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Effect of Solvent on Two-Photon Absorption by Vinyl Benzene Derivatives

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Two-photon absorption cross sections and spectral profiles were determined for three centrosymmetric vinyl benzenes in solvents of differing polarity and polarizability. The data do not correlate with parameters that characterize dielectric properties of the solvents. Rather, the effect of solvent depends on the solute, and even subtle structural changes in the latter can result in pronounced solvent-dependent differences in the absorption cross section. Our data highlight the need for more sophisticated models that can simulate the perturbing effects of a solvent in the two-photon process.

Introduction

The process of simultaneously absorbing two photons to populate an excited electronic state of an organic molecule has received a great deal of attention over the last 40 years.[1–4] This nonlinear optical phenomenon complements the more dominant linear one-photon process and provides a new dimension for the study and application of interactions between light and matter.

Fundamental efforts in this field have thus far principally focused on attempts to elucidate how changes in the chromophore (e.g., substituents, conjugation length, and symmetry) influence two-photon absorption as reflected both in the absorption spectrum and in the probability of a transition to a given state.[5–10] The latter is conventionally expressed in terms of the two-photon absorption cross section, δ, which is given in units of GM to honor Maria Göppert-Mayer, a pioneer in the field (1 GM $= 10^{-50}$ cm^4 s photon^{-1}).

Other efforts in this field have focused on developing applications that exploit features unique to the two-photon excitation of a chromophore. Principal among these is the feature that two-photon absorption only occurs where the incident photon flux is sufficiently large, and this constraint can be used to define very small volumes of excitation. Such spatial localization has been used to great effect with microscopes that provide 3D images with submicrometer resolution.[11] Similarly, localized excitation can be used to initiate reactions that can be used, for example, as a mechanistic tool to examine spatially resolved photoinduced phenomena or to build microscopic 3D structures using photoinduced polymerizations.[12]

Of interest in our research program is the development and use of molecules that can sensitize the production of singlet molecular oxygen, $O_2(a^1\Delta_g)$, upon the simultaneous absorption of two photons (Figure 1). Singlet oxygen is an important reactive intermediate in many processes,[13] and it is known to be involved in spatially resolved events that result in the photoinitiated death of biological cells (i.e., both apoptotic and necrotic processes).[14] As such, we are interested in the spatially resolved aspects of two-photon photosensitized singlet oxygen production as a tool for (1) the creation of singlet-oxygen-based images of a cell, and (2) mechanistic studies of photoinduced, oxygen-dependent cell death.[15–17]

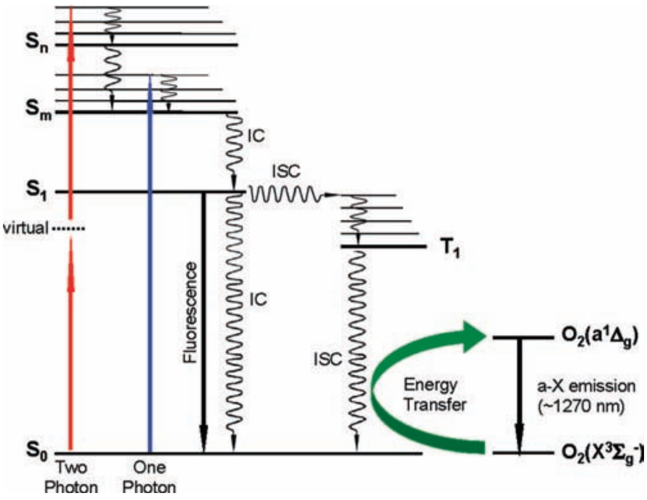

Figure 1. Diagram depicting both the one- and two-photon triplet state photosensitized production of singlet oxygen. Sensitizers of greatest interest will have a large absorption cross section and, after internal conversion (IC) to produce the lowest excited singlet state (S_1), will efficiently intersystem cross (ISC) into the triplet manifold to produce the lowest excited triplet state (T_1). In the bimolecular collision between the T_1 state and ground state oxygen, $O_2(X^3\Sigma_g^-)$, the ideal sensitizer will produce $O_2(a^1\Delta_g)$ in high yield. The excitation scheme shown is that for a centrosymmetric molecule where selection rules dictate that one- and two-photon irradiation do not populate the same state.

In our studies thus far, we have established that features of a chromophore that generally enhance two-photon absorption are often not conducive to the efficient photosensitized production of singlet oxygen.[18,19] Key in this regard is the extent of photoinduced charge transfer (CT), not just in the chromophore itself but also in complexes of the chromophore with oxygen. It is well established that substituents that promote intramolecular charge transfer can result in comparatively large transition dipole moments and, in turn, give rise to large absorption cross sections. In contrast, an increase in the extent of CT character in the sensitizer and in the sensitizer−oxygen complex generally provides mechanisms for deactivation of the excited state sensitizer that compete with energy transfer to produce singlet oxygen.[20–23] These CT-mediated processes can be quite

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pronounced in polar solvents, and are clearly reflected in solvent-dependent yields of singlet oxygen produced in photosensitized experiments.[18–20,23,24] Both the radiative and nonradiative deactivation of singlet oxygen are likewise sensitive to solvent effects.[20,25,26] Nevertheless, as with events that result in the photosensitized production of singlet oxygen, these solvent effects have been extensively examined and are now well understood.

In contrast to the work on singlet oxygen and to studies of one-photon transitions in organic molecules, the study of solvent effects on two-photon absorption is still in its infancy. Although a number of theoretical and computational studies have addressed the issue,[27–34] the results published indicate a general lack of consensus.

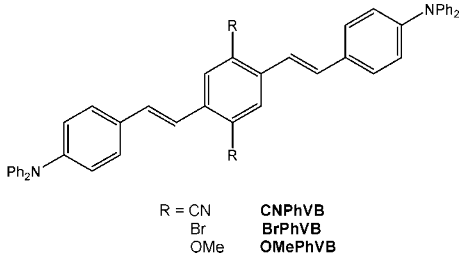
From the experimental side, the effect of solvent on two-photon absorption has yet to be addressed in systematic and detailed studies. Indeed, we are aware of only a few studies in which this issue has been considered. In a paper published in 1997, He et al.[35] reported two-photon absorption cross sections for a given molecule in five solvents. Appreciable solvent effects were observed on the values of δ recorded [e.g., δ(benzene) $\sim$ 2δ(THF)]. Unfortunately, these experiments were performed using a nanosecond (ns) excitation source which appears to have complicated and compromised the data obtained. Indeed, it was suggested in subsequent reports that the effects of excited state absorption likely contributed to the δ values obtained.[36,37] This is a common and accepted criticism of ns-based two-photon experiments. To avoid such problems, it is now generally acknowledged that, in the least, quantitative two-photon experiments should be performed using femtosecond (fs) laser pulses.[38]

To our knowledge, the only systematic study published thus far in which fs laser pulses were used to quantify solvent-dependent two-photon absorption parameters is that of Woo et al.[39] In this work, two-photon absorption cross sections and excitation spectra for a distyrylbenzene were recorded in five solvents: toluene, THF, acetone, DMSO and water (the chromophore was dressed with hydrophilic substituents for the experiments in water). The two-photon spectral profile of this chromophore did not change appreciably with a change in solvent, and a significant change in δ was observed [e.g., δ(THF) = 1540 GM, δ(toluene) = 910 GM].

