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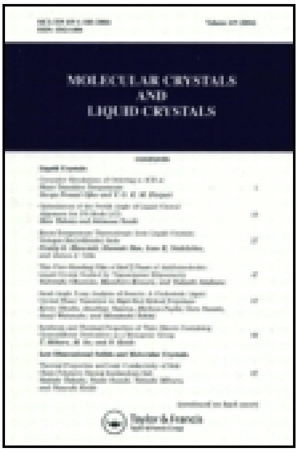

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Large Two-Photon Absorption Properties of Polyphenyls and Polyfluorenes

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Large Two-Photon Absorption Properties of Polyphenyls and Polyfluorenes

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The theoretical study of two-photon absorption (TPA) properties of polyphenyls and polyfluorenes (with the number of phenyl rings $N = 2$ to 6) was related to cooperative effects between monomers. These effects lead to an increase of the TPA cross-section with N without saturation according to a power law.

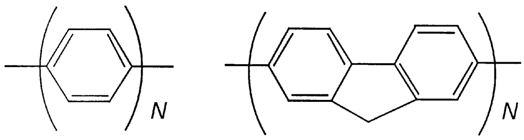
Keywords Two-photon absorption; polyfluorenes; polyphenyls; CNDO/S calculations.

INTRODUCTION

Two-photon absorption (TPA) properties of organic compounds are being involved in many applications [1]. Several organic molecules optimized for these applications, consisted generally in symmetrically substituted molecules, in which the role of electroactive groups was studied [2-4].

Recently efficient nonlinear absorption properties based on TPA processes were found in unsubstituted dimers, a bistilbene molecule (the Stilbene-3) [5], and the bifluorene [6], and a polyfluorene (60 monomers units) [7].

In this paper, we present theoretical TPA properties, using semi-empirical CNDO/S calculations, of two oligomers systems, the polyphenyls **I** and the polyfluorenes **II** (Fig. 1), in order to dissect the TPA cross-section on the basis of the two-level model and provide the origin of the enhanced properties of these systems. Preliminary results concerning this study were reported for polyphenyls [8].



I II

FIGURE 1 Molecular structures of oligomers $\mathbf{I}_N$ and $\mathbf{II}_N$

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CALCULATIONS METHOD

The molecule geometry was optimized by using Sybyl, i.e. Tripos force field and AM1 from the MOPAC package [9] ; the selected geometry corresponds to the lowest energy. For each molecule, the electronic state characteristics, i.e. singlet state energies, and dipole moments, were obtained by a configuration interaction (CI) procedure based on the CNDO/S method using the QCPE program #333. The CI calculations included 100 singly (SCI), and 100 doubly (DCI) excited configurations.

The TPA cross-section σ_{TPA} is proportional to the imaginary part of the average second hyperpolarizability:

$$\sigma_{TPA} = \frac{3}{10}\hbar\frac{\omega^2}{n^2c^2\varepsilon_0}f^4\,\mathrm{Im}<\gamma(-\omega;\omega,-\omega,\omega)> \qquad (1)$$

$$\langle\gamma\rangle = \frac{1}{5}\left(\gamma_{xxxx}+\gamma_{yyyy}+\gamma_{zzzz}+\gamma_{xxyy}+\gamma_{yyxx}+\gamma_{yyzz}+\gamma_{zzyy}+\gamma_{xxzz}+\gamma_{zzxx}\right) \qquad (2)$$

The tensor components γ_{jkl} were computed using Orr and Ward's equation based on the time-dependent perturbation theory [10]. TPA spectra were evaluated by using the parameters of the 19 lowest excited states to obtain a good convergence of σ_{TPA} values (Fig. 3). The damping factors Γ were taken to be 1000 cm^{-1} for all states, and the refractive index was assumed to be 1.

