

Probing Exciton Localization/Delocalization: Transient dc Photoconductivity Studies of Excited States of Symmetrical Porphyrin Monomers, Oligomers, and Supramolecular Assemblies

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Solution-phase transient dc photoconductivity (TDCP) measurements are used to address the question of exciton localization/delocalization in strongly coupled oligomeric porphyrins and in well-defined, higher-order assemblies of oligomers (ladder and prism assemblies). The approach used is determination of the excited-state excess polarizability volume, $\Delta\alpha_v$ —a quantity known to report on exciton delocalization. The measurements reveal for the oligomers that singlet excitons are substantially delocalized but that triplet excitons are much more localized. For each of the two higher-order assemblies, the measurements reveal that excitons are transiently confined to individual oligomeric subunits rather than being delocalized over the entire assembly.

Introduction

Macrocyclic tetrapyrrolic compounds and their derivatives (e.g., chlorins, chlorophylls, porphyrins) comprise essential pigments in natural photosynthetic systems and attractive building blocks for artificial light-harvesting systems.¹ Organized arrays of these chromophores can facilitate extended energy and/or charge transfer. Dipolar coupling is important for the former while electronic coupling is important for the latter. In the limit of very strong electronic coupling, exchange interactions yield excitons that are delocalized across multiple porphyrins² and thus extensively broaden porphyrin absorption spectra. Here we report on the application of transient dc photoconductivity (TDCP) measurements to the question of exciton localization/delocalization in monomeric, dimeric, trimeric, and tetrameric porphyrins. In addition, we report on the behavior of well-defined supramolecular assemblies of dimers and trimers.

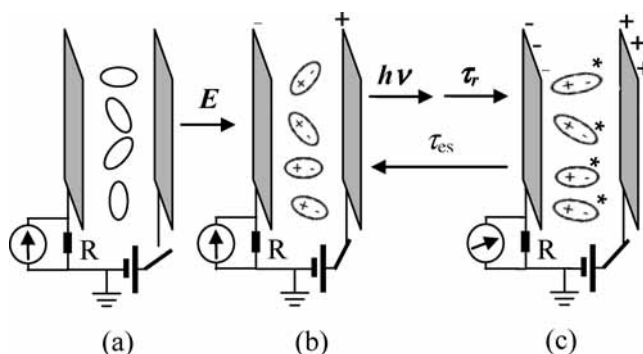
The TDCP technique measures changes in solution electric polarization, ΔP , upon photoexcitation of a chromophoric solute.³ These changes give rise to transient charge displacements that, in the presence of an externally applied electric field (E), can be detected capacitively with cell-defining conductive plates; see Scheme 1. The measured changes in polarization reflect differences in solute excited-state versus ground-state dipole moment—both the permanent dipole moment, $\Delta\mu$, and the field-induced dipole moment, $\Delta\mu^*$, which is the product of E and the change in molecular polarizability, $\Delta\alpha$. Assuming (for simplicity) that there is only one excited species and that the solute does not strongly couple to the solvent,^{3b} the change in solute electric polarization depends on the time-varying excited state concentration, $n_e(t)$, as follows

$$\Delta P_{\text{solution}}(t) = \Delta P_{\text{solute}}(t) = n_e(t)E\left(\Delta\alpha + \frac{\Delta\mu^2}{3k_B T}\right) \quad (1)$$

where k_B is the Boltzmann constant.

TDCP measurements have previously been used to characterize molecular photoprocesses involving charge transfer, either photoexcitation followed by electron transfer or optical transitions that directly entail charge transfer.^{3,4} By assuming that contributions from changes in polarizability are small enough to be neglected, the resulting values of ΔP have been used to obtain permanent-dipole-moment differences and, therefore, charge-transfer directions and distances.^{4a} In contrast, here we have intentionally examined symmetrical systems lacking permanent dipole moments in both ground and lowest excited states (see compounds 1–7 in Chart 1); as a consequence, the

SCHEME 1: A Simplified Representation of the TDCP Experiment, Showing: (a) Randomly Oriented Molecules in the Absence of a Field, (b) Preferential Orientation of Molecular Dipoles (or Induced Dipoles) by an External Electric Field, (c) Instantaneous Induced Dipole-Moment Change with Excitation and Further Preferential Molecular Orientation (Rotation; Time Scale τ_r)^a



