the assignments analysis was shown in Table 1.

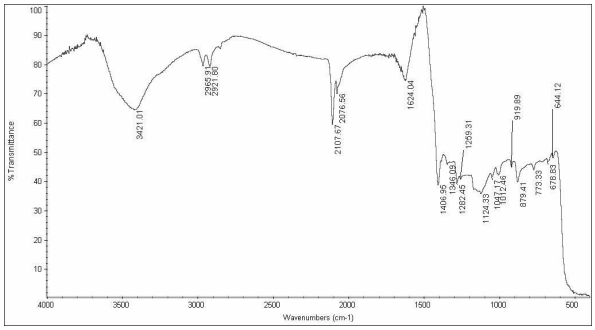


Fig. 1. IR spectrum of $ET_2Hg(SCN)_2Cl$.

Table 1. IR spectra data and their assignments for $ET_2Hg(SCN)_2Cl$ in the range of 400-4000 cm^{-1}.

IR spectra (cm^{-1})	Assignments
3421.01, 2965.91, 2921.80,	ν_{CH}
2107.67, 2076.56,	ν_{CN}
1624.04,	$\nu_{C=C}$
1406.95, 1346.09,	δ_{CH}
1282.45, 1259.31, 1124.33,	ν_{C-C}
1047.17, 1012.46,	δ_{SCN}
919.89, 879.41,	δ_{SCS}
773.33,	ν_{CS}
678.83, 644.12	ν_{HgS}

3.2 Linear absorption coefficient, ground state absorption cross-section (σ_0) and linear refractive indices

At λ = 532 nm the absorbance was A = 0.092, so the linear absorption coefficient α_0 was deduced to be 0.212 cm^{-1} with equation $\alpha_0 = \frac{A}{0.434L}$ where L is the length of the cuvette. In this case, L = 1 cm, and the ground state absorption cross-section (σ_0) was estimated to be 6.57×10^{-18} cm^2 according $\sigma_0 = \frac{\alpha_0}{N_A d_0 10^{-3}}$ where N_A is the Avogadro number, and d_0 is the concentration (mol/L).

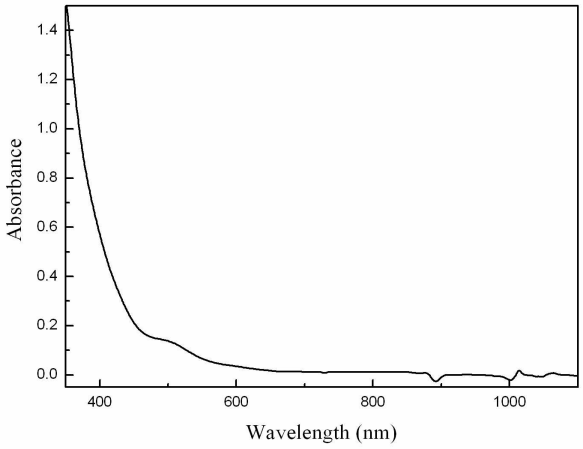


Fig. 2. Linear absorption spectrum of $ET_2Hg(SCN)_2Cl$ in acetonitrile (5.357×10^{-5} mol/L) in a cell of length 1 cm.

The respective linear refractive index (n_0) at 20 °C were 1.4548 at λ= 0.4861 μm, 1.4481 at λ= 0.5893 μm, 1.4462 at λ= 0.6563 μm, 1.4460 at λ= 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]

$$n_0 = A + (B/\lambda^2) + (C/\lambda^4) \quad (1)$$

(where A, B and C are constant parameters and λ in μm) with the above measured results gave A=1.4442, B=-0.00108 and C=0.00085 as shown in Fig. 3, so the linear refractive index n_0 at λ=0.532 μm was determined: n_0= 1.4510 at 20 °C.