Although other fs studies have addressed the effect of solvent on two-photon absorption, the number of solvents examined is limited, which makes it difficult to draw general conclusions.[40,41] In one case, data recorded from vinyl benzene derivatives did not show significant differences with a change in solvent from CH_2Cl_2 to water,[40] whereas in another case, δ values recorded for an azobenzene decreased as the amount of water in a DMSO solution was increased.[41] Terenziani et al.[32] recorded the two-photon absorption spectrum of a squaraine dye in toluene, DMSO and $CHCl_3$. Unfortunately, in this case, the experiment was limited by the spectral output of the laser used, and distinct absorption bands could not be discerned. Moreover, the authors indicated that data recorded in $CHCl_3$ may have been compromised by problems associated with photodegradation. Finally, on the basis of solvent-dependent hyperpolarizability measurements on *N,N*-dipropyl-*p*-nitroaniline, Shoute et al.[42] suggested that δ values for this molecule should not vary significantly with a change in solvent.

Given this rather limited base of experimental data, we initiated a project to systematically explore aspects of the effect of solvent on two-photon absorption. From the outset, our simplistic working hypothesis has been that the effect of solvent on the two-photon process cannot, a priori, be predicted based simply on data recorded from corresponding one-photon experiments. Rather, given the significance of the so-called virtual state in the two-photon transition (Figure 1, vide infra), and that this state could have a unique response to perturbation by the solvent, it is likely that solvent-dependent behavior observed for the two-photon absorption process would indeed differ from that observed for a one-photon process.

CHART 1: Structures of the Chromophores Studied



For our work, we were especially interested in using chromophores that could sensitize the production of singlet oxygen (Figure 1). Moreover, chromophores were selected to accommodate the ease and accuracy of our experiments, and to facilitate comparisons with two-photon data that has already been published. To these ends, we opted to work with three substituted vinyl benzenes (Chart 1): (*E*,*E*)-2,5-dicyano-1,4-bis(2-(4-diphenylaminophenyl)vinyl)benzene) (**CNPhVB**), (*E*,*E*)-2,5-dibromo-1,4-bis(2-(4-diphenylaminophenyl)vinyl)benzene) (**BrPhVB**), and (*E*,*E*)-2,5-dimethoxy-1,4-bis(2-(4-diphenylaminophenyl)vinyl)benzene) (**OMePhVB**). In particular, a substantial amount of two-photon data has already been accumulated for **CNPhVB** and **BrPhVB**, including data on the one- and two-photon photosensitized production of singlet oxygen.[19,43–45]

Results and Discussion

1. One-Photon Experiments. Absorption and fluorescence spectra recorded for **BrPhVB**, **OMePhVB** and **CNPhVB** are plotted in Figure 2, and the relevant photophysical data are summarized in Table 1. For these experiments, the three molecules were used at concentrations ranging from 1×10^{-7} to 2×10^{-4} M. Over this range, the spectral profile of the one-photon absorption and emission bands remained the same, and the absorbance followed linear Lambert–Beer behavior. These observations indicate that solvent-dependent solute aggregation does not present a problem.

All compounds display a distinct, broad, and structureless absorption band with λ_{max} between 420 and 470 nm. The solvent-dependent shifts in this absorption band are all relatively small, and there is no correlation between the position of the band maximum and any solvent polarity-related parameter. Nevertheless, for all molecules, this absorption band is most blue-shifted in cyclohexane and most red-shifted in benzonitrile. Appreciable solvent-dependent differences are observed in the molar extinction coefficient at the band maximum (equivalent solvent-dependent differences were observed in the integral of a Gaussian function fitted to this absorption band). We were likewise not able to find any correlation between a solvent polarity-related parameter and these manifestations of the transition probability.

In contrast, large solvent-dependent shifts appear in the fluorescence spectra. For all compounds, the most blue-shifted spectrum is recorded in cyclohexane (i.e., the smallest Stokes shift is recorded in this solvent). Moreover, this emission spectrum is unique in that it exhibits distinct vibronic structure.

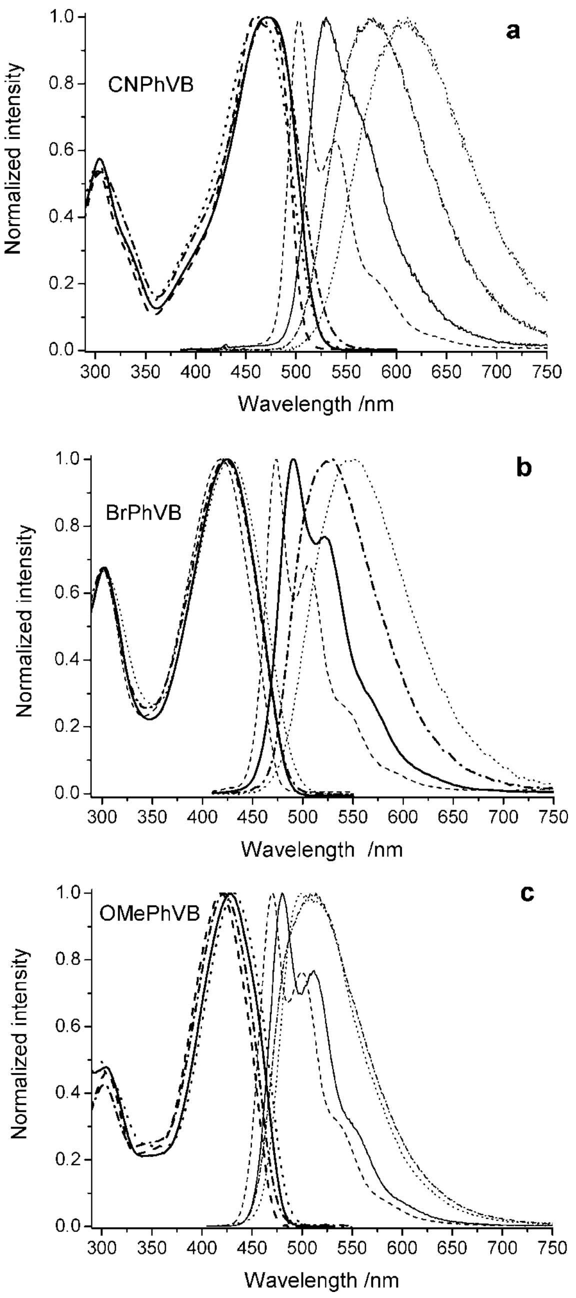


Figure 2. Absorption and fluorescence spectra of the molecules studied: (a) **CNPhVB**, (b) **BrPhVB**, (c) **OMePhVB**. For each molecule, data were recorded in four solvents: (—) toluene, (---) cyclohexane, (•••) benzonitrile, (—•—) THF or acetonitrile.

The fluorescence spectra recorded in the more polar and polarizable solvent toluene are red-shifted relative to those recorded in cyclohexane and, with the exception of the **OMePhVB** spectrum, the vibronic structure is less pronounced. Spectra recorded in THF, acetonitrile and benzonitrile are even further red-shifted and show no vibronic structure.

Interactions between the solvent and a solute are often described and interpreted using functions that depend on macroscopic dielectric properties of the solvent. Electronic transitions, in particular, are routinely examined against functions of the solvent static (ϵ_{st}) and optical (ϵ_{op}) dielectric constants, the latter expressed as the square of the solvent refractive index, n.[46] Common to most mathematical representations of Onsager's solvent–solute reaction field is the parameter Δf (eq 1).[46,47]

$$\Delta f = \frac{\epsilon_{st} - 1}{2\epsilon_{st} + 1} - \frac{n^2 - 1}{2n^2 + 1} \qquad (1)$$

As shown in Figure 3, there is a reasonably good correlation between our solvent-dependent Stokes shifts and Δf. Figure 3 also clearly illustrates that the Stokes shifts in **BrPhVB** and **CNPhVB** are most sensitive to the changes in solvent.

