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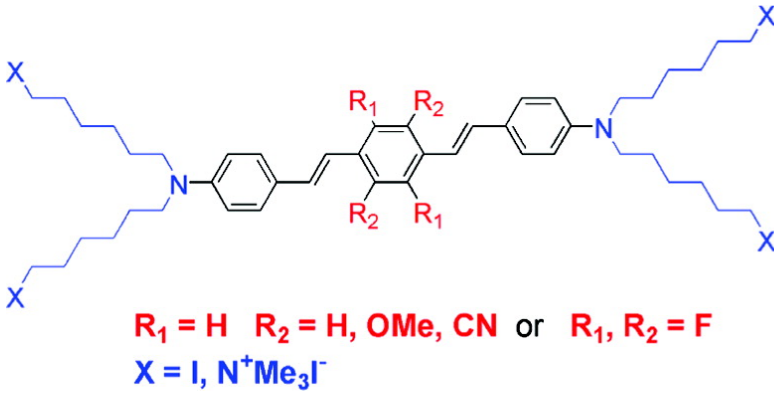

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Solvent Effects on the Two-Photon Absorption of Distyrylbenzene Chromophores

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Abstract: A series of organic- and water-soluble distyrylbenzene-based two-photon absorption (TPA) fluorophores containing dialkylamino donor groups at the termini was designed, synthesized, and characterized. The central core was systematically substituted to modulate intramolecular charge transfer (ICT). These molecules allow an examination of solvent effects on the TPA cross section (δ) and on the TPA action cross section. In toluene, the δ values follow the order of ICT strength. The effect of solvent on δ is nonmonotonic: maximum δ was measured in an intermediate polarity solvent (THF) and was lowest in water. We failed to find a correlation between the observed solvent effect and previous theoretical predictions. Hydrogen bonding to the donor groups and aggregation of the optical units in water, which are not included in calculational analysis, may be responsible for the discrepancies between experimental results and theory.

Introduction

Emerging technologies such as memory storage, photodynamic therapy, microfabrication techniques, and multiphoton microscopy, have stimulated substantial research activity on organic molecules that can simultaneously absorb two (or more) photons.[1−6] Structure−property relationships have emerged for the molecular design of efficient two-photon absorption (TPA) chromophores. The role of several factors, including the properties of the π-conjugated segment, the strength of donor and/or acceptor substituents, molecular symmetry, and the molecular dimensionality, have been examined.[7−9] In one particularly successful strategy, molecules containing quasilinear $D-\pi-D$ or $D-\pi-A-\pi-D$ structures, where D and A are donor or acceptor groups, respectively, and π represents a π-conjugated bridge, have shown exceptional performance. Their TPA cross sections (δ, expressed in $\mathrm{GM} = 1 \times 10^{-50}$ $\mathrm{cm}^4 \cdot \mathrm{s} \cdot \mathrm{photon}^{-1} \cdot \mathrm{molecule}^{-1}$), which reflect the probability of absorption, have been reported to be greater than 1000 GM. The magnitudes of δ depend on the degree of intramolecular charge transfer (ICT) upon excitation.[10,11]

In contrast to the extensive investigation of molecular design strategies[11] and the successful application of the resulting chromophores,[1−6] the effect of the surrounding medium and specifically the role of solvent on TPA has not been fully

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elucidated.[12-14] Since solvent polarity influences the magnitude of ICT, it is expected to change δ in D$-\pi-$D and D$-\pi-$A$-\pi-$D chromophores.

Understanding how aqueous media influence the linear spectroscopy and TPA[15-17] of π-conjugated systems is of importance for fully optimizing fluorescent tags used in two-photon fluorescence microscopy (TPM)[18] of biological samples, such as living cells.[19] For optimum TPM signal-to-noise and photostability, the two-photon action cross section, defined as $\eta\delta$ (where η is the fluorescence quantum yield), should be maximized. The majority of fluorophores currently used are those previously developed for one-photon excitation methods and display $\eta\delta$ values in the range of 1$-$50 GM.[16,20] We note that water not only has a high dielectric constant, which influences the ICT, but is capable of very effective hydrogen bonding and can therefore interact with the donor groups in the ground and the excited states. Perturbations on the optical properties of π-conjugated systems by water are poorly understood, relative to organic solvents, in part because there have been fewer molecular candidates available for study. Recent interest in using water-soluble conjugated polymers for the optical amplification of fluorescent biosensors has improved the synthetic methodologies for accessing these materials.[21,22]

Although extensive work (theoretical and experimental) has been devoted to understand the solvent dependence of linear spectroscopy,[23] theoretical efforts to address solvent effects on the TPA of conjugated molecules have been limited. Kogej et al. studied donor$-$acceptor stilbene derivatives using quantum-chemical calculations at the semiempirical level.[12] The TPA evolution was evaluated as a function of the degree of ground-state polarization by imposing an external field, directed to favor stabilization of charge transfer from the donor to the acceptor. In this work, the TPA peak ($\delta_{\max}$) and the difference ($\Delta\mu_{\mathrm{ge}}$) in dipole moments between the ground state (S_0) and the lowest singlet excited state (S_1) were observed at an intermediate value of bond order alternation (BOA)[24] between the neutral structure and the cyanine limit. The BOA can be considered to be related to the degree of ground-state polarization in media of different polarity. According to this work, it is necessary to optimize the combination between donor$-$acceptor strength, solvent polarity, and π-conjugation linker to maximize δ for a given structure.

The solvent effect on the TPA of the push$-$pull polyene structure $NO_2(C_2H_2)_2NH_2$ was studied.[13a] In this set of calculations, δ displayed a strong dependence on the geometrical changes that take place as a function of the polarity of the medium. The calculated δ showed an initial pseudolinear dependence on solvent polarity, with higher values in more polar solvents, ultimately reaching saturation at the highest dielectric constants.

Solvent effects on the conformational changes of a pyridinium *N*-phenolate betaine dye and the resulting impact on δ were calculated using the semiempirical GRINDOL method.[13b] The TPA cross section in the gas phase is enhanced several times at an interplanar angle (between the pyridinium and the phenolate rings) close to 80°, as compared to the planar structure. Moreover, the δ values in water were found to be lower than in the gas phase, and the dependence on the interplanar angle was less pronounced. A decrease of oscillator strength and an increase of the transition energy to the charge transfer state were given as the cause for the decrease of δ in water.

Another theoretical approach to study the solvent effects on molecular geometry, electronic structures, and the TPA of 4-*trans*-[*p*-(*N*,*N*-dibutylamino)-*p*-stilbenylvinyl]pyridine was published.[14] A typical D$-\pi-$A molecular structure was used in these calculations. The δ calculated from a two-state model and the solvatochromism of the ICT state were found to be solvent-dependent. A nonmonotonic behavior of δ with respect to the polarity of the solvents was observed. The δ value increases with respect to the solvent polarity and reaches a maximum at $\epsilon = 20.7$. It is noted that the maximum δ is approximately 2 times larger than in the gas phase and 1.3 times of the value in the nonpolar solvent of cyclohexane. It was suggested that the presence of solvent results in an increase of the charge separation in both ground and ICT excited states and that the electronic structure change by the solvent is the main reason behind the δ increase.