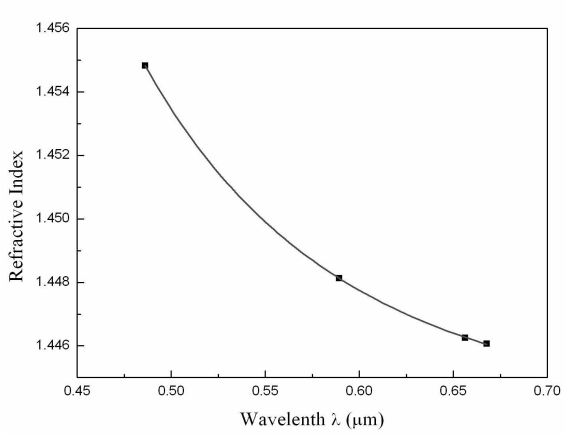


Fig. 3. Curve fitting result of linear refractive indices of solution of $ET_2Hg(SCN)_2Cl$ in acetonitrile (5.357×10^{-5} mol/L) at 20 °C with equation (1).

3.3 The molecular second hyperpolarizability γ

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 $\chi_{solution}^{(3)}$ was much less than nonlinear refraction, i.e. $\mathrm{Im}\{\chi_{solution}^{(3)}\} \ll \mathrm{Re}\{\chi_{solution}^{(3)}\}$. 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 $\Delta\Phi_0 = 0.64$

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

Where $x = z / z_0$, with equation (3) Δn_0 was obtained to be 5.5×10^{-5}

$$\Delta\phi_0 = k\Delta n_0 L_{eff} \qquad (3)$$

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

$\mathrm{Re}\{\chi^{(3)}\}(esu) = n_0^2\gamma(cm^2W^{-1})/0.0395$ and $\chi^{(3)} = \sqrt{\chi^{(3)}{}_{\mathrm{Re}}{}^2 + \chi^{(3)}{}_{\mathrm{Im}}{}^2} \approx \chi^{(3)}{}_{\mathrm{Re}}$ so $\chi_{solution}^{(3)}$ was 3.29×10^{-14} esu. For a solution of noninteracting particles, the effective $\chi^{(3)}$ assuming a pairwise additive model is given by [7]

$$\chi_{solution.}^{(3)} = L^4(N_{solvent.}\gamma_{solvent.} + N_{solute}\gamma_{solute})\cdots$$

where L^4 is the local field correction factor given by $[(n_0^2+2)/3]^4$ in this case L^4=3.5, $N_{solvent}$ and N_{solute} are the number densities of molecules per mL of the solute and solvent. For dilute solutions $N_{solute} = N_A C/M$ 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 g/mol, $C=6.0\times10^{-5}$ g/mL (5.357×10^{-5} mol/L). We may write

$\chi_{solution}^{(3)} = \chi_{solvent}^{(3)} + (L^4\gamma_{solute}N_A/M)C\cdots$. For acetonitrile $\chi_{solvent}^{(3)}=2.54\times10^{-14}$ esu [8] so γ_{solute} i.e. values of $ET_2Hg(SCN)_2Cl$'s molecular second hyperpolarizability is 6.64×10^{-32} esu. This is a high value and nearly the same order as lots of reported of metal porphyrin in recent years [9].

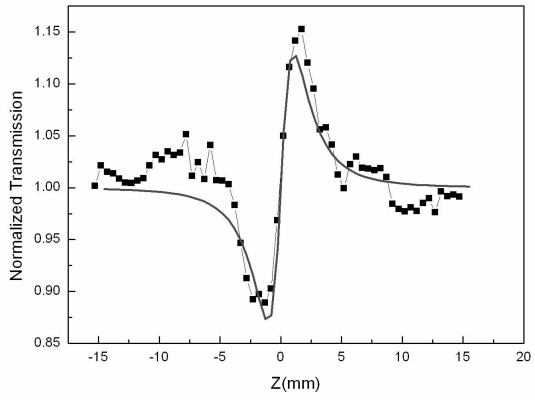


Fig. 4. Normalized z-scan transmittance of acetonitrile solution of $ET_2Hg(SCN)_2Cl$ measured with picosecond pulses at λ=532 nm with I_0=89 GW/cm^2. The solid line is curve fitting line using equation (2).

4. Conclusion

In conclusion with electrochemical method we have successfully synthesized $ET_2Hg(SCN)_2Cl$. 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.

Acknowledgement

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