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Strong Two Photon Absorption and Photophysical Properties of Symmetrical Chromophores with Electron Accepting Edge Substituents

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Two photon absorption (TPA) and photophysical properties of three new symmetrical chromophores with electron accepting phthalimide edge substituents have been studied. The three chromophores contain fluorene, alkoxy-substituted divinyl benzene, and carbazole moieties as central cores, respectively. The femtosecond time-resolved fluorescence upconversion spectroscopy and two photon excited fluorescence technique have been carried out. The effect of solvent polarity on TPA and on photophysics has also been determined. Ultrafast fluorescence dynamics, with decay times ranging from 1 to 13 ps, are revealed in polar solvents. This is attributed to the relaxation of the chromophores to the intramolecular charge transfer state. The chromophore bearing fluorene central core, being of the type A- π -A, is the most efficient concerning TPA. Strong TPA, with a cross section value as high as 2100 GM at an excitation wavelength of 770 nm is found in acetophenone which is a solvent of intermediate polarity. The TPA spectra were also reproduced using a sum over states three-state model. A study of the TPA induced photobleaching of the fluorene molecule, doped in a solid poly(methyl-methacrylate) film, has shown that this material is very promising for efficient TPA optical data storage.

Introduction

Two photon absorption, TPA, has received great attention by a large number of experimental and theoretical groups in order to understand the factors that determine TPA properties and to find materials with large TPA cross sections to be used in TPA microscopy,¹ three-dimensional (3D) optical data storage,^{2–4} 3D microfabrication,^{5–7} upconverted lasing,⁸ optical limiting,^{9,10} photodynamic therapy,^{11,12} and so forth. In contrast to one photon absorption (OPA), TPA offers highly confined excitation, three-dimensional resolution and increased penetration depth into a sample. These advantages of TPA, compared to OPA, are exploited toward 3D optical data storage. This can be practically achieved by TPA photopolymerization¹³ and TPA photobleaching.^{14–17} Specifically, in the latter case, materials exhibiting fast photobleaching at low excitation intensities are needed.

Organic materials with enhanced TPA properties have, in general, a large electron delocalization length and are able to experience intramolecular charge transfer from the edges to the center of the molecule or vice versa. For this reason, π -conjugated organic molecules of the general type D- π -D, D- π -A- π -D, and A- π -D- π -A, where D and A denote electron donating and accepting groups, have been studied.^{18–25} Another synthetic route for achieving good TPA materials is the design of multibranched molecules. In these, the TPA efficiency of the branches can be added and a charge transfer from the core to the periphery or vice-versa occurs.^{26,27}

The molecular environment also plays a significant role on TPA. Specifically, the solvent polarity affects the dipole moment of the ground and excited states, and consequently, it affects

the TPA as well as the photophysical properties. It was shown that the TPA cross section of a symmetrical nonlinear dye reaches a maximum in a solvent of intermediate polarity such as acetophenone (dielectric constant equal to 17.3).²⁸ Although, several experimental and theoretical reports have been published,^{21,22,29,30} a clear understanding of how the solvent polarity affects the TPA properties is still a matter of investigation.

In this work, we present the photophysics and strong two-photon absorption properties of three symmetrical molecules containing electron accepting edge substituents. Phthalimide has been used as electron acceptor while fluorene, alkoxy substituted divinyl-benzene, and carbazole have been used as central cores. Fluorene is a π -conjugated central link while alkoxy substituted divinyl-benzene and carbazole play the role of an electron donor. Thus, molecules of the type A- π -A and A- π -D- π -A have been studied. The effect of solvent polarity on photophysics and TPA properties has also been examined. Fluorescence decays taken under femtosecond temporal resolution have revealed an ultrafast decay mechanism in polar solvents. Additionally, strong two photon absorption with cross section values as high as 2100 GM have been obtained in solvents of intermediate polarity. The TPA spectra have also been reproduced using the sum over states (SOS) method for a three-state model. Finally, initial experiments on TPA photobleaching of solid poly(methyl-methacrylate) films doped with the fluorene molecule are also presented indicating that this is a very promising TPA storage medium.

Experimental Section

Materials. The chemical structures of the three TPA molecules and their synthetic route are shown in Figure 1 together with their abbreviations. All molecules bear phthalimide (PHT) edge substituents while the central cores are fluorene (F-PHT),