As shown by the different expectations in the above calculations, there is no general agreement. Moreover, there are few experimental data available to guide theoretical analysis of solvent effects.[15,25] One exception concerns a study on the molecular environment effects on TPA behavior of fluorene-based heterocyclic chromophores using a nonlinear absorption

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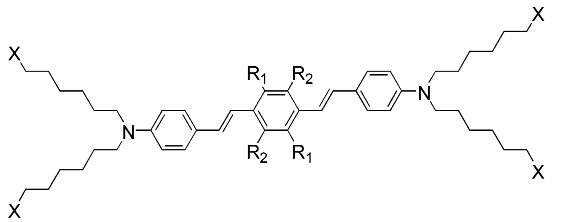
Scheme 1. Molecular Structures of Neutral and Ionic Distyrylbenzene Chromophores



$\mathbf{R_1 = H \quad R_2 = H, OMe, CN}$ or $\mathbf{R_1 = R_2 = F}$

$\mathbf{X = I, N^+Me_3I^-}$

method.[25c,26] In this work, the measured effective TPA cross section depends on the solvent used. The solvent dependence of the effective TPA cross section proved to be associated with absorption by a solvent sensitive excited state.

In this contribution, we provide a synthetic entry into distyrylbenzene chromophores of general D−π−A−π−D structures, which are soluble across a range of solvents (Scheme 1). Different substituents were chosen to allow the molecules to be neutral, and soluble in nonpolar organic solvents, or charged, and water-soluble. The internal ring was systematically substituted to modulate the electronic property of the core and the overall ICT from the terminal donor groups. TPA spectra for both the neutral and ionic chromophores in a range of solvents are also presented and compared. The overall set of compounds allows the examination of the solvent influence on δ and the effect of ICT on $\eta\delta$.

Results and Discussion

Synthesis and Characterization. Scheme 2 provides the synthetic entry into the molecules in Scheme 1. Using a modified literature method, the reaction of aniline with 6-chlorohexanol in *n*-butanol provides **1** in 60% yield.[27] Further treatment of **1** with phosphorus oxychloride in DMF introduces the aldehyde group and affords *N*,*N*-bis(6′-chlorohexyl)-4-aminobenzaldehyde (**2**) in 75% yield. With the motivation of activating halogen/amine substitution, chloride/iodide exchange is accomplished via a Finkelstein-type reaction to afford *N*,*N*-bis(6′-iodohexyl)-4-aminobenzaldehyde (**3**) in 80% yield. In the ^{1}H NMR spectra, the peak at ~3.55 ppm from the methylene adjacent to chloride disappeared and a new peak appeared at approximately 3.2 ppm originating from the methylene adjacent to iodide. The core phosphonates **4**−**7** are known in the literature[28−31] and were prepared by treatment of the corresponding bromomethyl compounds with excess triethyl phosphite in DMF.

Coupling 2 equiv of aldehyde **3** with phosphonates **4**−**7** under Horner−Emmons−Wittig coupling conditions using sodium hydride or potassium *tert*-butoxide in THF at room temperature affords the precursor neutral chromophores **8N**−**11N** in 35−67% yields. Potassium *tert*-butoxide must be used for the synthesis of **10N**. The water-soluble chromophores **8C**−**11C** are obtained by treatment of **8N**−**11N** with condensed trimethylamine in a THF/water mixture for 24 h. After addition of trimethylamine, a precipitate gradually forms as the reaction proceeds, consistent with the formation of ionic groups via quaternization. To ensure that the reaction proceeds to completion, it is recommended that the precipitate be dissolved by adding water and an excess of trimethylamine. Removal of unreacted trimethylamine does not impose a problem, because of its low boiling point.

Both the neutral precursors and the water-soluble chromophores were characterized by mass spectrometry, elemental analysis, and NMR spectroscopy. The conjugated framework exhibits characteristic ^{1}H NMR spectroscopy patterns: two doublets for the outer phenyl rings, two doublets of half the intensity for the vinyl protons, and a singlet (where appropriate) for the central phenyl ring. The trans stereochemistry of the olefin linkages was established by the coupling constant of the vinylic protons in the ^{1}H NMR spectra ($J = \sim 16$ Hz). After quaternization, the signal characteristic for the $-CH_2I$ protons (~3.2 ppm in $CDCl_3$ for **8N**, **10N**, and **11N**; 2.7 ppm for **9N** in C_6D_6) disappeared, while new peaks appeared at ~3.3 ppm ($-CH_2N^+(CH_3)_3I^-$) and ~3.05 ppm ($-CH_2N^+(CH_3)_3I^-$) for the water-soluble chromophores, indicative of >99% quaternization. Further evidence of the identity of **8C**−**11C** was obtained by electrospray ionization mass spectrometry (ESI-MS). Peaks corresponding to the correct molecular mass were detected, and the elemental results are in agreement with the proposed structures.

Linear Absorption and Photoluminescence Spectroscopy. Table 1 summarizes the linear absorption and photoluminescence (PL) spectra for **8**−**10** in different solvents.

Absorption spectra of toluene solutions containing **11** showed degradation under ambient illumination. For example, the absorption maximum decreased by approximately 20% after solutions were left standing on a lab bench for 30 min (Supporting Information). This instability prevented us from making careful measurements of photoluminescence quantum yields and TPA. In nonpolar solvents such as toluene, the neutral chromophores **8N**−**10N** display maxima and peak shapes (Figure 1) that are typical for this type of molecule.[7a,32] The absorption maxima range from 409 nm for **8N** to 485 nm for the cyano-substituted **10N**, while the corresponding emission changes from 449 nm for **8N** to 526 nm for **10N**. Introduction of methoxy groups into the central core produces a red-shift of 18 nm in the absorption and 26 nm in the emission, relative to **8N**. For each chromophore, the PL spectra show a progressive red-shift and a loss of vibronic structure, together with a decrease in η, as the solvent polarity increases, consistent with the strong ICT character of the solvent relaxed emissive state (Table 1).[33,34]

The PL of **10N** is the most sensitive to solvent effects, with the λ_{em} shifting from 526 nm in toluene to 636 nm in DMSO

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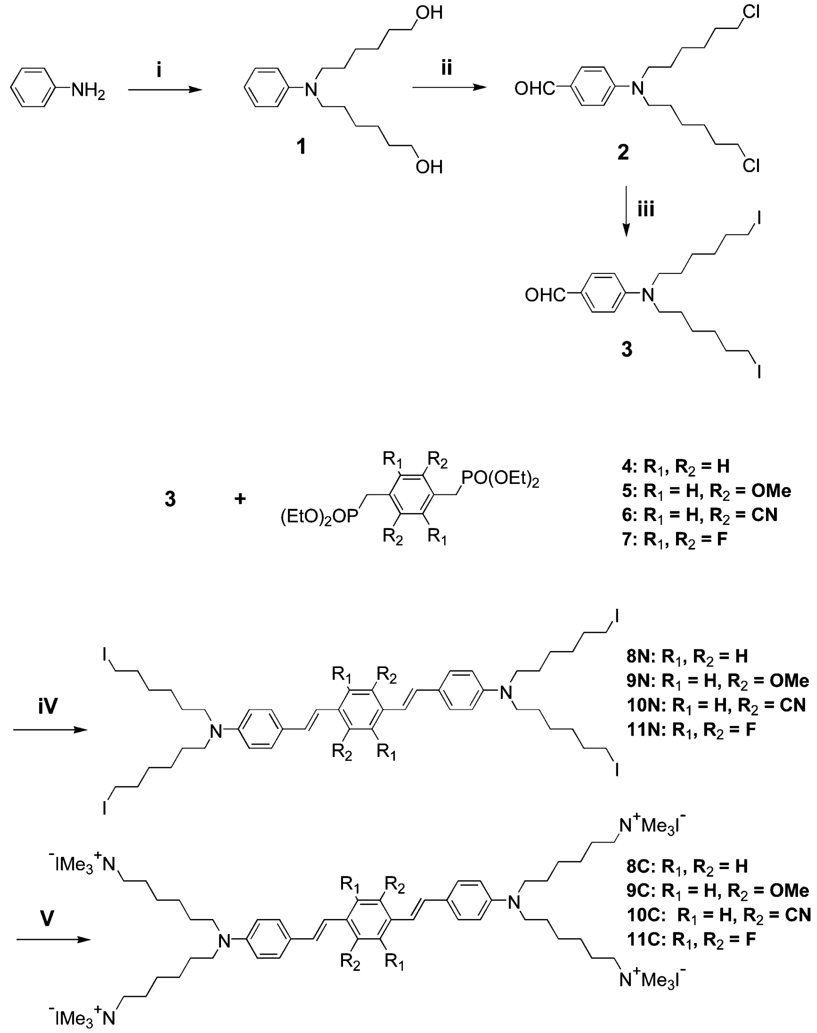
Scheme 2. Synthetic Procedure for Accessing Neutral and Water-Soluble TPA Chromophores[a]



