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Physical origin of the third order nonlinear optical response of orthogonal pyrrolo-tetrathiafulvalene derivatives

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We present the third order nonlinear optical study of tetrathiafulvalene-based molecular corners. Degenerate four-wave mixing measurements have been done to provide information about the magnitude and the origin of the nonlinearity, while the nonlinear absorption has been separately measured by performing "open aperture" Z-scan measurements. The response has been found to be strongly dependent upon the structure of the molecular corners. © 2010 American Institute of Physics. [doi:10.1063/1.3482943]

During the past few years the nonlinear optical (NLO) response of organic materials was studied in order to find suitable systems for optoelectronic/photonic applications. In this direction tetrathiafulvalene (TTF)-based molecules have been widely investigated.¹⁻⁵ Due to their extended π system and the strong electron donating character of the TTF-moiety (leading to charge transfer within the molecule), such systems exhibit very interesting NLO properties. In this work we report on the third order nonlinear optical response of orthogonal tetrathiafulvalene-based bricks (Fig. 1), which can be self-organized into orthogonal dimers through metal assisted assembly with Pd(II) or Pt(II) salts. The details of the synthetic procedure have been reported recently in Ref. 6.

The third order nonlinear optical response of the samples has been investigated by the well known degenerate fourwave mixing (DFWM) method.⁷ For the needs of the measurements the frequency doubled exit (532 nm) of a modelocked Nd:YAG laser, providing 30 ps duration laser pulses with 1 Hz repetition rate has been utilized, while the details of the experimental setup are given elsewhere.⁸ With this experimental setup and by changing the polarization of the pump and probe waves, the different elements of the third order susceptibility $\chi^{(3)}$ were determined, by reference to the CS₂ solvent. For the third order nonlinear optical investigation several solutions for each of the systems, exhibiting different concentrations in CH₂Cl₂ have been prepared and put into 1 mm thick quartz cells. In Fig. 2 the intensity of the DFWM signal I₄ as a function of the intensity of the pump beam I₁ is shown, for different concentrations of the sample S1 as well as of the neat solvent CH₂Cl₂. It is obvious that there is good dependence of the DFWM signal upon the pump intensity as theoretically expected.⁹ Similar procedure has been followed for the other two systems S2 and S3. From these measurements the optimal concentration C_{opt} has been determined as the concentration which results to the maximum I₄ signal. The C_{opt} has been found to be 2.5 $\times 10^{-4}$ mol/L, 5.0×10^{-4} mol/L, and 5.0×10^{-4} mol/L for the systems S1, S2, and S3, respectively. In Table I the $\chi^{(3)}$ values corresponding to the optimal concentrations, as well as the determined second order hyperpolarizability (γ) val-

ues of the molecules can be seen. In the same table the value of CS₂ is shown for comparison reasons. By comparing the results between the different TTF-based corners, it can be seen that S2 exhibits higher nonlinearity than S_1 by about a factor of 2. This result could be expected because changing the Pt(II) by a Pd(II) corner complex can change the charge transfer efficiency in the molecule. Moreover by comparing with the molecule S3 the effective γ values are enhanced by a factor of about 5 and 2.5 compared with that of the molecules S1 and S2, respectively, an effect which in this case, is assignable to the introduction of two triethyphosphine ligands in a cis position on the metal (S3), instead of a 1,3bis(diphenylphosphino)propane ligand (S1 and S2). Moreover the second order hyperpolarizability of the TTF compounds (S1-S3) is higher compared with that of neat CS_2 , by about four orders of magnitude, showing that the investigated compounds exhibit significant nonlinear optical response.

In the picosecond regime and for isotropic materials the electronic and nuclear contributions to the nonlinearity are



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FIG. 1. Chemical structures of the investigated systems.



FIG. 2. (Color online) Reflectivity of the DFWM as a function of the pump intensity for several concentrations of the S1 sample and the neat solvent.

dominant. In order to find out the physical origin of the nonlinearity further DFWM measurements have been carried out by changing the polarizations of the pump and the probe beams. In this way the relations between the elements of the third order susceptibility tensor were derived and are given below, in the following Eqs. (1) and (2), for the molecules S1 and S2, respectively:

$$\chi_{xxxx}^{(3)} \approx 1.6 \chi_{xxyy}^{(3)\text{exp}} \approx 2.0 \chi_{yxyx}^{(3)\text{exp}} \approx 1.8 \chi_{yxxy}^{(3)\text{exp}}, \tag{1}$$

$$\chi_{xxxx}^{(3)} \approx 1.8 \chi_{xxyy}^{(3)exp} \approx 2.1 \chi_{yxyx}^{(3)exp} \approx 2.0 \chi_{yxxy}^{(3)exp}.$$
 (2)

By comparing these results with the theoretically predicted for nuclear and electronic contributions¹⁰ it becomes clear that the electronic contribution to the nonlinearity is stronger. To provide quantitative results of the two contributions, the ratios $\chi_{XXXX}^{(3)el}/\chi_{XXXX}^{(3)}$ and $\chi_{XXXX}^{(3)nu}/\chi_{XXXX}^{(3)}$ were determined and have been found to be around 1.10 and 0.10, respectively, for all three systems. This result could be expected as the TTF is a well known electron donor and as a result strong charge transfer takes place along these molecules, leading to strong electronic contribution on the response.