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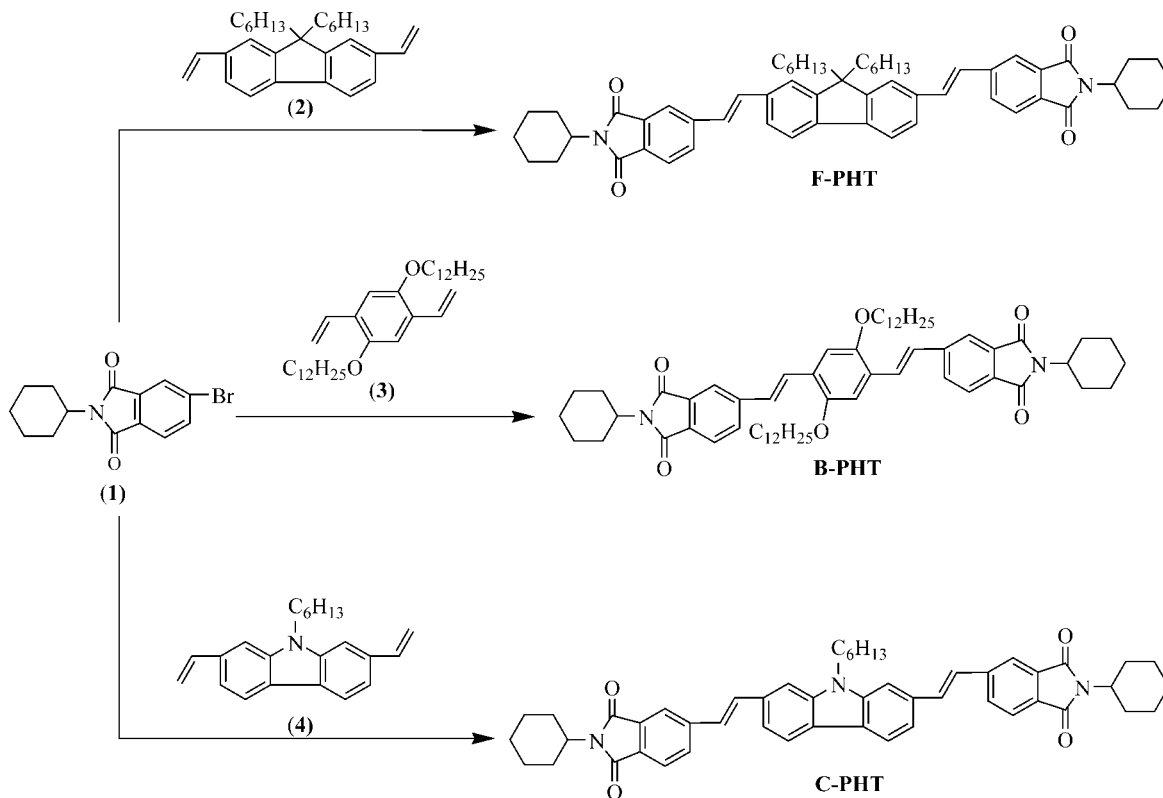


Figure 1. Chemical structures, the synthetic route, and the abbreviations of the three molecules.

divinyl-benzene (**B-PHT**), and carbazole (**C-PHT**). They have been synthesized by Heck coupling. In particular, bromide **1** reacted with divinyl compounds **2**, **3**, and **4** in a mole ratio 2:1 to afford **F-PHT**, **B-PHT**, and **C-PHT**, respectively (Figure 1). They were characterized by elemental analysis as well as FT-IR and ¹H NMR spectroscopy.³¹

Techniques. The photoluminescence excitation and fluorescence spectra were taken from 10⁻⁴ M solutions of the molecules using a Perkin-Elmer LS55B spectrometer.

Fluorescence dynamics of the molecules have been studied with a time-resolved fluorescence upconversion technique using a mode-locked Ti:sapphire femtosecond laser (100 fs pulse duration) as the light source. The experimental setup has previously been described in detail.^{32,33} Briefly, the second harmonic of the Ti:sapphire laser (at 400 nm) was used for the one photon excitation of the samples which were 10⁻⁴ M solutions of **F-PHT** and **B-PHT** in toluene, chlorobenzene (CB), tetrahydrofuran (THF), acetophenone, and dimethylformamide (DMF). The fluorescence of the samples was collected and mixed together with the delayed remaining fundamental laser beam into a BBO crystal generating an upconversion beam. This beam passed through a monochromator, and it was detected through a photomultiplier as a function of the temporal delay between the fundamental laser beam and the fluorescence. Thus, the fluorescence decay of the samples was detected under magic angle conditions.

TPA cross sections were measured by means of a two photon excited fluorescence (TPEF) method using the Ti:sapphire laser.^{34,28} For the detection of the TPA excitation spectra, the laser was tuned from 750 to 840 nm. The laser beam is expanded through a fivefold expanding telescope in order to uniformly illuminate the back aperture of an objective lens (NA = 0.32), which is used to excite the samples. TPA fluorescence intensity was collected backward with the same objective lens and was detected by a photomultiplier as a function of the excitation

power. The samples used for the TPA study were 10⁻⁴ M solutions of the molecules in tetrahydrofuran (THF). Two of the molecules, **F-PHT** and **B-PHT**, were also studied in solvents of different polarities, that is, toluene, CB, acetophenone, and DMF. The two-photon fluorescence cross sections, δ , were determined within the power regime where the fluorescence was proportional to the square of the excitation power, using rhodamine B (10⁻⁴ M in methanol) as a reference.

In order to study the TPA induced photobleaching in solid samples, films of PMMA doped with **F-PHT** were prepared with 1 wt % concentration. For the preparation of the films, appropriate amounts of PMMA and **F-PHT** were mixed and dissolved in THF under magnetic stirring for 24 h. Then, a viscous and homogeneous solution was obtained. The film was prepared by casting the solution onto clean glass slides and was left to dry in air. The technique used to study photobleaching was almost the same as that described previously for the measurement of the TPA cross sections. The samples were placed onto an *x-y-z* computer controlled stage and were illuminated by the same femtosecond laser through a 100 \times oil immersion objective lens.^{14,15} The main difference from the TPEF technique described above is that the photon counting electronics were synchronized with a fast shutter system (risetime 3 ms) in order to record the sharp decay of fluorescence because of photobleaching.

Results and Discussion

Photophysics. The photoluminescence excitation and fluorescence spectra of molecules **F-PHT**, **B-PHT**, and **C-PHT** are shown in Figure 2. The excitation and fluorescence maxima of **F-PHT**, **B-PHT**, and **C-PHT** together with their quantum yields are summarized in Table 1. All three molecules emit light in the blue-green spectral region with maxima at 483 nm, 522 nm, and 511 nm for **F-PHT**, **B-PHT**, and **C-PHT**, respectively.