The data in Figures 2 and 3 indicate that the solvent-equilibrated emitting state of our vinyl benzene derivatives is quite susceptible to the effects of the solvent and is stabilized in more polar/polarizable solvents. Analogous data have been recorded from other, related compounds.[8,32,39] In turn, these data imply that the emitting state may have a certain amount of charge-transfer (CT) character. Evidence to support the existence of a solvent-stabilized intramolecular CT excited state has been presented for related PV oligomers.[48]

In previous experiments on analogous vinyl benzenes, we have seen a corresponding decrease in the yield of sensitized singlet oxygen production in cases where fluorescence data implies excited state CT character.[8] In the present solvent-dependent work, we do not see a pronounced correlation between the singlet oxygen yield and the nature of the fluorescence spectrum (Table 2). This may indicate that, for the present molecules, (1) the extent of solvent-dependent CT character in the immediate precursor to singlet oxygen (the T_1 state) is not the same as that in the fluorescent S_1 state, or (2) S_1 simply has a larger dipole moment or is more polarizable than S_0, and CT character is not at all pronounced in the excited state.

2. Two-Photon Experiments. ***2.1. General Background.*** Two-photon absorption is illustrated in Figure 1 in the context of the photosensitized production of singlet oxygen. In this process, an excited state of the sensitizer, S_n, is produced from the ground state, S_0, via the simultaneous absorption of two photons. One can think of this transition as proceeding via a so-called virtual state which is denoted in the figure using a dashed line. This virtual state is not a real state of the molecule but can be described mathematically as a linear combination of all the real states of the molecule, ψ_i, including the ground state (eq 2).

$$\psi_{vir} = \sum_i c_i \psi_i \qquad (2)$$

This concept of the virtual state is integrally incorporated in expressions that can be derived for the two-photon absorption cross section, δ. This is seen in eq 3, obtained using time-dependent perturbation theory, for a transition between a ground (g) and a final (f) state under conditions where two photons of identical energy are absorbed and where only electric dipole transitions are considered.[50]

$$\delta = \frac{\pi^2 e^4}{c^2 \varepsilon_0^{\,2} h^2} \nu_L \left| \sum_i \frac{\langle \psi_f | \bar{r} \cdot \bar{e} | \psi_i \rangle \langle \psi_i | \bar{r} \cdot \bar{e} | \psi_g \rangle}{\nu_{ig} - \nu_L} \right|^2 g_f(2\nu_L) \qquad (3)$$

Here ν_L is the frequency of the light absorbed, ν_{ig} the frequency of the transition from the ground state to the ith state considered in the sum, $\bar{e}$ is the polarization vector of the radiation field, $\bar{r}$ is the dipole moment vector, and $g_f(2\nu_L)$ is a function describing the band shape of the final state. The latter reflects the fact that a given transition will be broadened by the presence of vibrational and rotational sublevels.[51]

Embodied in Figure 1 and eq 3 is the rule that, for centrosymmetric molecules, g → f transitions between states of opposite parity will be allowed for a one-photon process,

TABLE 1: Selected Photophysical Properties of CNPhVB, BrPhVB, and OMePhVB Obtained from One-Photon Experiments[a]

compound	solvent	λ_{max}(ab) (nm)	λ_{max}(em) (nm)	Stokes shift (cm^{-1})	$\Delta E_{0,0}$ (kJ/mol)	ε_{400} (M^{-1}cm^{-1})	ε_{max} (M^{-1}cm^{-1})	τ (ns)
CNPhVB	TOL	471	530	2364	236	19950	65900	1.48 ± 0.08
	CHX	459	504	1945	243	20800	72300	1.4 ± 0.1
	THF	463	575	4207	233	27000	72200	2.08 ± 0.08
	BZN	471	610	4838	226	22600	63400	2.7 ± 0.4
BrPhVB	TOL	425	491	3163	255	47600	62600	0.65 ± 0.05
	CHX	419	473	2725	261	44800	51900	0.65 ± 0.04
	THF	423	528	4701	252	52300	65000	0.73 ± 0.06
	BZN	427	550	5237	247	45000	59800	0.94 ± 0.07
OMePhVB	TOL	427	480	2586	258	57000	84500	1.13 ± 0.06
	CHX	420	470	2533	264	76200	93400	1.17 ± 0.08
	ACN	422	511	4127	258	62600	82000	1.45 ± 0.08
	BZN	433	503	3214	253	41800	68200	1.33 ± 0.12

[a] Absorption (ab) and emission (em) data were recorded in toluene (TOL), cyclohexane (CHX), tetrahydrofuran (THF), benzonitrile (BZN) and acetonitrile (ACN). **CNPhVB** and **BrPhVB** are not soluble in ACN (see Experimental Section). The energy difference between the S_0 and S_1 states, $\Delta E_{0,0}$, was obtained from the crossing point of the intensity-normalized absorption and fluorescence spectra. Molar extinction coefficients are reported at the absorption band maximum, ε_{max}, and at 400 nm, ε_{400}. As discussed in section 2, the latter is important in the approach used to quantify two-photon absorption cross sections. The lifetime of the S_1 state, τ, was obtained from a time-resolved fluorescence experiment.

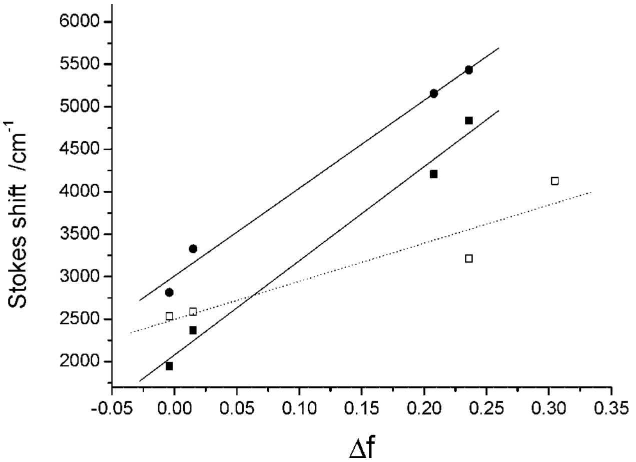


Figure 3. Plots of the Stokes shift for the three vinyl benzene derivatives studied (□, **OMePhVB**; ●, **BrPhVB**; ■, **CNPhVB**) against the reaction field parameter Δf for the solvents shown in Table 1. Although the lines shown derive from a linear fit to each data set, they are included only to highlight the overall trend.

TABLE 2: Solvent-Dependent Singlet Oxygen Yields Sensitized by BrPhVB

solvent[a]	Φ_Δ
TOL	0.37 ± 0.04[b]
THF	0.28 ± 0.03
BNZ	0.32 ± 0.03
CHX	0.26 ± 0.03

[a] Data were recorded in toluene (TOL), cyclohexane (CHX), tetrahydrofuran (THF), and benzonitrile (BZN). [b] We have previously reported a value of 0.45 ± 0.05 for **BrPhVB** in toluene,[49] and the present number, although smaller, is still within the error limits.

whereas the two-photon g → f process will only couple states of the same parity.[2] In short, the state f initially populated upon light absorption will be different in these respective processes. This selection rule applies quite generally, even for many of the large molecules typically used as singlet oxygen sensitizers.[49] Nevertheless, interesting cases can arise when dealing with molecules that readily interconvert between ground state isomers of different symmetry,[52] and where the presence of solvent and counterions influences the overall symmetry.[53]

On the basis solely of eq 2, we can see how a two-photon transition could indeed have a unique response to a change in solvent, certainly in comparison to a corresponding one-photon transition to the same state. Simply expressed, the real states that define the virtual state all have different electronic distributions, each of which will respond differently to a change in solvent. We can carry this discussion further with reference to eq 3. First, recall that, in the transition g → *i*, the surrounding solvent will retain the polarization established by the charge distribution of the ground state solute, and any state *i* initially populated upon light absorption will not be in equilibrium with the surrounding solvent. The extent to which a given excited state will be destabilized relative to the solvent-equilibrated condition will depend on the solvent and will be reflected in the parameter υ_{ig}. Second, because each electronic state of the solute will have a different orbital occupancy and charge distribution, and each charge distribution will respond differently to a given solvent, it is reasonable to expect that the transition dipole moments, $\langle\psi_f|\bar{r}\cdot\bar{e}|\psi_i\rangle$ and $\langle\psi_i|\bar{r}\cdot\bar{e}|\psi_g\rangle$, will likewise vary with the solvent. Finally, the solvent will influence the band shape function g_f by perturbing vibrational and rotational levels.