[a] Reagents and conditions: (i) 6-chloro-1-hexanol/*n*-butanol, K_2CO_3, reflux, 4 days; (ii) $POCl_3$/DMF, 100 °C, 2 h; (iii) NaI/dry acetone, reflux, 2 days; (iv) NaH (or t-BuOK) in dry THF, room temperature; (v) NMe_3, THF/H_2O, room temperature, 24 h.

Table 1. Summary of Absorption and Photoluminescence Spectroscopies in Different Solvents

	toluene		THF		DMSO		water	
	λ_{abs} (ϵ_{max})[a]	λ_{em} (η)[b]	λ_{abs} (ϵ_{max})	λ_{em} (η)	λ_{abs} (ϵ_{max})	λ_{em} (η)	λ_{abs} (ϵ_{max})	λ_{em} (η)
8N	409 (7.5)	449 (0.93)	409 (8.6)	461 (0.77)	418 (7.8)	506 (0.63)		
8C					418 (6.2)	506 (0.59)	406 (3.9)	558 (0.27)
9N	427 (6.5)	475 (0.92)	428 (6.5)	479 (0.92)	439 (6.3)	515 (0.52)		
9C					439 (5.3)	515 (0.55)	423 (4.9)	567 (0.40)
10N	485 (6.5)	526 (0.58)	483 (7.0)	559 (0.63)	497 (6.5)	636 (0.19)		
10C					495 (4.9)	635 (0.22)	469 (3.8)	–

[a] Molar absorption coefficient at λ_{abs} (10^4•mol^{-1}•cm^{-1}). [b] Quantum yields were measured relative to 9,10-diphenylanthracene in cyclohexane and fluorescein in water at pH ≈11.

(Table 1 and Figure 2). In these D−π−A−π−D systems, the cyano functionality is the stronger acceptor group, gives rise to more pronounced ICT in the excited state, and produces larger changes by solvent stabilization.

The absorption and emission spectra of **8C**−**10C** in water are shown in Figure 3. Perturbations by the central ring acceptor functionalities are similar to those observed for the **N** series. The λ_{abs} values in water are slightly blue-shifted, relative to those in toluene, in structurally related pairs [(in nm) **8N**/**8C**, 409/406; **9N**/**9C**, 427/ 423; **10N**/**10C**, 485/469]. This blue-shift may be attributed to a modified geometry with partially restricted delocalization due to the hydrophobic nature of the conjugated backbone. It is also possible that water can perturb the donor strength of the nitrogen atom via hydrogen bonding and ultimately the ICT process.[33a,35] The PL spectra are broad and

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(34) Absorption maxima are less sensitive to solvent polarity (Table 1). The ICT excited state is polar, with a large dipole moment due to a substantial charge redistribution, and is expected to be sensitive to solvent polarity. Direct transition from the ground state to the ICT state may be forbidden. The less sensitive absorption maxima to the solvent polarity suggest that the ICT state is derived following relaxation of the initially formed Franck−Condon excited state (ref 32a). See: (a) Leinhos, U.; Kühnle, W.; Zachariasse, K. A. *J. Phys. Chem.* **1991**, *95*, 2013. (b) Strehmel, B.; Sarker, A. M.; Malpert, J. H.; Strehmel, V.; Seifert, H.; Neckers, D. C. *J. Am. Chem. Soc.* **1999**, *121*, 1226.

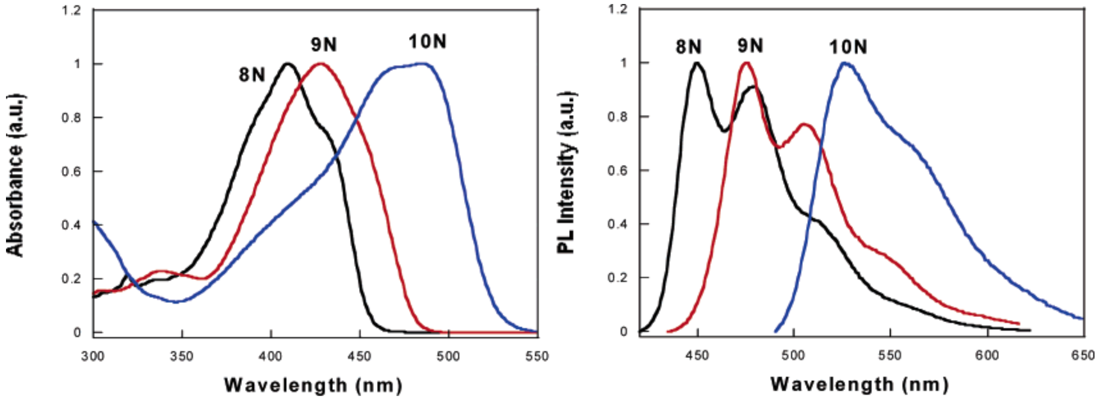

Figure 1. Normalized absorption and emission spectra of **8N**−**10N** in toluene. Emission scans were collected by exciting at the absorption maximum (λ_{abs}) of each sample.

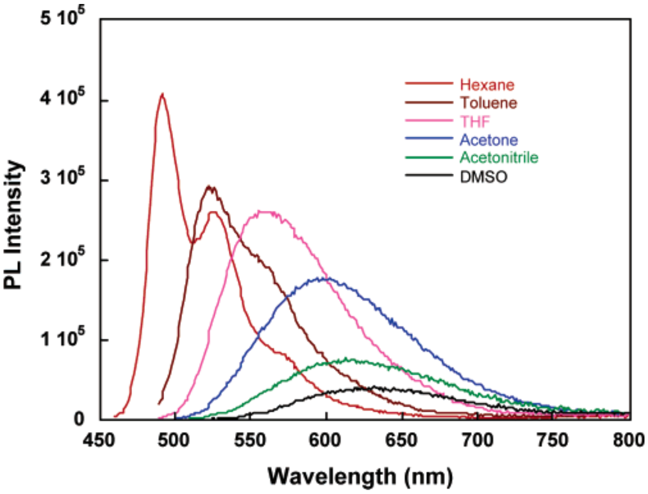

Figure 2. PL spectra of **10N** in different solvents. The areas under the spectra are proportional to the η in each solvent.