In order to separately determine the nonlinear absorption of the molecules S1-S3, "open aperture" Z-scan measurements have been carried out, following the procedure described elsewhere.^{11,12} For these measurements the same laser system has been employed. Briefly, the transmittance after the sample is measured, while moving it along the transmission axis of the laser beam. By fitting the experimental data according to equations which can be found in the literature^{11,12} the nonlinear absorption parameter (β), the Im $\chi^{(3)}$ and Im γ values are obtained.

TABLE I. Nonlinear optical parameters determined from the DFWM measurements (30 ps, 532 nm).

Sample (optimal concentration)	$\chi^{(3)} imes 10^{-21} \ (m^2/V^2)$	$\gamma \times 10^{-45}$ (m ⁵ /V ²)
$S1 (2.50 \times 10^{-4} \text{ mol/L})$	1.13	1.32
S2 $(5.00 \times 10^{-4} \text{ mol/L})$	1.11	2.71
S3 $(5.00 \times 10^{-4} \text{ mol/L})$	2.29	6.44
CS ₂	19.4	4.71×10^{-4}



FIG. 3. "Open-aperture Z-scan" obtained for the S1 system (1.0 mM in $CH_2Cl_2)$ at E=5.1 $\,\mu J.$

Prior to the measurements calibration of the nonlinear absorption setup has been done by investigating samples of C_{60} fullerene, which is a well known optical limiter. The imaginary part of the second order hyperpolarizability (Im γ) has been measured to be 0.21×10^{-45} m⁵/V², corresponding to 0.15×10^{-31} esu, which is in very good agreement with already reported values.^{12,13} Then "open aperture" Z-scan measurements have been done for several concentrations of each of the TTF compounds and for various incident laser intensities. The corresponding solvent (CH₂Cl₂) has been separately measured in all cases and the contribution to the nonlinear absorption, under the same experimental conditions, has been found to be negligible, so the nonlinear absorption of the solutions can be totally attributed to the dissolved TTF-corners. Transmittance minima have been found around the focal plane indicating reverse saturable absorption (RSA) character of the samples. In Fig. 3 a characteristic "open aperture" Z-scan of the system S1 exhibiting 1 mM concentration in CH₂Cl₂ can be seen, obtained at E =5.1 μ J, while in Fig. 4 the Im $\chi^{(3)}$ values for all investigated systems are shown as a function of concentration. Very good concentration dependence is obtained for all the systems, verifying that no aggregation or saturation of the nonlinear optical response was present during the measurements.



FIG. 4. (Color online) Concentration dependence of the nonlinear absorption for the S1–S3 molecules.

TABLE II. Nonlinear optical parameters determined from the nonlinear absorption measurements (30 ps, 532 nm).

Sample	β^{a} (10 ⁻¹¹ m/W)	$ Im \chi^{(3) \ a} \\ (10^{-13} \ \text{esu}) $	$\frac{\text{Im }\chi^{(3) \ a}}{(10^{-21} \ \text{m}^2/\text{V}^2)}$	$\operatorname{Im} \frac{\gamma \times 10^{-31}}{(\text{esu})}$	$\frac{\text{Im } \gamma \times 10^{-45}}{(\text{m}^{5}/\text{V}^{2})}$
S1	0.55	0.33	0.46	0.12	0.17
S2	0.32	0.19	0.27	0.07	0.10
S3	1.19	0.71	0.99	0.26	0.37

^aCorresponding to concentration 1 mM of the samples in CH₂Cl₂.

In Table II the determined β and Im $\chi^{(3)}$ values corresponding to 1 mM concentration samples can be seen, as well as the imaginary part of the second order hyperpolarizability (Im γ) which was determined from the concentration dependent investigation. It is obvious that the S3 system exhibits higher RSA than the other two systems, following the same trend with the second order hyperpolarizability values of the systems (Table I). On the contrary, the S2 system exhibits lower nonlinear absorption than S1. Additional measurements which were carried out for the B1 ligand revealed that it has negligible nonlinear absorption, compared with the other two systems, under the same experimental conditions.

By comparing the results of Tables I and II it is derived that the contribution of nonlinear refraction to the total response is dominant. In particular the Im γ values are at least one order of magnitude lower than the γ values, while the Im γ/γ ratios are 0.13, 0.04, and 0.06 for the S1, S2, and S3 molecules respectively.

In this work the physical origin of the third order NLO response, as well as the corresponding NLO parameters have been determined by a combination of DFWM and "open aperture" Z-scan measurements, while strong dependence upon the structure of the systems has been found. The high NLO response of the corners combined with the possibility to further tune it by changing the molecular structure makes these systems very promising candidates for a variety of optoelectronic/photonic applications.

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