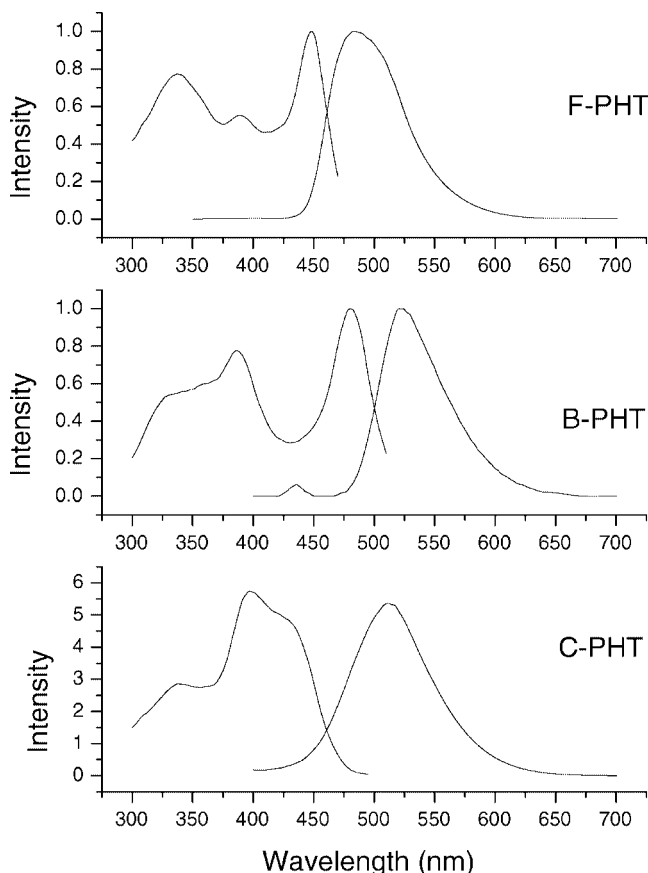


Figure 2. Photoluminescence excitation and fluorescence spectra of **F-PHT**, **B-PHT**, and **C-PHT** in 10^{-4} M THF solutions.

TABLE 1: Photophysical Properties and Quantum Yields of F-PHT, B-PHT, and C-PHT in THF

	$\lambda_{\text{exc}}^{\text{max}}$ (nm)	$\lambda_{\text{flu}}^{\text{max}}$ (nm)	Q.Y.
F-PHT	447	483	0.36
B-PHT	480	522	0.26
C-PHT	398, 430	511	0.17

B-PHT has its fluorescence and excitation maxima at longer wavelengths than the other two molecules which can be attributed to its alkoxy side substituents.

Figure 3 and Figure 4 show the excitation and fluorescence spectra of **F-PHT** and **B-PHT** in solvents of different polarities. Toluene is the less polar solvent with a dielectric constant equal to 2.38 while DMF is the most polar one with a dielectric constant equal to 38. The spectra of **B-PHT** are not shown in DMF because this chromophore was not soluble in this solvent. In both excitation and fluorescence spectra, a gradual red-shift is observed as the solvent polarity increases. This is due to the formation of an ICT state which is energetically lower than the first singlet state. Molecules relax to the ICT state which is responsible for the gradual red-shift of the spectra. In the spectra shown in Figure 3 and Figure 4, an exception to the gradual red-shift is observed in CB. This solvent is less polar than THF, and thus, the spectra in it are expected to be blue-shifted compared with the spectra in THF. However, this is not observed, and the spectra in CB are similar to those in THF. We attribute this to the fact that CB is an aromatic solvent while THF is a nonaromatic one. In the aromatic solvent, the molecule adopts a more conjugated and planar conformation leading to a shift of the spectra to longer wavelengths.

The fluorescence dynamics of **F-PHT** and **B-PHT** are shown in Figure 5 and Figure 6, respectively. All decays were detected

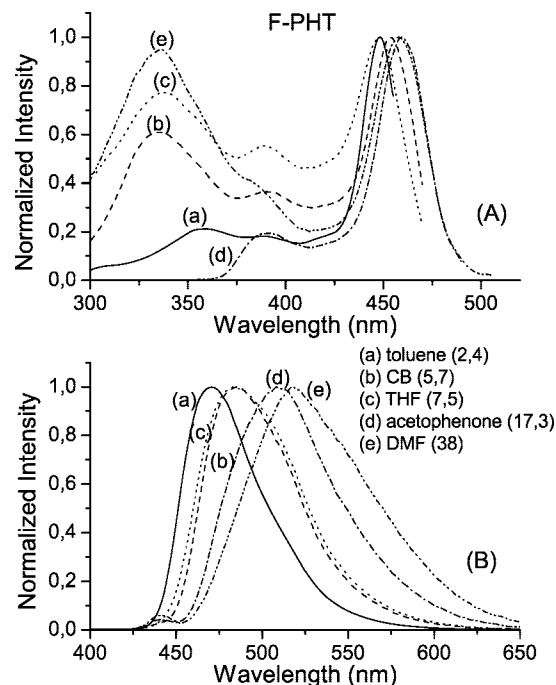


Figure 3. (A) Photoluminescence excitation and (B) fluorescence spectra of **F-PHT** in toluene, CB, THF, acetophenone, and DMF. The dielectric constants of the solvents are shown in parentheses.

at the maximum of the fluorescence spectra. In the three less polar solvents, that is, toluene, CB, and THF, the fluorescence dynamics of both molecules show an exponential decay with time constants ranging from 150 to 260 ps (all decay times are summarized in Table 2). This exponential decay in the less polar solvents is attributed to a simple fluorescence decay from the first singlet excited-state to the ground one. However, in the two most polar solvents, that is, acetophenone and DMF, the decay becomes biexponential, indicating the existence of two decay mechanisms. The time constant of the fast mechanism is