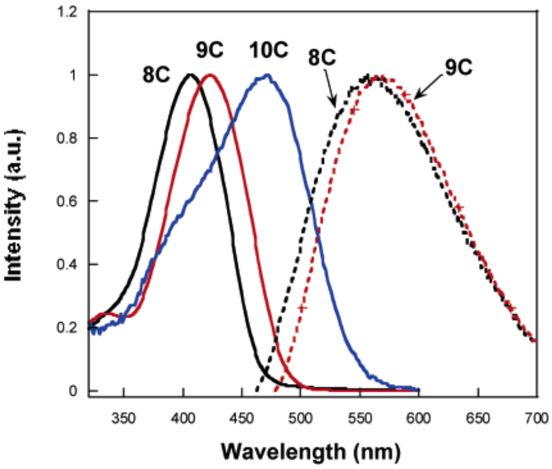

Figure 3. Normalized absorption and PL spectra of **8C**−**10C** in water. Emission scans were collected by exciting at the λ_{abs} of each sample. Compound **10C** has no detectable emission in water.

featureless and are further red-shifted from the absorption spectra in the charged compounds ($\Delta\nu_{abs-em} = 6709$ cm^{-1} for **8C**, 6004 cm^{-1} for **9C**), compared to their neutral counterparts in toluene ($\Delta\nu_{abs-em} = 2178$ cm^{-1} for **8N**, 2367 cm^{-1} for **9N**). Compounds **8N** and **8C** have η values of 0.93 and 0.27 in toluene and water, respectively. With the cyano-substituted pair (**10N**/**10C**), one observes a more dramatic change. For compound **10N** in toluene, $\eta = 0.58$, but **10C** shows no detectable emission in water with our instrumentation.[36] We also note that in a solvent of intermediate polarity (DMSO), there are no measurable differences in the linear spectroscopy for structurally related neutral (**N**) and charged (**C**) pairs. The charged end groups do not appear to be interacting with the electronic structure of the chromophores and do not modify spectral properties (Supporting Information).

Acceptor group strengths were probed through a study of the oxidation potential of the chromophores using cyclic voltammetry (CV). The measured electrochemical $E_{M^+/M}$ are 240 mV for **8N**, 140 mV for **9N**, and 410 mV for **10N**, relative to a Ag/AgNO$_3$ reference (Figure 4). CV measurements were carried out in 0.1 M n-Bu$_4$NPF$_6$ solution in THF at a scan rate of 100 mV/s. Coupling this information to the data in Table 1, we note that η in water (0.27 for **8C**, 0.40 for **9C** and no emission for **10C**) is inversely proportional to the strength of the acceptor group (**10C** > **8C** > **9C**).

In Figure 5, the absorption and emission spectra of **8C** in water are given as a function of HCl concentration. Table 2 contains a summary of similar experiments for **9C** and **10C**. With increasing [HCl], the nitrogen atoms at the termini of the chromophore are protonated and three different species are expected: unprotonated, monoprotonated, and doubly protonated. The absorption spectra of solutions of **8C** with HCl at intermediate levels of [HCl] were deconvoluted using a general equilibrium analysis technique,[20] and the absorption from the monoprotonated species was observed to have $\lambda_{abs} = 370$ nm (Supporting Information). The PL spectra, however, contain contributions from only the neutral and the doubly protonated species. Indeed, the effective η of the solution decreases first

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(35) Halpern, A. M.; Ruggles, C. J.; Zhang, X. *J. Am. Chem. Soc.* **1987**, *109*, 3748.

(36) The ICT often produces PL quenching by charge separation after excitation, increasing the rates of the radiationless decay processes. Several mechanisms for the ICT-related quenching were suggested. See: (a) Schuddeboom, W.; Jonker, S. A.; Warman, J. M.; Leinhos, U.; Kühnle, W.; Zachariasse, K. A. *J. Phys. Chem.* **1992**, *96*, 10809. (b) Jager, W. F.; Volkers, A. A.; Neckers, D. C. *Macromolecules* **1995**, *28*, 8153. (c) Lipinski, J.; Chojnacki, H.; Grabowski, Z. R.; Rotkiewicz, K. *Chem. Phys. Lett.* **1980**, *70*, 449. (d) Catalán, J.; Díaz, C.; López, V.; Pérez, P.; Claramunt, R. M. *J. Phys. Chem.* **1996**, *100*, 18392. (e) Baumann, W.; Bischof, H.; Fröhling, J.-C.; Brittinger, C.; Rettig, W.; Rotkiewicz, K. *J. Photochem. Photobiol. A*: *Chem.* **1992**, *63*, 49. In addition, PL quenching by specific solute−solvent interaction such as hydrogen bonding should be considered in water. The excited-state complex via hydrogen bonding may activate radiationless depopulation channels, for example, energy dissipation through the vibrations connected with hydrogen bonding. See: (f) Herbich, J.; Waluk, J. *Chem. Phys.* **1994**, *188*, 247. (g) Kumar, C. V.; Tolosa, L. M. *J. Photochem. Photobiol. A*: *Chem.* **1994**, *78*, 63.

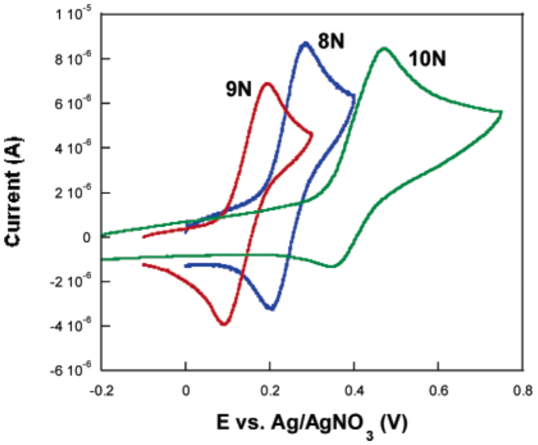

Figure 4. Cyclic voltammograms of **8N**−**10N** (1 mg/mL concentration) relative to Ag/AgNO$_3$ in 0.1 M n-Bu$_4$NPF$_6$ in THF at a scan rate of 100 mV/s.

and subsequently increases with increasing [HCl], suggesting that the monoprotonated species has a very low η or is nonfluorescent. When [HCl] = 10^{-2} M, conditions where only the doubly protonated species of each chromophore is expected to be present (i.e. **8CH$_2$$^+$**, **9CH$_2$$^+$**, and **10CH$_2$$^+$**), one observes blue-shifted λ_{abs} and λ_{em} values (Table 2) and an increase in η. Analogous spectral shifts were made with metal ion sensing two-photon fluorophores.[20]

Comparison of the data in Tables 1 and 2 shows that there is a difference in the order of the absorption and emission maxima for the doubly protonated chromophores, relative to the unprotonated counterparts. In the doubly protonated species, the internal ring becomes the electron rich fragment, and we expect a net charge transfer to the outer aromatic fragments bearing the ammonium groups. The donating ability of the groups is MeO > H > CN, which corresponds to the order in λ_{abs}. Furthermore, **10C** is not fluorescent in water, but strong emission from **10CH$_2$$^{2+}$** is observed. Overall, linear optical properties, such as λ_{abs}, λ_{em}, and η, are strongly perturbed by protonation on the terminal nitrogen atoms, which may be considered an extreme case of hydrogen bonding in water. As will be discussed later, hydrogen bonding can also be expected to modify overall ICT, leading to a change of TPA.

Two-Photon Absorption Spectroscopy. TPA spectra were obtained by using the two-photon induced fluorescence (TPIF) measurement technique with femtosecond laser pulses, as described previously in the literature.[7a,18a] Complete details can be found in the Supporting Information. The TPA spectra of **8N**−**10N** in toluene are presented in Figure 6 and are summarized in Table 3. The TPA maximum wavelength (λ_{TPA}) and the peak δ for **8N** in toluene (720 nm and 910 GM, respectively) are similar to those previously reported for 1,4-bis(4′-(*N*,*N*-dibutylamino)styryl)benzene (730 nm and 995 GM),[7a] which indicates negligible influence by the terminal iodide groups. The TPA spectra of **9N** and **10N** are also in good agreement with previous measurements of the corresponding structures bearing dibutylamino substituents.[7a,32]

It is interesting to note the effect of the core substituents (**8N**, −H; **9N**, −OMe; **10N**, −CN) on λ_{TPA} and δ. In toluene, the maximum δ observed are 910 GM at 720 nm for **8N**, 890 GM at 725 nm for **9N**, and 1710 GM at 815 nm for **10N**. The trend in λ_{TPA} values (toluene) is similar to that observed for λ_{abs} [(in nm) 409 and 720 for **7N**, 427 and 725 for **8N**, 485 and 815 for **9N**] and depends on the effective conjugation and the ICT over the entire molecule.[10,11] Increasing the acceptor strength of the core results in an enhanced ICT from dialkylamino donor units to the core, giving **10N** the largest δ. The δ value of **9N** is lowest due to methoxy being the poorest acceptor.