However, perhaps the simplest way to see how solvent could influence a two-photon transition through eq 3 is to recognize that, properly defined, the wave functions ψ will describe the *entire* system of solvent and solute.[54]

2.2. Two-Photon Excitation Spectra. Two-photon excitation spectra of the three vinyl benzenes (**CNPhVB**, **BrPhVB**, and **OMePhVB**) were recorded in the solvents listed in Table 1. These spectra, shown in Figure 4, were recorded against standard molecules for which the two-photon absorption profile has been independently established (see Experimental Section). The spectra were recorded using the sample fluorescence as the optical probe.

Recording such two-photon excitation spectra against that of an established standard accounts for changes in the fluorescence intensity that derive from wavelength-dependent differences in the temporal and spatial profiles of the exciting laser beam; one only has to account for the overall spectral profile of the standard. On the other hand, for experiments performed in different solvents, one must account for any wavelength-dependent effects that may arise as a consequence of light absorption by the solvent. These latter effects are readily quantified, however (see Experimental Section and Supporting Information). The excitation spectra shown in Figure 4 were corrected for solvent absorption, when necessary, and we

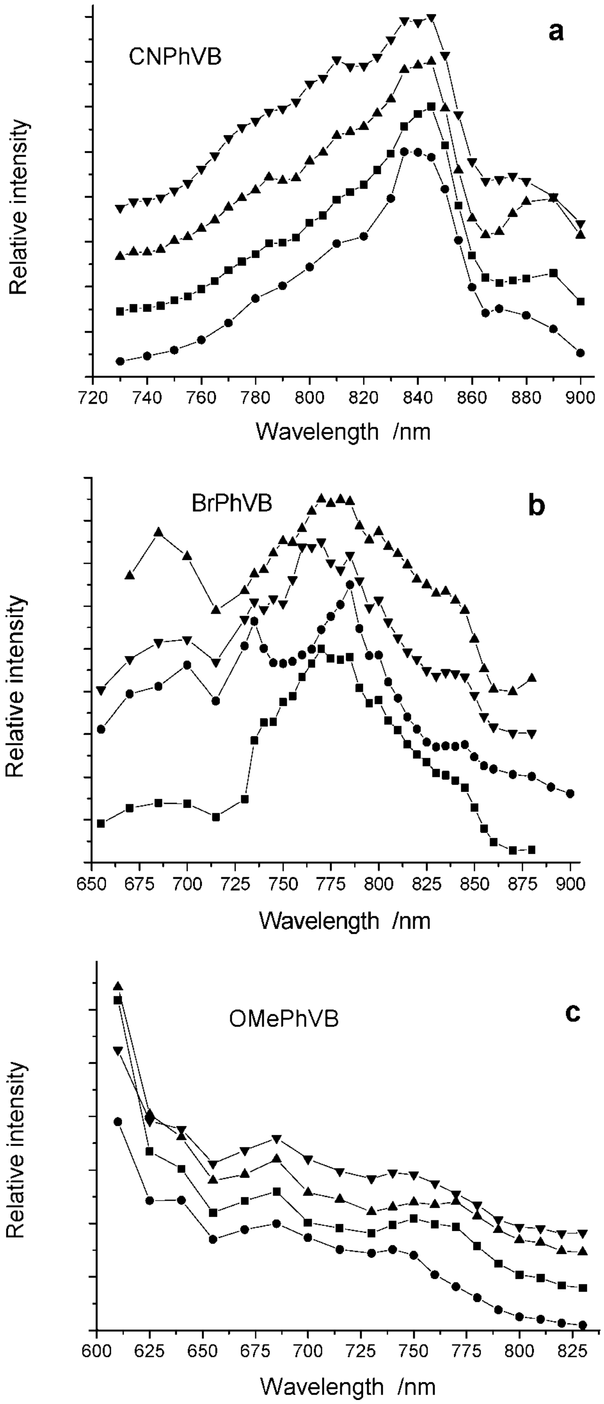


Figure 4. Two-photon excitation spectra for (a) **CNPhVB**, (b) **BrPhVB** and (c) **OMePhVB**. The **CNPhVB** and **BrPhVB** data were recorded in four solvents: toluene (■), cyclohexane (●), benzonitrile (▲) and THF (▼). For **OMePhVB**, acetonitrile was used instead of THF. Each point shown has an error of ~8%. To more clearly show the relative effects of a change in solvent, the spectra have been displaced vertically by an arbitrary factor.

ascertained that the fluorescence signals correctly scaled quadratically with incident laser power at all excitation wavelengths.

When examining the data shown in Figure 4, it is first important to recognize that these experiments were performed using a fs laser system as the excitation source. Thus, at each excitation wavelength, the spectral width of the laser pulse is comparatively broad (i.e., wavelength-dependent fwhm ~ 10−20 nm).[44] Second, our principle concern is to show relative, solvent-dependent changes in the spectral profiles of the respective molecules. As such, we have not included a numerical scale on the *y*-axes. However, using two-photon absorption cross sections independently obtained (section 2.3, vide infra), each of these spectra can be plotted with values of δ on the *y*-axis. These 12 spectra are included in the Supporting Information.

Although one can clearly discern solvent-dependent changes in the spectra of **CNPhVB** and **OMePhVB** (Figure 4a,c), these changes are not pronounced. These results are consistent with those obtained by Woo et al.[39] who likewise observed only small solvent-dependent changes in the spectra of a related *N,N*-dialkyl-substituted aminophenyl vinylene. On the other hand, more pronounced solvent-dependent changes are observed in the **BrPhVB** spectra (Figure 4b). Thus, our data clearly indicate that even when the principal molecular features of the chromophore remain the same, slight changes in a substituent (i.e., CN → OMe → Br) can have significant effects both on the two-photon spectral profile and on the sensitivity of this spectral profile to a change in solvent.

In Figure 5, we show the one- and two-photon spectra recorded in toluene for each of our vinyl benzene derivatives. The data are plotted such that the *x*-axis shows the transition energy. We clearly see that our results meet the expectation based on parity-derived selection rules (vide supra): For these centrosymmetric molecules, the initial state populated in a two-photon transition is different from that populated in a one-photon transition.

2.3. Two-Photon Absorption Cross Sections. We noted in the Introduction that singlet oxygen can be produced upon two-photon excitation of a sensitizer (Figure 1). We have established that one can use the 1270 nm phosphorescence of the singlet oxygen thus produced ($O_2(a^1\Delta_g) \rightarrow O_2(X^3\Sigma_g^-)$) as a probe to quantify the efficiency with which light is absorbed by that sensitizer in the two-photon process.[8,19,43,44] This singlet-oxygen-based approach complements other methods by which nonlinear light absorption can be studied in a given molecule (e.g., fluorescence,[38] z-scan[55,56]) and, in fact, has a number of distinct advantages, particularly for a solvent-dependent study.[44]

2.3.1. Experimental Technique. Two-photon absorption cross sections, δ, were obtained using the singlet-oxygen-based technique that has been described in detail elsewhere.[8,19,44]