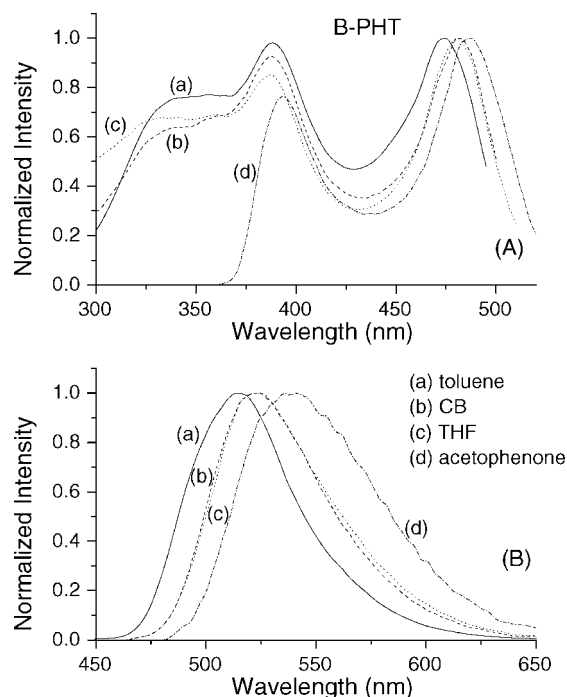


Figure 4. (A) Photoluminescence excitation and (B) fluorescence spectra of **B-PHT** in toluene, CB, THF, and acetophenone.

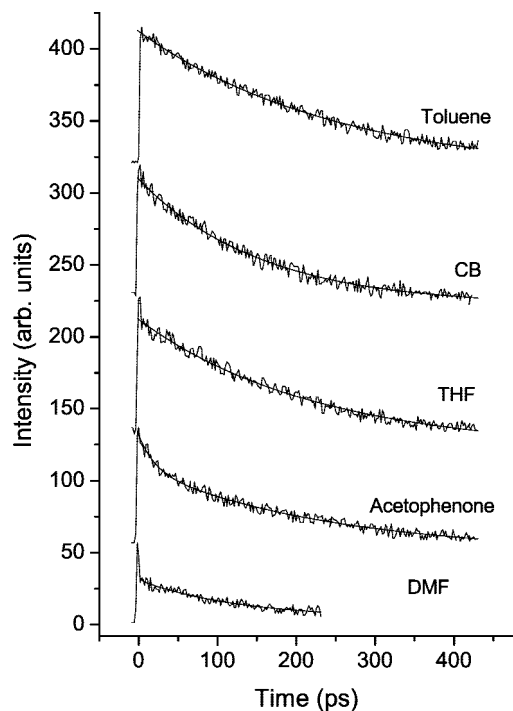


Figure 5. Fluorescence dynamics of **F-PHT** in five solvents showing an ultrafast decay mechanism in the most polar ones (acetophenone and DMF) attributed to the relaxation to the ICT state.

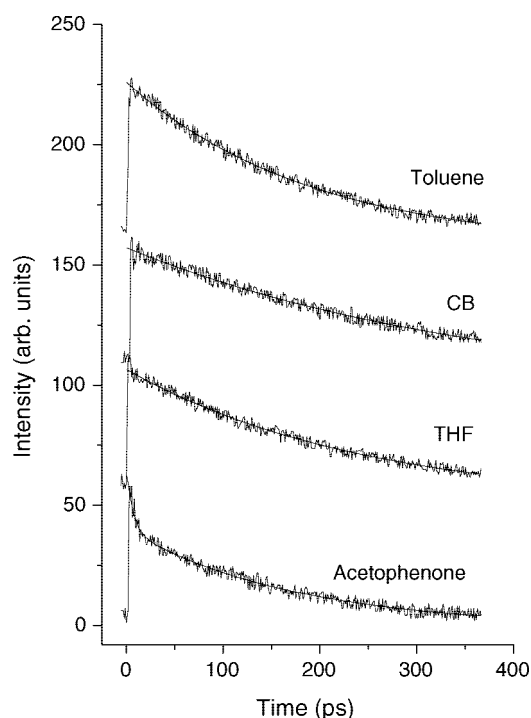


Figure 6. Fluorescence dynamics of **B-PHT** in four solvents. In the most polar solvent, acetophenone, a fast decay mechanism is observed attributed to the relaxation to the ICT state.

13 ps and 1 ps for **F-PHT** in acetophenone and DMF, respectively. In the case of **B-PHT** in acetophenone, the fast mechanism decays within 4 ps. On the other hand, the time constant of the slow decay mechanism is of the order of few hundreds of picoseconds. The biexponential decay in the polar solvents is observed because the molecules decay by both solvent relaxation and fluorescence. The fast decay mechanism is attributed to the relaxation of the molecules from the first excited state to the energetically lower lying ICT state, while

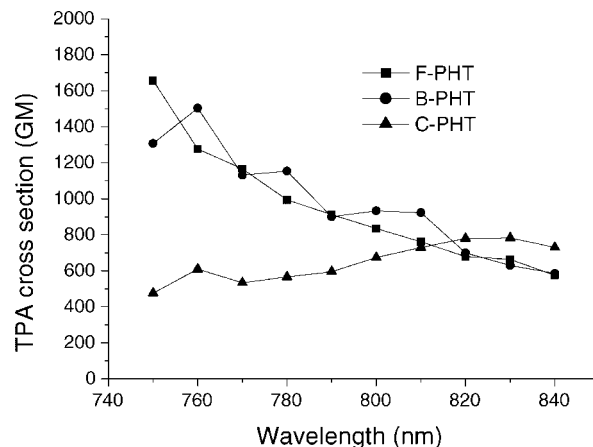


Figure 7. TPA cross section values of **F-PHT**, **B-PHT**, and **C-PHT** in THF for different excitation wavelengths. The experimental uncertainty is estimated 10%.