Figure 7 shows the TPA spectra of **8N** and **8C** in different solvents. The spectra display similar band shape and λ_{TPA} and variations in δ [(in GM) 910 in toluene, 1540 in THF, 1200 in acetone; ~900 GM in DMSO, and 330 GM in water]. Plotting δ vs dielectric constant shows a nonmonotonic dependence (Figure 8). We note here that a similar trend was obtained for [2.2]paracyclophene-based TPA chromophores.[15,37]

Figure 9 shows that, in water, the TPA of **8C** and **9C** show similar λ_{TPA} and band structure, relative to the measurements of the neutral counterparts in organic solvents. However, the δ values are considerably lower (Table 3). The δ of **10C** could not be determined with our technique because **10C** is not fluorescent in water. We also note that in a solvent of intermediate polarity (DMSO), the TPA spectra of the **N** and **C** series are similar. The charged or neutral terminal groups therefore are not a major consideration.

Our measurements are best accommodated by the theoretical calculations by Wang et al.,[14] where a maximum δ was anticipated in a solvent of intermediate polarity. The enhancement of δ was explained in terms of increased charge separation assisted by solvent, and they suggested that the resulting change in electronic structure provides the main perturbation on δ. However, there are still substantial deviations between the measured quantities and these calculations, which suggest that other factors need to be considered, such as solute−solvent interactions and solubility differences. Low solubility and hydrophobic interactions can lead to aggregation or structure changes (for example, by distortion), with a corresponding modification of linear and nonlinear optical responses.[38,39] Fluorescence and near-field scanning optical microscopy (NSOM) studies of conjugated polymer aggregates show different solvatochromism, relative to amorphous polymer regions.[40] Additionally, strong enhancement (30-fold) of δ from a J aggregate of a porphyrin-type molecule in water was also observed.[17] Evidence for structural changes and aggregation in the molecular systems described in this paper can be obtained from a comparison of the linear absorption spectra of the **N** series in toluene with those of the **C** series in water, which are broad, lack vibronic structure, and have blue-shifted λ_{abs} values that are concentration-dependent (Supporting Information).

Water can also influence the electronic structure of D−π−A−π−D chromophores via hydrogen bonding and a corre-

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(37) We observed a similar trend on the solvent dependence of the measured TPA cross section of the structure that contains two fragments of **8** held together via the [2.2]paracyclophane core: 1290 GM in toluene, 2180 GM in THF, 1300 GM in DMSO, and 370 GM in water. For the synthesis of these compounds see: (a) Bartholomew, G. P.; Rumi, M.; Pond, S. J. K.; Perry J. W.; Tretiak, S.; Bazan, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 11529. (b) Bartholomew, G. P.; Bazan, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 5183.

(38) (a) Siddiqui, S.; Spano, F. C. *Chem. Phys. Lett.* **1999**, *308*, 99. (b) Song, Q.; Evans, C. E.; Bohn, P. W. *J. Phys. Chem.* **1993**, *97*, 13736. (c) Evans, C. E.; Song, Q.; Bohn, P. W. *J. Phys. Chem.* **1993**, *97*, 12302. (d) Manas, E. S.; Spano, F. C. *J. Chem. Phys.* **1998**, *109*, 8087.

(39) The absorption of **8N** in toluene is invariant in the 10^{-6}−10^{-4} M range. For **8C** in water, one observes a blue-shift in λ_{abs} with increasing [**8C**], which indicates different levels of aggregation (See Supporting Information).

(40) (a) Nguyen, T.-Q.; Martel, R.; Avouris, P.; Bushey, M. L.; Brus, L.; Nuckolls, C. *J. Am. Chem. Soc.* **2004**, *126*, 5234. (b) Nguyen, T.-Q.; Schwartz, B. J.; Schaller, R. D.; Johnson, J. C.; Lee, L. F.; Haber, L. H.; Saykally, R. J. *J. Phys. Chem. B* **2001**, *105*, 5153.

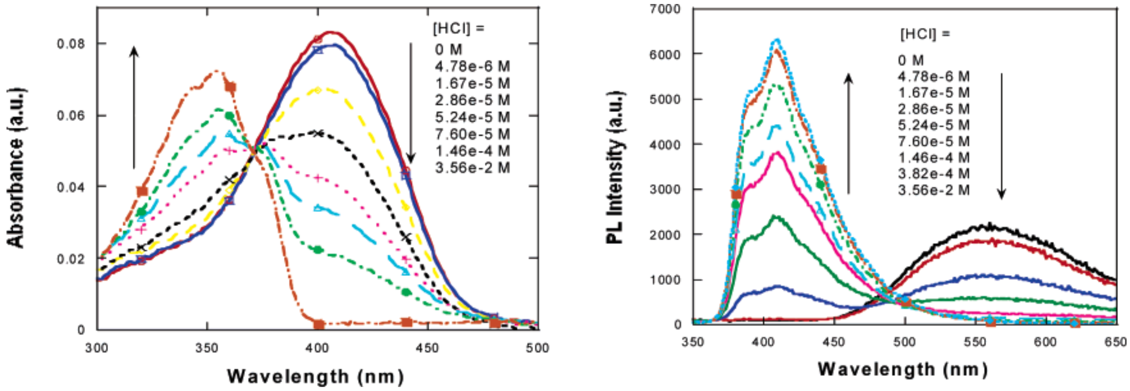

Figure 5. Absorption and emission spectra of **8C** ([**8C**] = 2 × 10^{-6} M) as a function of HCl concentration in water. The areas under the spectra are proportional to η.

Table 2. Summary of Absorption and Photoluminescence Spectra at [HCl] = 10^{-2} M and [**8C**−**10C**] = 10^{-6} M

	λ_{abs} (nm)	λ_{em} (nm)	η
$8CH_2^{2+}$	355	406	0.36
$9CH_2^{2+}$	379	461	0.57
$10CH_2^{2+}$	346	420	0.45

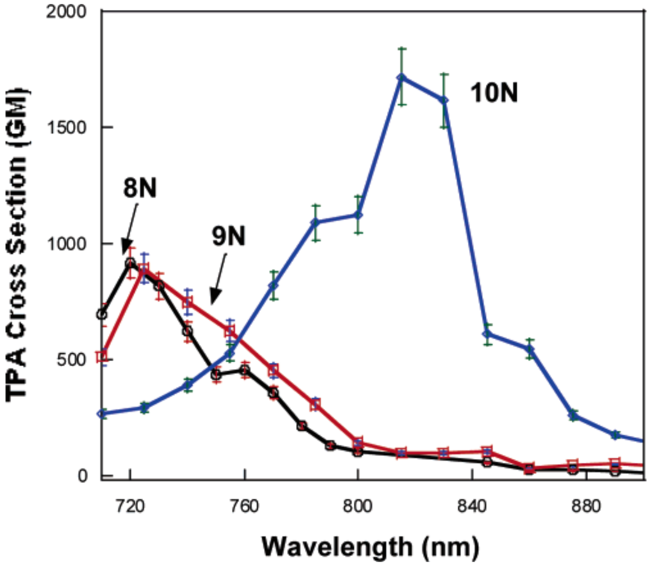

Figure 6. Two-photon absorption spectra of **8N**−**10N** in toluene.