Briefly, the intensity of singlet oxygen phosphorescence detected upon two-photon excitation of the molecule, I_2, was compared to the intensity of singlet oxygen phosphorescence detected upon one-photon excitation of the same molecule, I_1. The number of excited states produced upon light absorption in the one-photon process, N_1, which is proportional to I_1, is given by eq 4,

$$N_1 = \frac{P_1\lambda_1(1 - 10^{-A})}{f_{\text{rep}}hc} \tag{4}$$

where P_1 is the average power of the laser used to irradiate the system at the wavelength λ_1, f_{rep} is the laser repetition rate, h is Planck's constant, c is the speed of light, and A is the sample absorbance at λ_1. The number of excited states produced upon light absorption in the two-photon process, N_2, which is proportional to I_2, can be similarly expressed,

$$N_2 = \frac{\delta P_2^{\,2}\lambda_2^{\,2}C}{2f_{\text{rep}}^{\,2}h^2c^2}g_{\text{T}}g_{\text{S}} \tag{5}$$

where P_2 is the average laser power incident on the sample at the irradiation wavelength λ_2, C is the concentration of the molecule under study, δ is the two-photon absorption cross section, and g_{T} and g_{S} are the temporal and spatial coherence

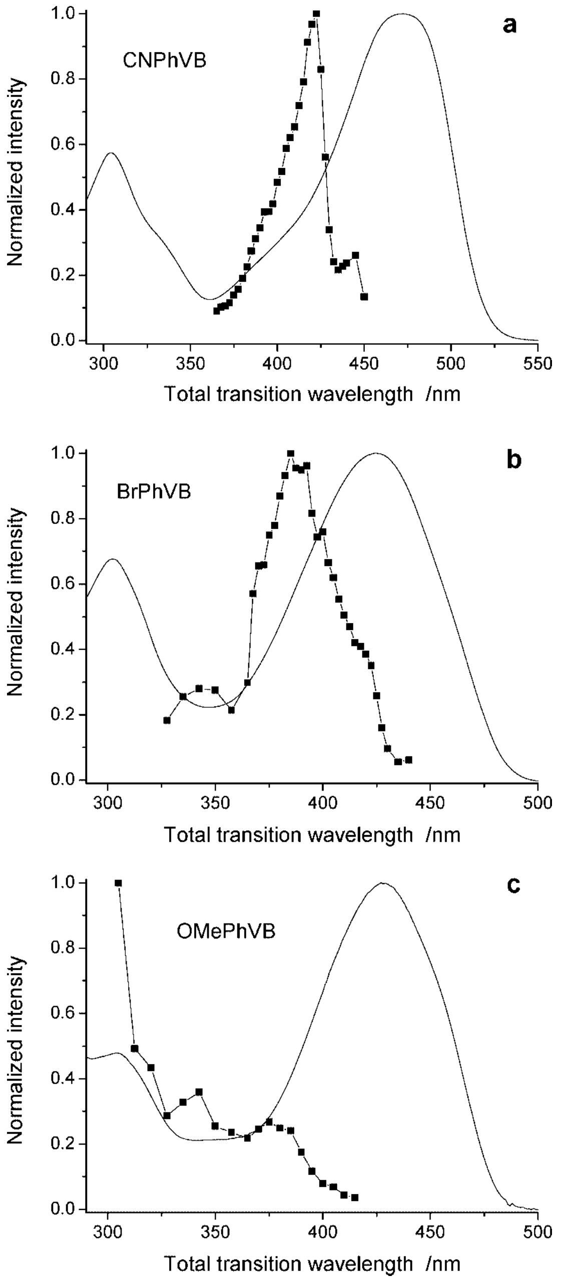


Figure 5. One-photon absorption spectra (solid line) and two-photon excitation spectra (■) for the three vinyl benzenes recorded in toluene: (a) **CNPhVB**. (b) **BrPhVB**. (c) **OMePhVB**. Shown on the *x*-axis is the total transition energy, given as a wavelength in nm.

factors for the irradiating laser beam, respectively.[4,38,44] In this experiment, the irradiation wavelengths were chosen such that $2\lambda_1 = \lambda_2$ (i.e., the two-photon experiments were performed at 800 nm which is an easily accessible wavelength and which, in turn, is readily frequency-doubled to yield 400 nm light for the one-photon experiments).

Upon the absorption of light, we assume that rapid intramolecular relaxation produces the same state (i.e., S_1) and the subsequent photosensitized production of singlet oxygen occurs with the same efficiency (see Figure 1). Given the way that this experiment is done, the same multiplicative factor relates the intensities of the singlet oxygen phosphorescence signals, I_1 and I_2, to N_1 and N_2, respectively.[44] Thus, the combination of eqs 4 and 5 makes it possible to obtain a value for δ at a given wavelength. When experiments are performed in different solvents, the inherent effect of solvent on the value of δ is recorded (i.e., corrections for changes in the refractive index are not necessary). Therefore, this approach is readily used to obtain relative δ values for experiments performed in different solvents.

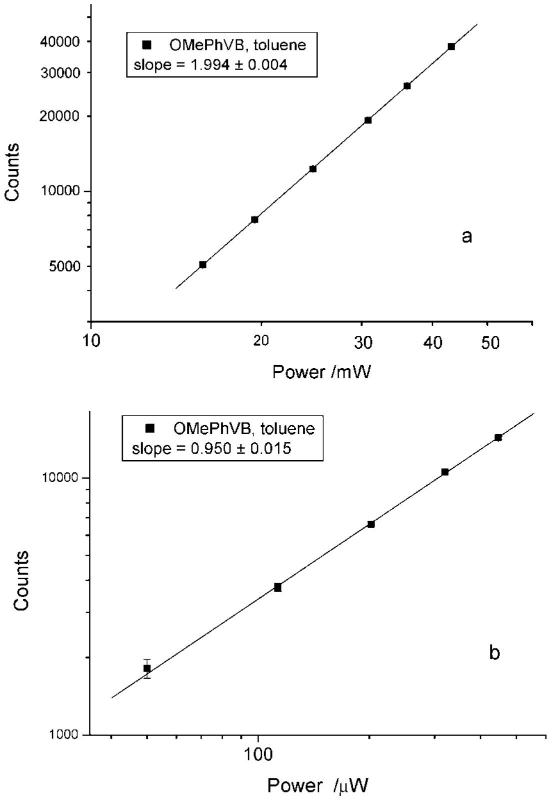


Figure 6. Double logarithmic plots of the singlet oxygen phosphorescence signal against incident laser power recorded upon (a) 800 nm, and (b) 400 nm irradiation (background corrected) of **OMePhVB** in toluene.

One disadvantage of our approach is that the temporal and spatial coherence factors for the irradiating laser, g_T and g_S, must be quantified if an absolute value for δ is to be reported at any given wavelength.[19,44] To report absolute δ values, relative δ values can be normalized against a reference molecule with established wavelength-dependent δ values. In our case, this is readily done using **CNPhVB** in toluene as the standard.

2.3.2. Solvent Absorption. The data recorded from solutions of our vinyl benzenes following irradiation at 800 nm scaled quadratically with the incident power (Figure 6a), as expected for a two-photon transition. In these experiments with 800 nm irradiation, we did not observe a signal from any of the neat solvents and, thus, a background correction was not required.

Upon 400 nm irradiation, the signals detected from cyclohexane, THF and acetonitrile solutions of the sensitizers scaled linearly with the incident power as expected for a one-photon transition. Moreover, a signal was not observed upon 400 nm irradiation of these neat solvents and, thus, a background correction was likewise not required.