Results were interpreted on the basis of the three-level model (Eq.(3)and Fig. 2):

$$\gamma \propto \frac{\mu_{01}^2\mu_{12}^2}{(E_{01}-\frac{E_{02}}{2})^2} \qquad (3)$$

where μ_{01}, and μ_{12}, are the transition moment between the ground state S_0 and the lowest charge transfer excited-state S_1, and the transition moment between S_1 and the lowest two-photon excited state S_2, respectively. E_{01} and E_{02} are the energy of S_1 and S_2, respectively. [3]

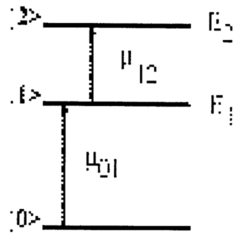

FIGURE 2 Three-level model scheme

As an illustration of the validity of this model for oligomers systems, variations of σ_{TPA} with the number of excited states was reported on Fig. 3 for the bifluorene $\mathbf{I_2}$ and tetraphenyl $\mathbf{II_2}$ molecules. A rapid convergence of σ_{TPA} is obtained for both molecules. Negative values corresponding to one-photon resonance saturation effects were obtained up to 5 excited states, while the maximum σ_{TPA} value was found for 7 states ; the subsequent decrease was ascribed to negative contribution of $\mu_{0i}\ \mu_{ij}\ \mu_{jk}\ \mu_{k0}$ terms.

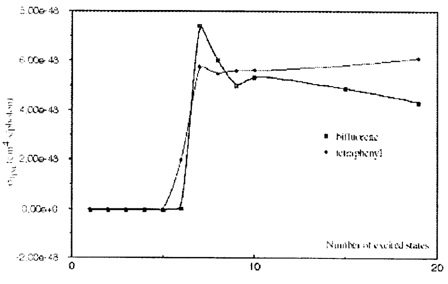

FIGURE 3 TPA cross-section as a function of the number of excited states included in calculations

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RESULTS

The spectral distribution of σ_{TPA} for oligomers **I** and **II** is presented on Fig. 4 for $N = 2$ and 6. The theoretical spectrum consists mainly in a band centered at an energy of $\frac{E_{02}}{2}$ (Eq(3)). A weak wavelength shift is obtained with N for the spectral distribution of σ_{TPA} in the case of the polyfluorenes **II** (see also Fig.6).

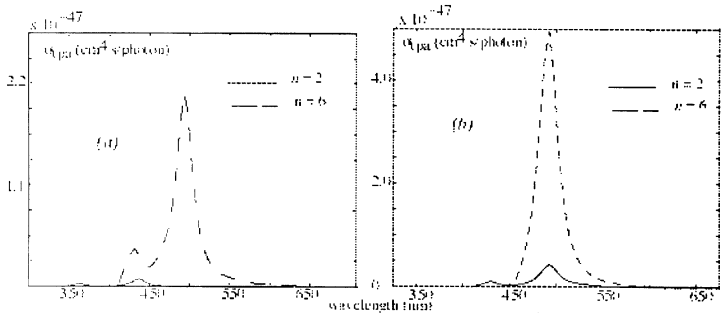

FIGURE 4 TPA spectrum for **I** (a) and **II** (b).

Values of σ_{TPA} are reported on Table 1 as a function of N. When comparing values of σ_{TPA} for a same number of monomers N (a benzene ring for **I** and a fluorene for **II**), **II** leads to higher values σ_{TPA}.

N	**I**	**II**
2	80	430
3	330	1502
4	610	2289
5	1260	3290
6	2090	4940

TABLE 1 TPA cross-sections (10^{-50} cm^4 s/photon) of polyphenyls and polyfluorenes as a function of the monomers number N.

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Variations of σ_{TPA} are presented on Fig. 5. A In order to compare TPA properties of **I** and **II**, these variations were plotted versus N' according to the system (4).

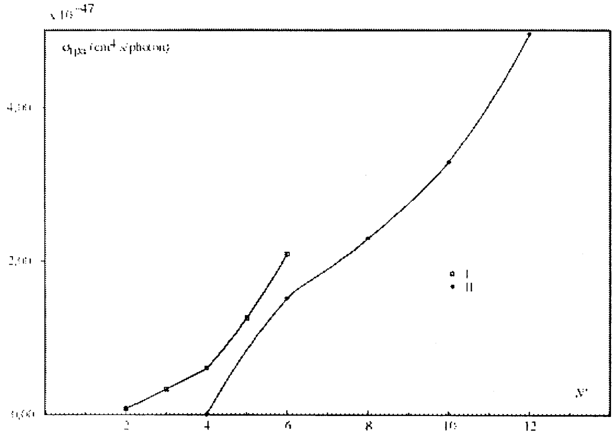

FIGURE 5 σ_{TPA} versus the number of moieties for **I** and **II**

$$N' = N$$
$$N' = 2N$$

A continuous increase of σ_{TPA} was obtained for N = 1 to 6 for **I** and **II**. However, when comparing values for a same number of benzene rings N', polyphenyls **I** give rise higher values σ_{TPA} (Fig. 5). These large variations of σ_{TPA} could be quantified following the power law (5) :

$$P = KN^{\alpha} \qquad (5)$$

These variations are in good agreement with recent theoretical results obtained for polyene oligomers, for which a strong correlation between TPA properties and the length of theses systems was established [11]. Values of the exponent α obtained for **I** and **II** for σ_{TPA} are reported on Table 2. These values of α are in good agreement with found for other oligomers (α = 5-6[7c]).