TABLE 2: Fluorescence Decay Times and TPA Cross Section Values of F-PHT and B-PHT in Various Solvents

	toluene		CB		THF		acetophenone		DMF	
	τ (ps)	δ (GM)	τ (ps)	δ (GM)	τ (ps)	δ (GM)	τ_1, τ_2 (ps)	δ (GM)	τ_1, τ_2 (ps)	δ (GM)
F-PHT	225	640	150	1820	180	1660	13, 195	2100	1, 190	1300
B-PHT	170	240	260	440	235	1500	4, 170	1440		

the slow one is attributed to the direct fluorescence decay from the first excited singlet state to the ground state.

Two Photon Absorption. Figure 7 shows the TPA absorption cross sections of **F-PHT**, **B-PHT**, and **C-PHT** in 10^{-4} M THF solutions as a function of the excitation wavelength. High TPA cross section values, δ , equal to 1660 GM and 1500 GM are obtained from **F-PHT** and **B-PHT** at 750 and 760 nm, respectively. On the other hand, **C-PHT** exhibits lower δ values with a maximum of 785 GM at 830 nm. It is well-known nowadays that molecules with high δ values should be of the general type D- π -A- π -D or A- π -D- π -A. However, it is interesting in our results that **F-PHT**, being of the type A- π -A, is the most efficient TPA molecule among the three molecules studied, even though there is no specific substituent acting as an electron donating group. On the other hand, **B-PHT** and **C-PHT** are of the general type A- π -D- π -A since the alkoxy substituted divinyl benzene and carbazole central cores act as electron donors. Even though one could expect higher δ in **B-PHT** and **C-PHT** than in **F-PHT**, this is not observed. This may be due to the short electron delocalization length from the center to the edges of the molecules. Additionally, **F-PHT** has also the highest fluorescence quantum yield and thus it is the most promising molecule toward TPA applications.

In order to identify the effect of solvent polarity on the TPA properties, we have measured the TPA spectra in different solvents, and the results are shown in Figure 8a,b for **F-PHT** and **B-PHT**, respectively. Concerning **F-PHT** (Figure 8a), the highest δ values, in the three less polar solvents (toluene, CB, and THF), are found at 750 nm, while in the two most polar ones (acetophenone and DMF), they are found at slightly longer wavelengths. This is more obvious in acetophenone where the highest δ value is obtained at 770 nm. Similarly, in **B-PHT**, the highest δ value in acetophenone is found at 770 nm, namely, at a longer wavelength than in THF. This is related to the red shift which is also observed in the linear excitation spectra of **F-PHT** and **B-PHT** as the solvent polarity increases (Figures 3 and 4).

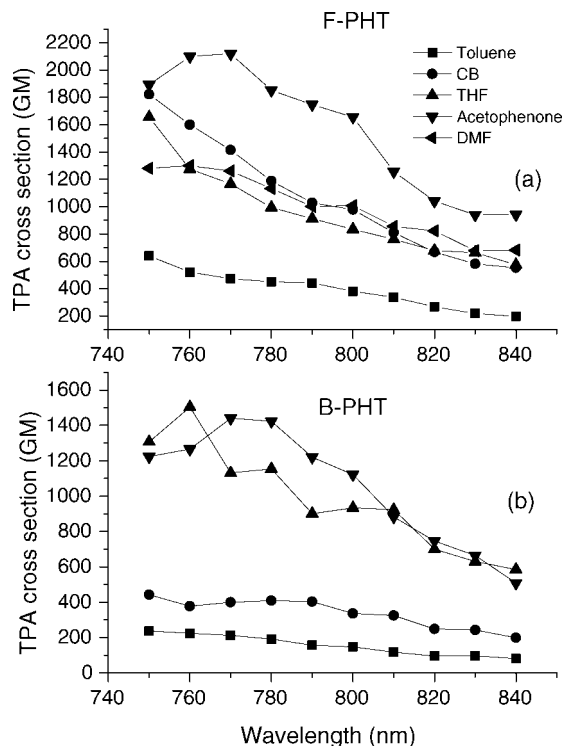


Figure 8. TPA cross section values of (a) **F-PHT** and (b) **B-PHT** in different solvents.

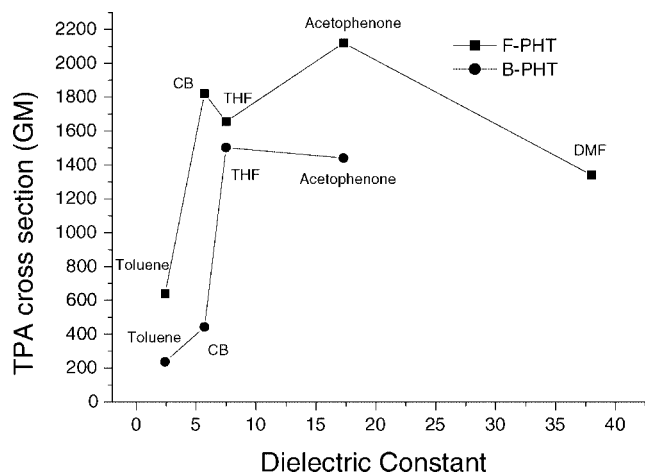


Figure 9. TPA cross sections of **F-PHT** and **B-PHT** as a function of solvent's dielectric constant showing a nonmonotonic dependence.