However, upon 400 nm irradiation of neat toluene and benzonitrile, a singlet oxygen phosphorescence signal was detected which scaled quadratically with the incident laser power. We have previously addressed this issue in detail with respect to similar experiments to quantify δ,[8,44] and have demonstrated that one can correct for this solvent-derived background signal simply by subtracting it from the signal detected from solutions of the sensitizers. Indeed, when the data obtained from solutions of toluene and benzonitrile were

TABLE 3: Solvent-Dependent Two-Photon Absorption Cross Sections at 800 nm and at the Maximum of a Given Band in the Two-Photon Spectrum

compound	solvent[a]	$\delta_{\mathrm{rel}}^{800}$[b]	$\lambda_{\max}$[c] (nm)	$\delta_{\mathrm{rel}}^{\max}$[d]	$\varepsilon_{\mathrm{rel}}^{\max}$[e]	$\delta_{\mathrm{relCNPhVB}}^{800}$[f]	δ^{800}[g] (GM)
CNPhVB	TOL	1.00	845	1.00	1.00	1.00	1365 ± 205
	CHX	1.23 ± 0.10	835	1.22 ± 0.10	1.10 ± 0.12		1679 ± 286
	THF	1.07 ± 0.16	845	0.74 ± 0.11	1.10 ± 0.12		1461 ± 309
	BZN	0.95 ± 0.06	845	0.83 ± 0.05	0.96 ± 0.10		1297 ± 211
BrPhVB	TOL	1.00	770	1.00	1.00	0.73 ± 0.05	990 ± 163
	CHX	0.58 ± 0.04	785	0.66 ± 0.05	0.83 ± 0.09		574 ± 102
	THF	0.83 ± 0.05	770	0.87 ± 0.05	1.04 ± 0.11		822 ± 144
	BZN	0.67 ± 0.06	770	0.60 ± 0.05	0.96 ± 0.10		663 ± 124
OMePhVB	TOL	1.00	685	1.00	1.00	0.43 ± 0.03	587 ± 97
	CHX	0.57 ± 0.05	685	1.00 ± 0.09	1.11 ± 0.12		335 ± 63
	ACN	0.40 ± 0.04	685	0.53 ± 0.05	0.97 ± 0.10		235 ± 45
	BZN	1.23 ± 0.11	685	1.1 ± 0.1	0.81 ± 0.09		722 ± 136

[a] Data were recorded in toluene (TOL), cyclohexane (CHX), tetrahydrofuran (THF), benzonitrile (BZN), and acetonitrile (ACN). The data were collected in 4−8 independent experiments and averaged. The errors shown reflect one standard deviation from the mean. [b] Values of δ determined at 800 nm relative to that obtained for the given molecule in toluene. [c] Maximum of a prominent band in the two-photon spectrum. See Figure 4. [d] Values of δ at the maximum of the band whose wavelength is shown in column 4 relative to the δ value obtained at the band maximum in toluene. [e] Values of the one-photon molar extinction coefficient, ε, at the maximum of the one-photon absorption band (see Table 1) relative to the ε value obtained at the band maximum in toluene. [f] Values of δ obtained at 800 nm relative to that obtained from **CNPhVB**. [g] Values of δ at 800 nm obtained using $\delta_{\mathrm{CNPhVB}}(\text{toluene}) = 1365 \pm 205$ as the standard. This value for δ_{CNPhVB} has been independently established.[44]

corrected for the solvent background, the resulting signal scaled linearly with the incident power, as expected (Figure 6b).

2.3.3. Solvent Effects on δ. It is first informative to compare relative values of the two-photon absorption cross section obtained at 800 nm in different solvents, $\delta_{\mathrm{rel}}^{800}$. Of course, in making such a comparison, we must always be aware that solvent-dependent changes in δ at a given wavelength could principally reflect the solvent-dependent spectral shift of a distinct band. Nevertheless, as seen in Figure 4, solvent-dependent changes in the respective spectra of these molecules indicate that direct comparison of δ data obtained at 800 nm is reasonable. On the basis of the respective excitation spectra, we can also compare relative values of the absorption cross section obtained at the maximum of a given band, $\delta_{\mathrm{rel}}^{\max}$. Using these two yardsticks, we see an appreciable solvent effect on δ for all three molecules examined (Table 3).

Although Woo et al.[39] also report values of δ that depend on the solvent, their results are not consistent with ours. Specifically, for the particular vinyl benzene examined in their study, they find a rather large increase in the absorption cross section at the band maximum as the solvent is changed from toluene to THF. In our case, we find that for both **CNPhVB** and **BrPhVB**, there is a distinct decrease in δ as the solvent is changed from toluene to THF. Although this difference between our data and those of Woo et al. could reflect a number of experiment-specific phenomena, we rather think that it reflects a more fundamental aspect of the role played by the solvent in influencing two-photon transitions in a given molecule. This point is developed further below.

Our data clearly show that values of δ for each of the vinyl benzenes respond differently to a given change in solvent. For example, with **CNPhVB**, $\delta_{\mathrm{rel}}^{800}$ and $\delta_{\mathrm{rel}}^{\max}$ increase with the change in solvent from toluene to cyclohexane. With **BrPhVB**, $\delta_{\mathrm{rel}}^{800}$ and $\delta_{\mathrm{rel}}^{\max}$ decrease with the same change in solvent. As such, we are not able to find a correlation between δ and any common parameters, or collection of parameters, which describe solvent properties (e.g., Δf in eq 1).

We indicated earlier that we were likewise unable to correlate values of the one-photon molar extinction coefficient, ε, for these vinyl benzenes with solvent parameters. We are also not able to correlate solvent dependent changes in δ with solvent dependent changes in ε (see values of $\delta_{\mathrm{rel}}^{\max}$ and $\varepsilon_{\mathrm{rel}}^{\max}$ in Table 3). Arguably, this latter lack of correlation could be expected on the basis of the fundamental differences between one- and two-photon transitions, particularly for centrosymmetric molecules where different states are involved. However, in the present context, the differences between one- and two-photon transitions are best exemplified by referring to eq 2; the virtual state involved in the two-photon process is a linear combination of all states in the system, and it is here that one can find a reasonable basis for a unique susceptibility of a two-photon transition to the effects of a solvent.

Our results clearly indicate that, for these vinyl benzenes, the effect of a solvent on δ depends significantly on the particular molecule involved. This conclusion is consistent with the fact that the results of Woo et al.,[39] who studied a different vinyl benzene, do not correlate with our results. At first, one might find this conclusion rather surprising given that the differences between the vinyl benzenes that we have studied might not seem to be pronounced (i.e., “simple” substituent change; CN → OMe → Br, Chart 1). However, as illustrated with the respective two-photon excitation spectra, these subtle structural differences have a marked effect on spectroscopic transitions and the energies of the corresponding states. With respect to δ, this molecule-specific solvent-dependence is again best seen through eqs 2 and 3. The virtual state key to the two-photon process is a linear combination of all states in the given system. As such, substituent-dependent changes in electronic structure will be manifested in this virtual state. For a given molecule at a given irradiation wavelength, some states will be more important than others in the linear combination that defines the virtual state.[8,51,57] In itself, this provides a sufficient foundation to explain intrinsic, molecule-dependent solvent effects on δ.

2.3.4. δ Values. Using data recorded from **CNPhVB** as a standard, δ values for **BrPhVB** and **OMePhVB** at 800 nm were obtained in toluene using the singlet-oxygen-based techniques described in this report (Table 3). The δ value for **BrPhVB** thus obtained is identical to that obtained in a previous study using an independent optoacoustic-based measurement.[44] These data can then be normalized using our relative solvent-dependent δ values to yield two-photon absorption cross sections (in GM units) for our vinyl benzenes in each of the solvents examined (Table 3). Using the spectral profiles shown in Figure 4, one can then plot the full spectrum of the vinyl benzene in the given solvent with δ values on the abscissa (see Supporting Information for the 12 spectra pertinent to this study).