Table 3. Summary of TPA Spectroscopy

	solvent	λ_{abs} (nm)	λ_{TPA}[a] (nm)	δ_{max} (GM)[b]	$\eta\delta$ (GM)[c]
8N	toluene	409	720	910	846
8C	water	406	720	330	89
9N	toluene	427	725	890	819
9C	water	423	730	360	144
10N	toluene	485	815	1710	992
10C	water	469			

[a] Wavelength of two-photon absorption maximum. [b] TPA cross section at λ_{TPA}. [c] Two-photon absorption action cross section.

sponding decrease of the ICT. Complexation via hydrogen bonding between an electronically excited amine and water is well-known and has been mentioned previously.[33a,35] The exact mechanism for the substantial drop of δ in water is, however, not clear at present stage and awaits detailed theoretical treatments that consider a comprehensive set of variables involved in the experimental measurements.

Despite the medium effect uncertainties, it is valuable to mention molecular design guidelines for the efficient TPM fluorophores for biological systems. The combined $\eta\delta$ values are 89 GM for **8C** and 144 GM for **9C**, respectively. However, the molecular framework of **10C**, which has the highest δ in toluene, is not a useful structure to consider for TPM applica-

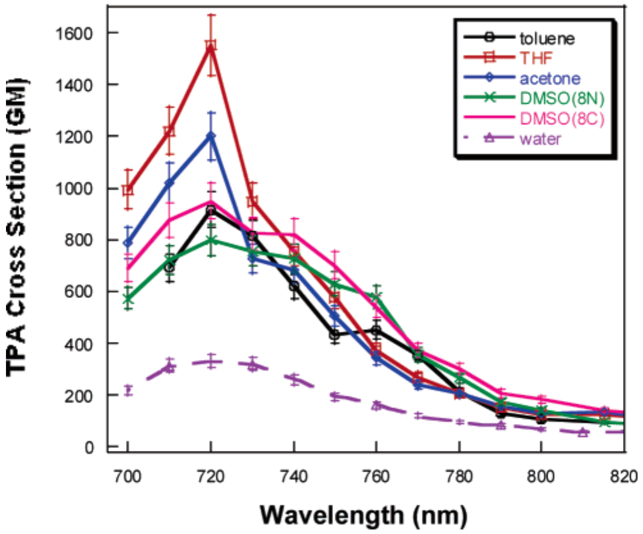

Figure 7. Solvent dependence of the measured TPA spectra of **8** (**8N** in toluene, THF, acetone, and DMSO and **8C** in DMSO and water).

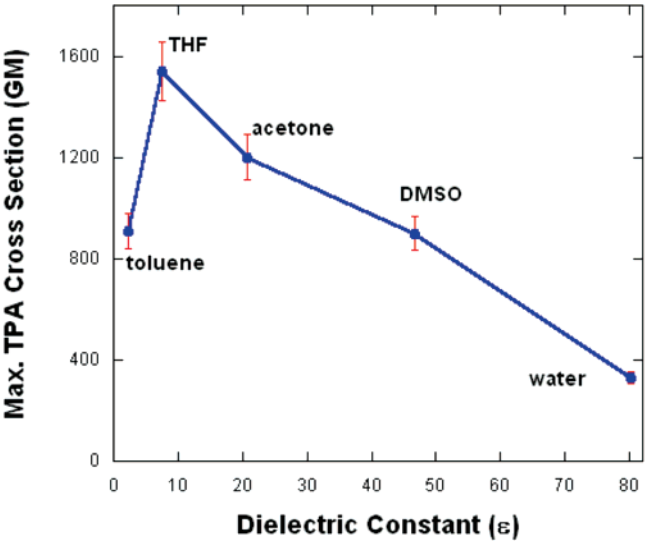

Figure 8. Maximum TPA cross section of **8** vs solvent polarity (**8N** in toluene, THF, acetone, and DMSO and **8C** in DMSO and water).

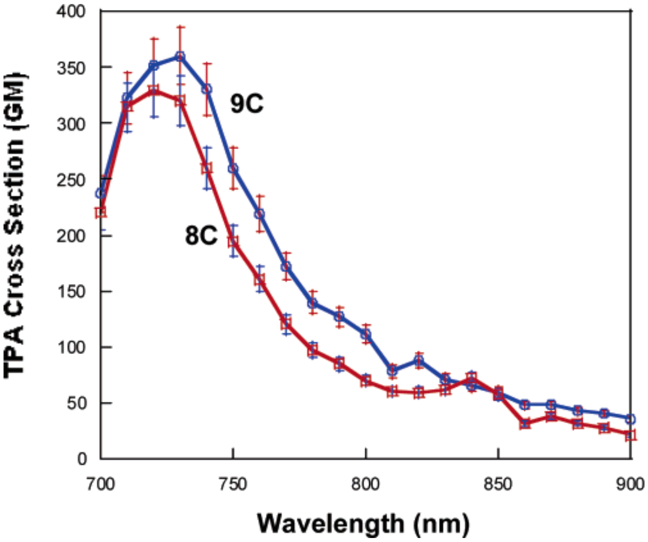

Figure 9. Two-photon absorption spectra of **8C** and **9C** in water.

tions in water, because of its negligible η. As previously demonstrated with [2.2]paracyclophane TPA chromophores,[15] acceptors and/or donors of intermediate strength are more likely to lead to enhanced $\eta\delta$.

Conclusion

In summary, we provide a synthetic entry to a series of organic-soluble and water-soluble TPA chromophores based on the distyrylbenzene framework. Introduction of alkyl halide terminal units in neutral precursors and subsequent quaternization using trimethylamine affords water-soluble TPM fluorophores. The neutral and charged molecules allowed us to measure the effect of the solvent polarity on δ as a function of acceptor strength. We observed a maximum δ in THF, which is of intermediate polarity. In water, δ shows a substantial decrease. The solvent dependence of TPA in the D$-\pi-$A$-\pi-$D distyrylbenzene structure is nonmonotonic when plotted against the solvent dielectric constant, and we failed to find an exact match against previous theoretical expectations. Closest agreement was with the predictions by Wang.[14] We suggest that future theoretical work should consider specific solute−solvent interactions, such as hydrogen bonding, which can substantially modify the ICT states. The effect of protonation, an extreme case of hydrogen bonding, on absorption and photoluminescence spectra highlights chemical effects. Additionally, changes in the chromophore geometry and/or multichromophore aggregation are likely of importance. Finally, we note that to obtain optimum two-photon action cross sections in water, the ICT strength must be moderated to retain high quantum efficiencies.

Experimental Section

General Details. Chemicals were purchased from Aldrich Co., except 2,5-dimethylterephthalonitrile, which was purchased from TCI America and were used without further purification. ^{1}H- and ^{13}C NMR spectra were collected on a Varian Unity 400 MHz (or 200 MHz) spectrometer. The UV−vis absorption spectra were recorded on a Shimadzu UV-2401 PC diode-array spectrometer. Photoluminescence spectra were obtained on a PTI Quantum Master fluorometer equipped with a Xenon lamp excitation source. Fluorescence quantum yields were measured relative to fluorescein ($\eta = 0.92$) and 9,10-diphenylanthracene ($\eta = 0.91$) and verified using the referenceless technique described previously.[41] Mass spectrometry and elemental analysis were performed by UC Santa Barbara Mass Spectrometry Laboratory and Elemental Analysis Center. 1,4-Bis(diethylphosphonatemethyl)benzene,[28] 1,4-bis(diethylphosphonatemethyl)-2,5-dimethoxybenzene,[29] 1,4-bis(diethylphosphonatemethyl)-2,5-dicyanobenzene,[30] and 1,4-bis(diethylphosphonatemethyl)-2,3,5,6-tetrafluorobenzene[31] were synthesized according to literature precedent.