In Figure 9, the highest δ values for both **F-PHT** and **B-PHT** are plotted as a function of the solvent's dielectric constant. A nonmonotonic dependence of δ on dielectric constant is obtained. Specifically, δ reaches a maximum in a solvent of intermediate polarity. The highest δ values for **F-PHT** and **B-PHT** are found in acetophenone (dielectric constant equal to 17.3) and in THF (dielectric constant equal to 7.5), respectively. Specifically, **F-PHT** in acetophenone has a δ value as high as 2100 GM showing a threefold increase compared with its value in toluene. Additionally, **B-PHT** in THF has a δ value as high as 1500 GM, meaning that there is an \sim sixfold increase by changing the solvent from toluene to THF. The obtained δ values for **F-PHT** and **B-PHT** are very high compared with other results at these wavelengths for similar molecules and using also the TPEF technique.^{24,25,35–38} In the results shown in Figure 8a for **F-PHT**, a discontinuity on the dependence of δ on the dielectric constant appears in CB (dielectric constant

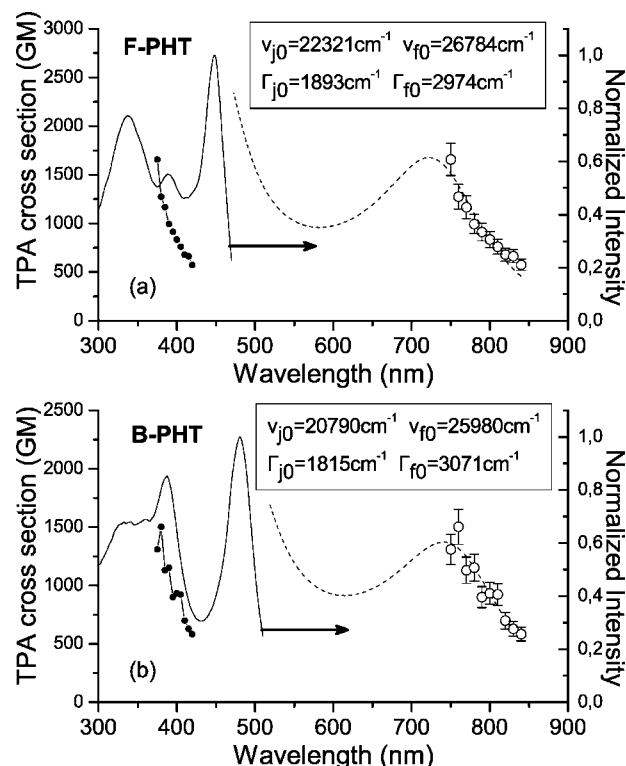


Figure 10. OPA excitation spectra (solid lines), TPA excitation spectra at half-wavelengths (solid circles) and at IR wavelengths (empty circles), and the reproduced TPA spectra using eq 1 (dotted lines) for (a) **F-PHT** and (b) **B-PHT**. The insets show the parameters of the reproduced spectra.

equal to 5.62). Specifically, δ is higher in CB than in THF. The reason for this may be the fact that CB is an aromatic solvent which leads to the extension of the molecular backbone. This could have various effects on the intramolecular charge transfer and/or solubility and consequently on the value of δ .

The above results on the dependence of δ on the solvent polarity are in agreement with previous results of ours for molecules with fluorene central core.²⁸ Additionally, there is an agreement with the experimental results by Woo et al.²¹ In a theoretical work, Wang et al. have also found a maximum δ value in a solvent of intermediate polarity²⁹ and a theoretical investigation by Luo et al. has shown that δ increases with solvent polarity but reaches saturation when the polarity is large enough.³⁰ On the other hand, in a recent work, Yan et al. using the z -scan technique have reported that, for a molecule of D- π -D type, δ increases from a solvent of low polarity (toluene) to a solvent of high polarity (DMF) without saturation.²² From all the above, a common conclusion is that enhanced TPA properties are not favored in low-polarity solvents. However, as the solvent polarity increases, no clear conclusion can be extracted. In most cases, there seems to be an optimum intermediate solvent polarity in which the TPA properties are enhanced. However, solute–solvent interactions and differences in solubilities and in aggregation have to be taken into account in order to optimize the TPA performance of a chromophore.

Admittedly, in some cases, the maximum δ value of the molecules may not be within the wavelength range of this study. However, it is fairly safe to conclude the following two conclusions: (a) **F-PHT** is the most efficient TPA molecule and (b) the highest TPA cross section is found in a solvent of intermediate polarity. By comparing the OPA with the TPA excitation spectra at half-wavelengths (Figure 10), it is seen that

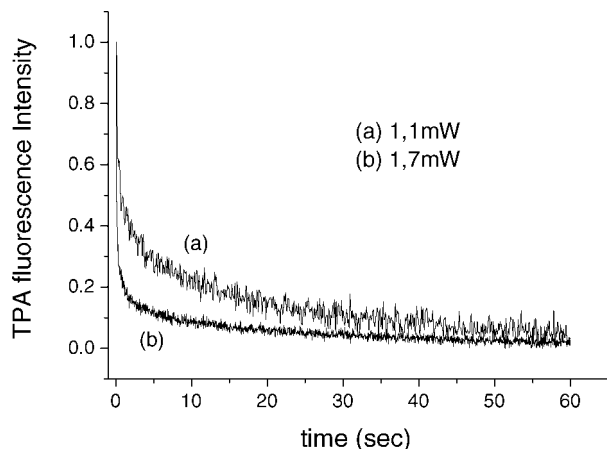


Figure 11. TPA induced fluorescence intensity of **F-PHT** doped in a PMMA solid film as a function of the illumination time. A clear and fast photobleaching is observed even at low excitation intensities.