Conclusions

The data reported herein indicate that the effect of solvent on the process of two-photon absorption by vinyl benzenes depends intrinsically on the solute; even subtle structural changes in the latter result in pronounced and seemingly random solvent-dependent differences in the absorption cross section. Our observations are arguably consistent with a model for two-photon absorption in which the transition is seen to proceed through a so-called virtual state that is a linear combination of all states in the system. Thus, subtle electronic structure changes in the excited state manifold can make the virtual state very susceptible to the effects of the solvent in ways that depend intrinsically on the molecule involved. Given the plethora of states that define the virtual state for a given molecule, one indeed may not find a systematic correlation between values of δ and common macroscopic dielectric parameters used to characterize solvents.

Our data reinforce the need for more sophisticated models that can simulate the perturbing effects of a solvent in the two-photon process, particularly with respect to how such perturbations influence the virtual state. It is expected that continuum-based solvation models will not be sufficient. Rather, one will need to consider specific solvent−solute interactions, certainly those that occur in the first solvation shell. To this end, hybrid quantum mechanics/molecular mechanics (QM/MM) methods[58] provide one promising approach. With this methodology, it is expected that the best results will occur when both the solute and the first solvation sphere are treated quantum mechanically. Furthermore, given the importance of the virtual state, it is expected that traditional sum-over-states models will likewise not be sufficient. Rather, methods such as response theory will be more desirable because they accurately represent all states of the system in a computationally tractable manner. The combination of the QM/MM and response methodologies has already been applied to the problem of calculating nonlinear optical properties of solvated molecules,[29,59] although more clearly needs to be done certainly with respect to comparatively large molecules in a range of solvents. It will also be essential to computationally consider the vibronic profiles of the solvated solute, and preliminary work has likewise addressed this issue with respect to two-photon transitions.[60]

In conclusion, experimental and computational investigations of solvent effects on two-photon optical transitions are seen to provide a new dimension for the study of fundamental interactions between light and matter, and how such interactions can be perturbed at the molecular level. Moreover, the results of such studies will directly influence projects ranging from the two-photon-based creation of images to two-photon-initiated chemical reactions, both of which are especially pertinent for current efforts to study the behavior of singlet oxygen at the level of a single cell.[16,17,61]

Experimental Section

The instruments and equipment used are described in detail elsewhere.[8,44] Nevertheless, a short description of these tools is provided in the Supporting Information for this report.

Two molecules were used as standards to calibrate the excitation spectra recorded; Over the wavelength range 730−900 nm, **CNPhVB** in toluene was used, whereas 1,4-bis(2-methylstyryl)benzene (**MSB**) dissolved in cyclohexane was used over the wavelength range 610−750 nm. Key features of this approach have likewise been published,[44,49] and a short synopsis is included in the Supporting Information.

The approach used to correct for background signals that derive from the solvent has been published,[8,44] and the data pertinent for the present study are included in the Supporting Information.

The solubility of **CNPhVB**, **BrPhVB** and **OMePhVB** was good in both toluene and benzonitrile, somewhat modest in THF, and quite low in cyclohexane and acetonitrile. The concentrations of the solutions used in the two-photon experiments ranged from $\sim 2 \times 10^{-5}$ to 2×10^{-4} M. Data recorded from one-photon experiments over this concentration range (see section 1) indicate that solute aggregation does not occur.

Sensitizer Preparation. CNPhVB, BrPhVB and**OMePhVB** were all synthesized via Horner−Wadsworth−Emmons reactions. The synthesis of **CNPhVB** and **BrPhVB** has previously been published,[19,43,45] and the approach for the synthesis of **OMePhVB** is completely analogous. Data used to characterize **OMePhVB** are included in the Supporting Information.

Materials. Toluene (≥99.5%, A.C.S spectrophotometric grade), cyclohexane (≥99%, A.C.S spectrophotometric grade), benzonitrile (99.9%, HPLC grade), acetonitrile (≥99.5%, spectrophotometric grade) and THF (99.5+%, spectrophotometric grade, inhibitor free) were all purchased from Sigma-Aldrich and were used as received. **MSB** (≥99%, Fluka) was used as received without any further purification.

Experiments performed in THF can be problematic. We have found that results can depend significantly on the age of the THF used, and on whether or not a stabilizer is present in the solvent (i.e., commercial THF is sometimes supplied with a radical trap). Our experiments were performed with fresh THF that did not contain a stabilizer. We ascertained that solute degradation did not occur during the course of our measurements in THF, or any other solvent.

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Supporting Information Available: Instrumentation, experimental techniques, and control experiments; two-photon spectra of **CNPhVB**, **BrPhVB**, and **OMePhVB** in all solvents examined; characterization data for **OMePhVB**. This information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Kershaw, S. In *Characterization Techniques and Tabulations for Organic Nonlinear Optical Materials*; Kuzyk, M. G., Dirk, C. W., Eds.; Marcel Dekker, Inc.: New York, 1998;pp 515−654.

(2) McClain, W. M. *Acc. Chem. Res.* **1974**, *7*, 129–135.

(3) Bhawalkar, J. D.; He, G. S.; Prasad, P. N. *Rep. Prog. Phys.* **1996**, *59*, 1041–1070.

(4) Birge, R. R. In *Ultrasensitive Laser Spectroscopy*; Kliger, D. S., Ed.; Academic Press, Inc.: New York, 1983, pp 109−174.

(5) Albota, M.; Beljonne, D.; Brédas, 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.; Röckel, H.; Rumi, M.; Subramaniam, G.; Webb, W. W.; Wu, X.-L.; Xu, C. *Science* **1998**, *281*, 1653–1656.

(6) Reinhardt, B. A.; Brott, L. L.; Clarson, S. J.; Dillard, A. G.; Bhatt, J. C.; Kannan, R.; Yuan, L.; He, G. S.; Prasad, P. N. *Chem. Mater.* **1998**, *10*, 1863–1874.

(7) Strehmel, B.; Sarker, A. M.; Detert, H. *Chem. Phys. Chem.* **2003**, *4*, 249–259.

(8) Johnsen, M.; Paterson, M. J.; Arnbjerg, J.; Christiansen, O.; Nielsen, C. B.; Jørgensen, M.; Ogilby, P. R. *Phys. Chem. Chem. Phys.* **2008**, *10*, 1177–1191.

(9) Wang, C.-K.; Macak, P.; Luo, Y.; Ågren, H. *J. Chem. Phys.* **2001**, *114*, 9813–9820.

(10) Drobizhev, M.; Meng, F.; Rebane, A.; Stepanenko, Y.; Nickel, E.; Spangler, C. *J. Phys. Chem. B* **2006**, *110*, 9802–9814.

(11) Denk, W.; Strickler, J. H.; Webb, W. W. *Science* **1990**, *248*, 73–76.

(12) Kawata, S.; Sun, H.-B.; Tanaka, T.; Takada, K. *Nature* **2001**, *412*, 697–698.

(13) Frimer, A. A., Ed. *Singlet Oxygen*; CRC Press: Boca Raton, FL, 1985; Vols I−IV.

(14) Redmond, R. W.; Kochevar, I. E. *Photochem. Photobiol.* **2006**, *82*, 1178–1186.

(15) Snyder, J. W.; Zebger, I.; Gao, Z.; Poulsen, L.; Frederiksen, P. K.; Skovsen, E.; McIlroy, S. P.; Klinger, M.; Andersen, L. K.; Ogilby, P. R. *Acc. Chem. Res.* **2004**, *37*, 894–901.

(16) Skovsen, E.; Snyder, J. W.; Ogilby, P. R. *Photochem. Photobiol.* **2006**, *82*, 1187–1197.

(17) Hatz, S.; Lambert, J. D. C.; Ogilby, P. R. *Photochem. Photobiol. Sci.* **2007**, *6*, 1106–1116.

(18) Nielsen, C. B.; Johnsen, M.; Arnbjerg, J.; Pittelkow, M.; McIlroy, S. P.; Ogilby, P. R.; Jørgensen, M. *J. Org. Chem.* **2005**, *70*, 7065–7079.