P	σ_{TPA}	$\mu 01$	$\mu 02$	$(E_{01}-\frac{E_{02}}{2})^{-1}$	$\sigma_{TPA}^{3-level}$
I	2.8	0.67	0.64	0.47	3.6
II	1.9	0.54	0.42	0.25	2.4

TABLE 2 Exponents α involved in Eq. (5) for parameters P describing the relationship (3) in oligomers **I** and **II**

DISCUSSION

In the following we will consider oligomers **I** and **II** as constituted of N monomers in excitonic coupling similarly to J-aggregates in order to interpret the above enhancement of σ_{TPA} of these oligomers. This assumption requires a dependence of the dipole moments μ_{ij}^{N} of the oligomer with that of the monomer μ_{ij}^{1} following the relationship (6) [12,13]:

$$\mu_{ij}^{N} = \sqrt{N}\mu_{ij}^{1} \qquad (6)$$

Values of $\mu 01$ and $\mu 12$ are reported on Fig. 6 for systems **I** and **II** with that of E_{01} and E_{02}. Variations with N of these parameters follows a power law of type (5), for which the values of the exponent α are reported on Table 2. These values, which are very close for $\mu 01$ and $\mu 12$ from the value of 0.5 proposed in the excitonic model (see Eq. (6)), valid our assumption of coupling interactions in oligomers **I** and **II**.

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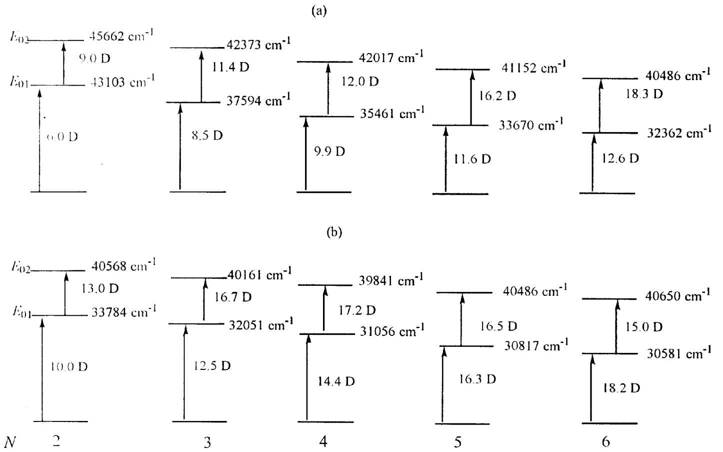

FIGURE 6 Energy diagram with $\mu 01$, $\mu 12$ values for systems **I** (a) and **II** (b).

We note on Fig. 6 that polyfluorenes **II** presents energies E_{01} and E_{02} shifted towards the red range with respect to those of a polyphenyls I. However, for systems **II** weaker variations with N of these energies are predicted ; furthermore, a decrease with N of $\mu 12$ is calculated. These observations is in good agreement with preliminary experimental data in fluorenes [14] and led to weaker α exponent values for $\mu 01$, $\mu 12$ and $(E_{01} - \frac{E_{02}}{2})^{-1}$ in the case of systems **II** (Table 2).

The above coupling model allows to interpret readily large variations of σ_{TPA} with N ; when replacing all parameters ($\mu 01$, $\mu 12$ and $(E_{01} - \frac{E_{02}}{2})^{-1}$) involved in the relationship of the three-level model (Eq. 3) by their power law expression, we obtained an α exponent value for $\sigma_{TPA}^{3\ level}$ similar to that obtained directly from variations of σ_{TPA} with N (Table 2).