the TPA excitation maximum lays at the short wavelength side of the OPA excitation maximum corresponding to the $S_0 \rightarrow S_2$ transition. This blue shift of the TPA excitation spectrum compared with the OPA one is common in symmetric molecules since the one photon allowed transitions are two photon forbidden. The dependence of δ on wavelength can be determined by the semiempirical SOS method. According to a simplified SOS expression for a three-state model, the TPA cross section spectrum is given by^{39–41}

$$\delta(\nu_p) \propto \frac{\nu_p^2}{(\nu_{j0} - \nu_p)^2 + \Gamma_{j0}^2} \frac{\Gamma_{f0}}{(\nu_{f0} - 2\nu_p)^2 + \Gamma_{f0}^2} \quad (1)$$

where ν_p is the laser frequency, ν_{j0} and ν_{f0} are the transition energies from the ground state to the intermediate and final state, respectively, and Γ_{j0} and Γ_{f0} are the dumping factors for the corresponding transitions. The TPA spectra for **F-PHT** and **B-PHT** were reproduced using eq 1 and experimental parameters from OPA excitation spectra. Specifically, ν_{j0} is obtained from the $S_0 \rightarrow S_1$ transition, and Γ_{j0} and Γ_{f0} correspond to the linewidths of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions. The amplitude as well as ν_{f0} were treated as adjustable parameters. The reproduced spectra together with the fitting parameters are shown in Figure 10, exhibiting good agreement with the experimental spectra. The increase of δ at wavelengths shorter than 600 nm is related to a resonance enhancement due to the one photon transition.

F-PHT, being an efficient TPA molecule, has also been studied concerning TPA photobleaching. This is a process in which a molecule after illumination with femtosecond IR pulses is no longer able to emit light and can be exploited as a writing mechanism for 3D optical storage.³⁴ Figure 11 shows the TPA induced fluorescence intensity of **F-PHT** doped into a PMMA polymeric matrix as a function of illumination time. The concentration of the film was 1 wt % of **F-PHT** in PMMA. The excitation wavelength was 780 nm, and two different excitation powers, that is, 1.1 and 1.7 mW, were used. Although, in all cases, the excitation power is kept low, a fast drop of fluorescence intensity is observed because of photobleaching. Especially, at 1.7 mW, the fluorescence decrease is very fast and steep. This means that photobleaching, which is the storing mechanism, is very fast and needs very low excitation power. These initial results are very promising toward the future use of **F-PHT** as a 3D storing medium.

Conclusions

Three strong TPA molecules with electron accepting phthalimide edge substituents have been studied concerning TPA and photophysics. The chromophores have fluorene, alkoxy-substituted divinyl benzene, and carbazole central cores. Fluorescence decays, have revealed an ultrafast decay mechanism in polar solvents. This mechanism, having a time constant equal to 1 ps in DMF, is attributed to the fast relaxation toward the ICT state which is formed in polar solvents. The molecule with fluorene core, being of the type A- π -A, has been found the most efficient TPA chromophore showing δ values as high as 2100 GM. The dependence of the δ on solvent polarity indicates that it reaches its highest value in solvents of intermediate polarities like THF and acetophenone. The TPA spectra have been reproduced following the SOS method for a three-state model showing good agreement with the experimental data. Finally, a study of the TPA induced photobleaching of solid PMMA films doped with the fluorene-core chromophore have demonstrated that this chromophore is very promising for efficient and fast TPA optical data storage.

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References and Notes

- (1) Diaspro, A.; Robello, M. *J. Photochem. Photobiol. B: Biol.* **2000**, 55, 1.
- (2) Jiang, B.; Shen, Z.; Cai, J.; Tang, H.; Xing, H.; Huang, W. *Proceedings of SPIE*, The International Society for Opt. Engineering 6150 II, article no. 61503Q.
- (3) Parthenopoulos, D. A.; Rentzepis, P. M. *Science* **1989**, 245, 843.
- (4) Sivarman, R.; Clarson, S. J.; Lee, B. K.; Steckl, A. J.; Reinhardt, B. A. *Appl. Phys. Lett.* **2000**, 77, 328.
- (5) Kawata, S.; Sun, H.-B.; Tanaka, T.; Takada, T. *Nature* **2001**, 412, 697.
- (6) Dyer, D. J.; Cumpston, B. H.; McCord-Maughon, D.; Thaynmanavan, S.; Barlow, S.; Perry, J. W.; Marder, S. R. *Nonlinear Optics Quantum Optics* **2004**, 31, 175.
- (7) Lu, Y.; Hasegawa, F.; Goto, T.; Ohkuma, S.; Fuguhara, S.; Kawazu, Y.; Totan, K.; Yamashita, T.; Watanabe, T. *J. Mater. Chem.* **2004**, 14, 75.
- (8) Abboto, A.; Beverina, L.; Bradamante, S.; Bozio, R.; Ferrante, C.; Pagni, A. G.; Signorini, R. *Adv. Mater.* **2000**, 12, 1963.
- (9) O'Flaherty, S. A.; Murphy, V.; Hold, S. V.; Cadek, M.; Coleman, J. N.; Blau, W. J. *J. Phys. Chem. B* **2003**, 107, 958.
- (10) Charlot, M.; Izard, N.; Mongin, O.; Riehl, D.; Blanchard-Desce, M. *Chem. Phys. Lett.* **2006**, 417, 297.
- (11) Fredriksen, P. K.; Nielsen, S. P.; Nikolajsen, L.; Jorgensen, M.; Mikkelsen, K. V.; Ogilby, P. R. *J. Am. Chem. Soc.* **2005**, 127, 255.
- (12) Drobizhev, M.; Stepanenko, Y.; Dzenis, Y.; Karotki, A.; Rebane, A.; Taylor, P. N.; Anderson, H. L. *J. Phys. Chem. B* **2005**, 109, 7223.
- (13) Tian, Y. P.; Zhang, M. L.; Yu, X. Q.; Xu, G. B.; Ren, Y.; Yang, J. X.; Wu, J. Y.; Zhang, X. J.; Tao, X. T.; Zhang, S. Y.; Jiang, M. H. *Chem. Phys. Lett.* **2004**, 388, 325.
- (14) Polyzos, I.; Tsigaridas, G.; Fakis, M.; Giannetas, V.; Persephonis, P. *Opt. Lett.* **2005**, 30, 2654.
- (15) Polyzos, I.; Tsigaridas, G.; Fakis, M.; Giannetas, V.; Persephonis, P.; Mikroyannidis, J. *J. of Phys. Chem. B* **2006**, 110, 2593.
- (16) Gavriluk, S.; Polyutov, S.; Jha, P. C.; Rinkevicius, Z.; Ågren, H.; Gel'mukhanov, F. *J. Phys. Chem. A* **2007**, 111, 11961.
- (17) Eggeling, C.; Widengren, J.; Brand, L.; Schaffer, J.; Felekyan, S.; Seidel, C. A. M. *J. Phys. Chem. A* **2006**, 110, 2979.
- (18) Albota, M.; Beljonne, D.; Bredas, J. L.; Ehrlich, J. E.; Fu, J. Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Rockel, H.; Rumi, M.; Subramaniam, C.; Webb, W. W.; Wu, X. L.; Xu, C. *Science* **1998**, 281, 1653.
- (19) Mazzucato, S.; Fortunati, I.; Sclaro, S.; Zerbetto, M.; Ferrante, C.; Signorini, R.; Pedron, D.; Bozio, R.; Locatelli, D.; Righetto, S.; Roberto, D.; Ugo, R.; Abboto, A.; Archetti, G.; Beverina, L.; Ghezzi, S. *Phys. Chem. Chem. Phys.* **2007**, 9, 2999.
- (20) Strehmel, S.; Strehmel, V. *Adv. In Photochemistry* **2007**, 29, 111.
- (21) Woo, H. Y.; Liu, B.; Kohler, B.; Korystov, D.; Mikhailovsky, A.; Bazan, G. C. *J. Am. Chem. Soc.* **2005**, 127, 14721.