***N,N*-Bis(6-hydroxyhexyl)aniline (1).** A mixture of 9.3 g (100 mmol) of freshly distilled aniline, 30.0 g (220 mmol) of 6-chloro-1-hexanol, and 30.4 g (220 mmol) potassium carbonate was heated in 50 mL of *n*-butanol under reflux for 4 days. After cooling, the remaining solids were filtered off, and the solvent was removed under reduced pressure to afford the crude product. Purification by silica gel chromatography (ethyl acetate/hexane = 2:1) yielded 17.6 g (60%) of **1** as a colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.18 (m, 2H), 6.61 (m, 3H), 3.91 (t, $J = 6.4$ Hz, 4H), 3.67 (t, $J = 6.4$ Hz, 4H), 1.90−1.77 (m, 4H), 1.70−1.53 (m, 4H), 1.50−1.31 (m, 8H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 148.19, 129.31, 115.33, 111.86, 62.79, 51.06, 32.78, 27.30, 27.05, 25.76. HRMS (EI): $m/z = 293.2360$ (M$^+$), $\Delta = 1.7$ ppm.

***N,N*-Bis(6′-chlorohexyl)-4-aminobenzaldehyde (2).** Phosphorus oxychloride (17.5 g, 114 mmol) was added dropwise to 40 mL of dry DMF at 0 °C. After 30 min, 11.1 g (38 mmol) of **1** in 20 mL of DMF was added to the above solution. The resulting mixture was heated to 100 °C for 2 h. After cooling to 40 °C, the resulting mixture was poured into 200 mL of ice water. The pH of the mixture was adjusted to 7 by addition of saturated potassium acetate aqueous solution. The mixture was extracted with dichloromethane, and the combined organic phase was washed with water and dried over MgSO$_4$. The solvent was evaporated and the crude product was purified by silica gel chromatography (chloroform/hexane = 3:2) to afford **2** (10.2 g, 75%) as a light yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.71 (s, 1H), 7.71 (d, $J = 8.4$ Hz, 2H), 6.65 (d, $J = 8.4$ Hz, 2H), 3.55 (t, $J = 6.6$ Hz, 4H), 3.36 (t, $J = 7.2$ Hz, 4H), 1.89−1.81 (m, 4H), 1.64−1.60 (m, 4H), 1.48−1.36 (m, 8H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 190.18, 152.66, 132.46, 124.87, 110.90, 51.14, 45.17, 32.73, 27.23, 26.88, 26.51. HRMS (EI): $m/z = 357.1617$ (M$^+$), $\Delta = 2.6$ ppm. Anal. Calcd for C$_{19}$H$_{29}$Cl$_2$NO: C, 63.68; H, 8.16; N, 3.91. Found: C, 63.33; H, 8.05; N, 3.97.

***N,N*-Bis(6′-iodohexyl)-4-aminobenzaldehyde (3).** A mixture of **2** (8.9 g, 14.7 mmol) and 37.5 g (250 mmol) of sodium iodide was dissolved in 200 mL of dry acetone and heated under reflux for 2 days. The solvent was evaporated and the resulting mixture was diluted with 300 mL of dichloromethane and washed with water several times. The organic phase was dried over MgSO$_4$ and filtered. After removal of the solvent, the crude product was purified by silica gel chromatography (chloroform/hexane = 3:2) to afford **3** (10.7 g, 80%) as a light brown oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.70 (s, 1H), 7.69 (d, $J = 8.4$ Hz, 2H), 6.63 (d, $J = 8.4$ Hz, 2H), 3.34 (t, $J = 7.6$ Hz, 4H), 3.19 (t, $J = 6.8$ Hz, 4H), 1.86−1.81 (m, 4H), 1.64−1.60 (m, 4H), 1.47−1.33 (m, 8H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 190.07, 152.54, 132.32, 124.73, 110.82, 51.03, 33.38, 30.34, 27.06, 26.04, 7.19. EI-MS: 541 (M$^+$), 344 (M$^+$-C$_5$H$_{10}$I). Anal. Calcd for C$_{19}$H$_{29}$I$_2$NO: C, 42.16; H, 5.40; N, 2.59. Found: C, 41.91; H, 5.23; N, 2.63.

General Procedure for the Synthesis of the Neutral Chromophores. A solution containing 1 mmol of the phophonate (**4**, **5**, **6**, or **7**) and 2.5 mmol of the aldehyde **3** was prepared in dry THF. To the above mixture was added 2 mmol of base (sodium hydride or potassium *tert*-butoxide). The resulting suspension was stirred overnight at room temperature. The resulting mixture was diluted with 200 mL of dichloromethane and washed with brine. The organic layer was dried over MgSO$_4$, and the solvent was evaporated. The crude material was

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(41) (a) Greenham, N. C.; Samuel, I. D. W.; Hayes, G. R.; Phillips, R. T.; Kessener, Y. A. R. R.; Moratti, S. C.; Holmes, A. B.; Friend, R. H. *Chem. Phys. Lett.* **1995**, *241*, 89. (b) Maciejewski, A.; Steer, R. P. *J. Photochem.* **1986**, *35*, 59. (c) Meech, S. R.; Phillips, D. *J. Photochem.* **1983**, *23*, 193.

purified by silica gel chromatography (dichloromethane/hexane = 2:1) to afford the precursor chromophores **8N−11N** in yields in the range of 35−67%.

1,4-Bis(4′-(*N*,*N*-bis(6′′-iodohexyl)amino)styryl)benzene (8N). The pure **8N** was obtained in 39% yield as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (s, 4H), 7.39 (d, J = 8.8 Hz, 4H), 7.04 (d, J = 15.6 Hz, 2H), 6.89 (d, J = 15.6 Hz, 2H), 6.63 (d, J = 8.8 Hz, 4H), 3.30 (t, J = 7.6 Hz, 8H), 3.22 (t, J = 6.4 Hz, 8H), 1.89−1.82 (m, 8H), 1.64−1.57 (m, 8H), 1.49−1.43 (m, 8H), 1.41−1.35 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.73, 136.87, 128.32, 127.97, 126.41, 125.14, 123.89, 111.97, 51.15, 33.66, 30.59, 27.39, 26.32, 7.41. Anal. Calcd for $C_{46}H_{64}I_4N_2$: C, 47.93; H, 5.60; N, 2.43. Found: C, 48.15; H, 5.47; N, 2.60.

1,4-Bis(4′-(*N*,*N*-bis(6′′-iodohexyl)amino)styryl)-2,5-dimethoxybenzene (9N). The pure **9N** was obtained in 46% yield as a yellow solid. ^{1}H NMR (400 MHz, C_6D_6): δ 7.92 (d, J = 16.0 Hz, 2H), 7.65 (d, J = 8.8 Hz, 4H), 7.42 (d, J = 16.0 Hz, 2H), 7.28 (s, 2H), 6.65 (d, J = 8.8 Hz, 4H), 3.50 (s, 6H), 3.01 (t, J = 7.4 Hz, 8H), 2.73 (t, J = 6.8 Hz, 8H), 1.43 (m, 8H), 1.36 (m, 8H), 1.07 (m, 8H), 0.96 (m, 8H). ^{13}C NMR (100 MHz, C_6D_6): δ 152.53, 148.50, 129.69, 129.01, 127.77, 127.30, 120.19, 113.16, 109.50, 56.39, 51.67, 34.19, 31.06, 28.02, 26.78, 7.32. Anal. Calcd for $C_{48}H_{68}I_4N_2O_2$: C, 47.54; H, 5.65; N, 2.31. Found: C, 47.24; H, 5.75; N, 2.41.