CONCLUSION

This theoretical study shows that the two-photon absorption cross-section of polyphenyls and polyfluorenes increases with the number of monomer units. No saturation is predicted at least up to n=6. This TPA enhancement follows a power law that results from cooperative effects between monomers on excited state characteristics.

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REFERENCES

[1] B.A. Reihardt Photonics Science News **4**, 21 (1999).

[2] (a) J.E. Ehrlich, X.L. Wu, I.-Y.S. Lee, Z.-Y. Hu, H. Röckel, S.R. Marder, J.W. Perry Opt. Lett. **22**, 1843 (1997); (b) J.W. Perry, S. Barlow, J.E. Ehrlich, A.A. Heikal,Z.-Y. Hu, I.-Y.S. Lee, K. Mansour, S.R. Marder, H. Röckel, M. Rumi, S. Thayumanavan, X.-L. Wu Nonlinear Optics **21**, 225 (1999); (c) S. Delysse, P. Filloux, V. Dumarcher, C. Fiorini, J.-M. Nunzi Optical Materials **9**, 347 (1998); (d) P.-A. Chollet, V. Dumarcher, J.-M. Nunzi, P. Feneyrou, P Baldeck Nonlinear Optics **21**, 299 (1999); (e) C. Nguefack, T. Zabulon, R. Anémian, C. Andraud, A. Collet, S. Topçu, P.L. Baldeck Nonlinear Optics **21**, 309 (1999).

[3] M. Albota, D. Beljonne, J.L. Brédas, J.E. Ehrlich, J.-Y. Fu, A.A. Heikal, S.E. Hess, T. Kogej, M.D. levin, S.R. Marder, D. McCord-Maughon, J.W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W.W. Webb, X.-L. Wu, C. Xu Science **281**, 1653 (1998).

[4] C. Andraud, R. Anémian, A. Collet, J.-M. Nunzi, Y. Morel, P.L. Baldeck J. Opt. A : Pure Appl. Opt. **2**, 284 (2000) ; B. Paci, J.-M. Nunzi, R. Anémian, C. Andraud, A. Collet, Y. Morel, P.-L. Baldeck J. Opt. A : Pure Appl. Opt. **2**, 268 (2000).

[5] P.-A. Chollet, V. Dumarcher, J.-M. Nunzi, P. Feneyrou, and P.L. Baldeck Nonlinear Optics, **21**, 299 (1999); P.-A. Chollet, A. Sornin, B. Paci, V. Hully, J.-M. Nunzi, Y. Morel, and P.L. Baldeck, in Mat. Res. Soc. Symp. Proc., Thin Films for Optical Waveguide Devices and Materials for Optical Limiting, edited by K. Nashimoto, B.W. Wessels, J. Shmulovich, A.K-Y. Jen, K. Lewis, R. Pachter, R. Sutherland, J. Perry, (MRS Boston 1999), **Vol. 597**, in press.

[6] Y. Morel, A. Irimia, P. Najechalski, Y. Kervella, O. Stephan, P.L. Baldeck J. Chem. Phys. in press ; P. Najechalski, Y. Morel, O. Stephan, P.L. Baldeck Chem. Phys. Lett. in press.

[7] P. Najechalski, Y. Morel, O. Stéphan, P. L. Baldeck Chem. Phys. Lett. in press.

[8] C. Andraud, P.L. Baldeck Nonlinear Optics (in press).

[9] SYBYL 6.5, from Tripos, 1699 S. Hanley Road, St. Louis, MO 63144-2913. (Tripos force field ans AM1 calculation included in MOPAC package).

[10] B.J. Orr, J.F. Ward Mol. Phys. **20**, 513 (1971).

[11] (a) A.A. Said, C. Wamsmey, D.J. Hagan, E.W. Van Stryland, B.A. Reinhardt, P. Rodere, A. G. Dillard Chem. Phys. Lett. **228**, 646 (1994); (b) D. Beljonne, J.L. Brédas J. Opt. Soc. Am. B **11**, 1380 (1994); (c) P. Norman, Y. Luo, H. Agren Chem. Phys. Lett. **296**, 8 (1998); (d) P. Norman, Y. Luo, H. Agren J. Chem. Phys. **111**, 1 (1999).

[12] E.G. McRae, M. Kasha J. Chem. Phys. **28**, 721 (1958).

[13] A.S. Davidov Zhur. Eksptl. I Teort. Fiz. **18**, 515 (1948).

[14] Results to be published.