- (22) Yan, Y.; Li, B.; Liu, K.; Dong, Z.; Wang, X.; Qian, S. *J. Phys. Chem. A* **2007**, *111*, 4188.
- (23) Belfield, K. D.; Morales, A. R.; Hales, J. M.; Hagan, D. J.; Van Stryland, E. W.; Chapela, V. M.; Percino, J. *Chem. Mater.* **2004**, *16*, 2267.
- (24) Belfield, K. D.; Morales, A. R.; Kang, B. S.; Hales, J. M.; Hagan, D. J.; Van Stryland, E. W.; Chapela, V. M.; Percino, J. *Chem. Mater.* **2004**, *16*, 4634.
- (25) Shao, P.; Huang, B.; Chen, L.; Liu, Z.; Qin, J.; Gong, H.; Ding, S.; Wang, Q. *J. Mater. Chem.* **2005**, *15*, 4502.
- (26) Li, J.; Meng, F.; He, T.; Mi, J.; Ji, W. *Chem. Lett.* **2005**, *34*, 922.
- (27) Terenziani, F.; Droumaguet, C.; Katan, C.; Mongin, O.; Blanchard-Desce, M. *ChemPhysChem* **2007**, *8*, 723.
- (28) Ftilis, I.; Fakis, M.; Polyzos, I.; Giannetas, V.; Persephonis, P.; Vellis, P.; Mikroyannidis, J. *Chem. Phys. Lett.* **2007**, *447*, 300.
- (29) Wang, C. -K.; Zhao, K.; Su, Y.; Ren, Y.; Zhao, X.; Luo, Y. *J. Chem. Phys.* **2003**, *119*, 1208.
- (30) Luo, Y.; Norman, P.; Macak, P.; Ågren, H. *J. Phys. Chem. A* **2000**, *104*, 4718.
- (31) Mikroyannidis, J. unpublished results.
- (32) Fakis, M.; Anastopoulos, D.; Giannetas, V.; Persephonis, P.; Mikroyannidis, J. *J. Phys. Chem. B* **2006**, *110*, 12926.
- (33) Fakis, M.; Anastopoulos, D.; Giannetas, V.; Persephonis, J. *Phys. Chem. B* **2006**, *110*, 24897.
- (34) Polyzos, I.; Tsigaridas, G.; Fakis, M.; Giannetas, V.; Persephonis, P.; Mikroyannidis, J. *Chem. Phys. Lett.* **2003**, *369*, 264.
- (35) Yao, S.; Belfield, K. D. *J. Org. Chem.* **2005**, *70*, 5126.
- (36) Wang, X.; Wang, P.; Jiang, W.; Xu, G.; Guo, X. *Opt. Mater.* **2005**, *27*, 1163.
- (37) Halik, M.; Wenseleers, W.; Grasso, C.; Stellacci, F.; Zojer, E.; Barlow, S.; Bredas, J. L.; Perry, J. W.; Marder, S. R. *Chem. Commun.* **2003**, 1490.
- (38) Kim, O. -K.; Lee, K. -J.; Huang, Z.; Heuer, W. B.; Paik-Sung, C. S. *Opt. Mater.* **2002**, *21*, 559.
- (39) Kamada, K.; Ohta, K.; Iwase, Y.; Kondo, K. *Chem. Phys. Lett.* **2003**, *372*, 386.
- (40) De Boni, L.; Piovesan, E.; Misoguti, L.; Zilio, S. C.; Mendonca, C. R. *J. Phys. Chem. A* **2007**, *111*, 6222.
- (41) Neves, U. M.; De Boni, L.; Ye, Z.; Bu, X. R.; Mendonca, C. R. *Chem. Phys. Lett.* **2007**, *441*, 221.

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