1,4-Bis(4′-(*N*,*N*-bis(6′′-iodohexyl)amino)styryl)-2,5-dicyanobenzene (10N). The pure **10N** was obtained in 35% yield as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 2H), 7.45 (d, J = 8.8 Hz, 4H), 7.20 (d, J = 16.0 Hz, 2H), 7.11 (d, J = 16.0 Hz, 2H), 6.63 (d, J = 8.8 Hz, 4H), 3.33 (t, J = 7.6 Hz, 8H), 3.22 (t, J = 6.8 Hz, 8H), 1.84 (m, 8H), 1.63 (m, 8H), 1.46 (m, 8H), 1.39 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.04, 138.83, 129.27, 129.13, 123.21, 117.50, 116.86, 114.24, 111.86, 51.17, 33.65, 30.60, 27.40, 26.32, 7.31. Anal. Calcd for $C_{48}H_{62}I_4N_4$: C, 47.94; H, 5.20; N, 4.66. Found: C, 48.37; H, 5.30; N, 4.72.

1,4-Bis(4′-(*N*,*N*-bis(6′′-iodohexyl)amino)styryl)-2,3,5,6-tetrafluorobenzene (11N). Compound **11N** was obtained in 67% yield as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.8 Hz, 4H), 7.40 (d, J = 16.4 Hz, 2H), 6.85 (d, J = 16.4 Hz, 2H), 6.62 (d, J = 8.8 Hz, 4H), 3.32 (t, J = 7.6 Hz, 8H), 3.21 (t, J = 6.8 Hz, 8H), 1.89−1.82 (m, 8H), 1.64−1.57 (m, 8H), 1.49−1.43 (m, 8H), 1.41−1.35 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.56, 144.74 (d), 136.59, 128.61, 124.52, 114.79 (m), 111.82, 109.32, 51.14, 33.65, 30.58, 27.38, 26.31, 7.33. Anal. Calcd for $C_{46}H_{60}F_4I_4N_2$: C, 45.12; H, 4.94; N, 2.29. Found: C, 45.74; H, 4.96; N, 2.32.

General Procedure for the Synthesis of the Water-Soluble Chromophores. The neutral precursor chromophores (**8N−11N**, 200 mg) were dissolved in 30 mL of THF and the solution was cooled to −78 °C with dry ice/acetone bath. A large excess of condensed trimethylamine (∼2 mL) was added to the solution. The solution was allowed to warm to room temperature for 12 h and 20 mL of water was added to dissolve the precipitated compounds. Another portion (∼2 mL) of condensed trimethylamine was added at −78 °C, and the mixture was stirred for another 12 h for the complete quaternization. After removal of the solvents and an excess of trimethylamine under vacuum, the residue was dissolved in water and filtered. Evaporation of the water afforded the products, which were washed in acetone and dried under vacuum to afford the final water-soluble chromophores **8C−11C**. The product yields are close to 90%.

1,4-Bis(4′-(*N*,*N*-bis(6′′-(*N*,*N*,*N*-trimethylammonium)hexyl)amino)-styryl)benzene tetraiodide (8C) was obtained as a yellow solid (yield: 92%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.48 (s, 4H), 7.39 (d, J = 9.2 Hz, 4H), 7.09 (d, J = 16.4 Hz, 2H), 6.90 (d, J = 16.4 Hz, 2H), 6.64 (d, J = 9.2 Hz, 4H), 3.28 (m, 16H), 3.04 (s, 36H) 1.68 (m, 8H), 1.55 (m, 8H), 1.34 (m, 16H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 147.35, 136.22, 128.10, 127.70, 124.06, 112.75, 111.51, 65.23, 52.16, 49.93, 26.68, 25.96, 25.77, 22.10. Anal. Calcd for $C_{58}H_{100}I_4N_6$: C, 50.15; H, 7.26; N, 6.05. Found: C, 50.07; H, 7.17; N, 6.14.

1,4-Bis(4′-(*N*,*N*-bis(6′′-(*N*,*N*,*N*-trimethylammonium)hexyl)amino)-styryl)-2,5-dimethoxybenzene tetraiodide (9C) was obtained as a yellow solid (yield: 89%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.37 (d, J = 8.8 Hz, 4H), 7.21 (s, 2H), 7.15 (d, J = 16.4 Hz, 2H), 7.10 (d, J = 16.4 Hz, 2H), 6.65 (d, J = 8.8 Hz, 4H), 3.87 (s, 6H), 3.29 (m, 16H), 3.05 (s, 36H), 1.68 (m, 8H), 1.55 (m, 8H), 1.34 (m, 16H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.52, 147.31, 140.27, 128.61, 127.64, 125.55, 124.54, 117.19, 111.56, 65.24, 56.19, 52.16, 49.93, 26.68, 25.96, 25.76, 22.10. Anal. Calcd for $C_{60}H_{104}I_4N_6O_2$: C, 49.73; H, 7.23; N, 5.80. Found: C, 50.10; H, 7.12; N, 5.68.

1,4-Bis(4′-(*N*,*N*-bis(6′′-(*N*,*N*,*N*-trimethylammonium)hexyl)amino)-styryl)-2,5-dicyanobenzene tetraiodide (10C) was obtained as a dark red solid (yield: 87%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.41 (s, 2H), 7.58 (d, J = 16.4 Hz, 2H), 7.43 (d, J = 8.8 Hz, 4H), 6.97 (d, J = 16.4 Hz, 2H), 6.71 (d, J = 8.8 Hz, 4H), 3.33 (m, 16H), 3.07 (s, 36H), 1.68 (m, 8H), 1.59 (m, 8H), 1.34 (m, 16H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 148.57, 137.98, 135.10, 128.89, 122.52, 117.10, 115.47, 113.01, 111.55, 65.21, 52.16, 49.91, 44.23, 26.64, 25.89, 25.73, 22.08. Anal. Calcd for $C_{60}H_{98}I_4N_8$: C, 50.08; H, 6.86; N, 7.79. Found: C, 49.42; H, 6.95; N, 7.56.

1,4-Bis(4′-(*N*,*N*-bis(6′′-(*N*,*N*,*N*-trimethylammonium)hexyl)amino)-styryl)-2,3,5,6-tetrafluorobenzene tetraiodide (11C) was obtained as an orange solid (yield: 90%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.45 (d, J = 8.8 Hz, 4H), 7.33 (d, J = 16.8 Hz, 2H), 6.79 (d, J = 16.8 Hz, 2H), 6.67 (d, J = 8.8 Hz, 4H), 3.31 (m, 16H), 3.05 (s, 36H), 1.67 (m, 8H), 1.55 (m, 8H), 1.33 (m, 16H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 148.44, 143.73 (d), 137.01, 128.69, 112.92, 114.15, 111.45, 107.44, 65.21, 52.16, 26.64, 25.90, 25.73, 22.08. Anal. Calcd for $C_{58}H_{96}F_4I_4N_6$: C, 47.68; H, 6.62; N, 5.75. Found: C, 47.53; H, 6.30; N, 5.58.

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Supporting Information Available: Additional UV/vis and PL spectra (**11N**, **8N**/**8C**, **8C**/**8CH$^+$**/**8CH$_2$$^{2+}$**), TPA spectra measurements, concentration dependence of absorption in toluene (**8N**) and in water (**8C**), and complete refs 1b and 11. This material is available free of charge via the Internet at http://pubs.acs.org.

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