(19) Frederiksen, P. K.; McIlroy, S. P.; Nielsen, C. B.; Nikolajsen, L.; Skovsen, E.; Jørgensen, M.; Mikkelsen, K. V.; Ogilby, P. R. *J. Am. Chem. Soc.* **2005**, *127*, 255–269.

(20) Schweitzer, C.; Schmidt, R. *Chem. Rev.* **2003**, *103*, 1685–1757.

(21) Flors, C.; Ogilby, P. R.; Luis, J. G.; Grillo, T. A.; Izquierdo, L. R.; Gentili, P.-L.; Bussotti, L.; Nonell, S. *Photochem. Photobiol.* **2006**, *82*, 95–103.

(22) McGarvey, D. J.; Szekeres, P. G.; Wilkinson, F. *Chem. Phys. Lett.* **1992**, *199*, 314–319.

(23) Kristiansen, M.; Scurlock, R. D.; Iu, K.-K.; Ogilby, P. R. *J. Phys. Chem.* **1991**, *95*, 5190–5197.

(24) Wilkinson, F.; Abdel-Shafi, A. A. *J. Phys. Chem. A* **1999**, *103*, 5425–5435.

(25) Ogilby, P. R. *Acc. Chem. Res.* **1999**, *32*, 512–519.

(26) Keszthelyi, T.; Weldon, D.; Andersen, T. N.; Poulsen, T. D.; Mikkelsen, K. V.; Ogilby, P. R. *Photochem. Photobiol.* **1999**, *70*, 531–539.

(27) Luo, Y.; Norman, P.; Macak, P.; Ågren, H. *J. Phys. Chem. A* **2000**, *104*, 4718–4722.

(28) Ray, P. C.; Leszczynski, J. *J. Phys. Chem. A* **2005**, *109*, 6689–6696.

(29) Paterson, M. J.; Kongsted, J.; Christiansen, O.; Mikkelsen, K. V.; Nielsen, C. B. *J. Chem. Phys.* **2006**, *125*, 184501.

(30) Song, Y.-Z.; Li, D.-M.; Song, X.-N.; Huang, X.-M.; Wang, C.-K. *J. Mol. Struct. (THEOCHEM)* **2006**, *772*, 75–79.

(31) Zhao, K.; Ferrighi, L.; Frediani, L.; Wang, C.-K.; Luo, Y. *J. Chem. Phys.* **2007**, *126*, 204509.

(32) Terenziani, F.; Painelli, A.; Katan, C.; Charlot, M.; Blanchard-Desce, M. *J. Am. Chem. Soc.* **2006**, *128*, 15742–15755.

(33) Kogej, T.; Beljonne, D.; Meyers, F.; Perry, J. W.; Marder, S. R.; Brédas, J. L. *Chem. Phys. Lett.* **1998**, *298*, 1–6.

(34) Wang, C.-K.; Zhao, K.; Su, Y.; Ren, Y.; Zhao, X.; Luo, Y. *J. Chem. Phys.* **2003**, *119*, 1208–1213.

(35) He, G. S.; Yuan, L.; Cheng, N.; Bhawalkar, J. D.; Prasad, P. N.; Brott, L. L.; Clarson, S. J.; Reinhardt, B. A. *J. Opt. Soc. Am., B.* **1997**, *14*, 1079–1087.

(36) Baur, J. W.; Alexander, M. D.; Banach, M.; Denny, L. R.; Reinhardt, B. A.; Vaia, R. A.; Fleitz, P. A.; Kirkpatrick, S. M. *Chem. Mater.* **1999**, *11*, 2899–2906.

(37) Swiatkiewicz, J.; Prasad, P. N.; Reinhardt, B. A. *Opt. Commun.* **1998**, *157*, 135–138.

(38) Xu, C.; Webb, W. W. *J. Opt. Soc. Am., B.* **1996**, *13*, 481–491.

(39) Woo, H.-Y.; Liu, B.; Kohler, B.; Korystov, D.; Mikhailovsky, A.; Bazan, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 14721–14729.

(40) Hayek, A.; Bolze, F.; Nicoud, J. F.; Baldeck, P. L.; Mely, Y. *Photochem. Photobiol. Sci.* **2006**, *5*, 102–106.

(41) Antonov, L.; Kamada, K.; Nedeltcheva, D.; Ohta, K.; Kamounah, F. S. *J. Photochem. Photobiol, A: Chem.* **2006**, *181*, 274–282.

(42) Shoute, L. C. T.; Helburn, R.; Kelley, A. M. *J. Phys. Chem. A* **2007**, *111*, 1251–1258.

(43) Frederiksen, P. K.; Jørgensen, M.; Ogilby, P. R. *J. Am. Chem. Soc.* **2001**, *123*, 1215–1221.

(44) Arnbjerg, J.; Johnsen, M.; Frederiksen, P. K.; Braslavsky, S. E.; Ogilby, P. R. *J. Phys. Chem. A* **2006**, *110*, 7375–7385.

(45) Pond, S. J. K.; Rumi, M.; Levin, M. D.; Parker, T. C.; Beljonne, D.; Day, M. W.; Brédas, J.-L.; Marder, S. R.; Perry, J. W. *J. Phys. Chem. A* **2002**, *106*, 11470–11480.

(46) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, 1988.

(47) Billing, G. D.; Mikkelsen, K. V. *Introduction to Molecular Dynamics and Chemical Kinetics*; Wiley: New York, 1996.

(48) Bhaskar, A.; Ramakrishna, G.; Lu, Z.; Twieg, R. J.; Hales, J. M.; Hagan, D. J.; van Stryland, E.; Goodson, T. *J. Am. Chem. Soc.* **2006**, *128*, 11840–11849.

(49) Arnbjerg, J.; Paterson, M. J.; Nielsen, C. B.; Jørgensen, M.; Christiansen, O.; Ogilby, P. R. *J. Phys. Chem. A* **2007**, *111*, 5756–5767.

(50) Bischel, W. K.; Kelly, P. J.; Rhodes, C. K. *Phys. Rev. A.* **1976**, *13*, 1817–1828.

(51) Poulsen, T. D.; Frederiksen, P. K.; Jørgensen, M.; Mikkelsen, K. V.; Ogilby, P. R. *J. Phys. Chem. A* **2001**, *105*, 11488–11495.

(52) Arnbjerg, J.; Jiménez-Banzo, A.; Paterson, M. J.; Nonell, S.; Borrell, J. I.; Christiansen, O.; Ogilby, P. R. *J. Am. Chem. Soc.* **2007**, *129*, 5188–5199.

(53) Zoueu, J. T.; Fiorini-Debuisschert, C.; Charra, F.; Nunzi, J.-M. *Chem. Phys. Lett.* **2006**, *419*, 454–457.

(54) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1963**, *38*, 1187–1203.

(55) Sheik-Bahae, M.; Said, A. A.; Wei, T.-H.; Hagan, D. J.; VanStryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760–769.

(56) Belfield, K. D.; Bondar, M. V.; Hernandez, F. E.; Przhonska, O. V.; Yao, S. *J. Phys. Chem. B* **2007**, *111*, 12723–12729.

(57) Drobizhev, M.; Karotki, A.; Kruk, M.; Rebane, A. *Chem. Phys. Lett.* **2002**, *355*, 175–182.

(58) Gao, J. *Acc. Chem. Res.* **1996**, *29*, 298–305.

(59) Poulsen, T. D.; Ogilby, P. R.; Mikkelsen, K. V. *J. Chem. Phys.* **2001**, *115*, 7843–7851.

(60) Macak, P.; Luo, Y.; Ågren, H. *Chem. Phys. Lett.* **2000**, *330*, 447–456.

(61) Snyder, J. W.; Skovsen, E.; Lambert, J. D. C.; Poulsen, L.; Ogilby, P. R. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4280–4293.

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