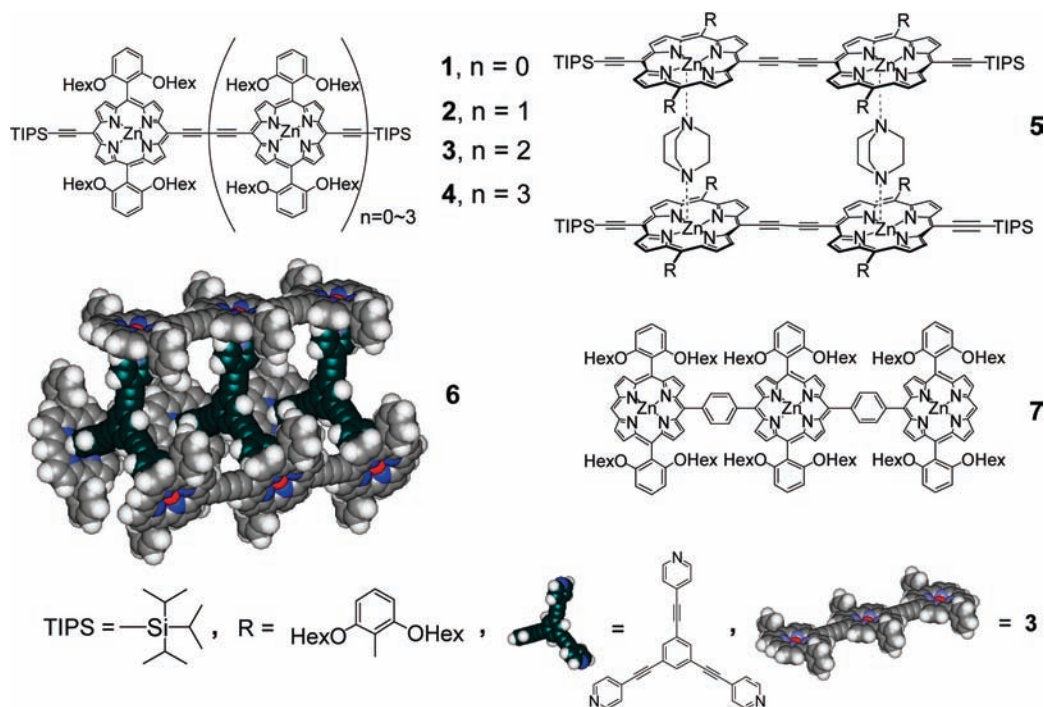
^a (c) returns to (b) after decay of the excited states (time = τ_{es}).

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CHART 1: Structures of Porphyrinic Chromophores 1–7^a

^a For clarity, solubilizing groups have been omitted from the space-filled representations of **3** and **6**.

polarization difference measurements have returned values for $\Delta\alpha$ (or more precisely, the excess polarizability volume,⁵ $\Delta\alpha_v$), rather than $\Delta\mu$. As discussed previously by Warman et al.,^{2f,g,6} the excess polarizability volume of the excited state can be related qualitatively to exciton delocalization. Consistent with earlier observations for closely related compounds (via alternative methods, transient microwave conductivity^{2f,g} and ESR^{2b}), we find that highly conjugated structures facilitate delocalization of singlet excitons but leave triplet excitons much more localized. In addition, for the two supramolecular assemblies, we find that singlet excitons localized on single oligomeric subunit rather than delocalizing over entire assemblies.

Experimental Section

Zinc tetraphenylporphyrin, 4-dimethylamino-4-nitrostilbene (DMANS), and 1,4-diazabicyclo[2.2.2]octane (dabco) were obtained from Aldrich. **1–5** and **7** are variants of known compounds.^{2f,7} Their synthesis and characterization are included in Supporting Information. **6** is characterized in a previous publication.^{8a}

All photophysical measurements were made at ambient in spectroscopic grade toluene. Absorption spectra were collected on a CARY 5000 UV–vis–NIR spectrophotometer. Luminescence spectra were collected on a Jobin-Yvon Fluorolog 3 fluorimeter using a red-sensitive Hamamatsu R928 photomultiplier tube. All fluorescence spectra were corrected for instrumental responsivity. Quantum yields for **1** and **2** were evaluated relative to zinc tetraphenylporphyrin ($\phi_f = 0.033$).⁹ Yields for **2**, **3**, **4**, and **7** were measured in Durham with the intensity of the spectra being calibrated to that of **2**. Fluorescence lifetime measurements were made using a Hamamatsu C4780 ps fluorescence lifetime measurement system, consisting of a C4334 Streakscope and a C4792-01 synchronous delay generator. The samples were excited by a home-built Ti:sapphire laser (cavity dumped at 820 kHz) described elsewhere.¹⁰

Photoacoustic calorimetry was performed with a previously described apparatus using ferrocene as an external reference.¹¹

Estimates of singlet energy, ${}^1E_{00}$, were obtained by normalizing the intensity of the lowest energy absorption band and the fluorescence spectrum and equating the crossing point with ${}^1E_{00}$. The intersystem crossing yield, ϕ_{isc} , was determined from the following equation

$$\phi_{isc} = \frac{(1 - h)E_{hv} - \phi_f {}^1E_{00}}{{}^3E_{00}} \quad (2)$$

where h is the ratio of heat instantaneously released to the total heat released in the photoacoustic calorimetry experiment, ϕ_f is fluorescence quantum yield, and E_{hv} is the photon energy of the excitation laser. On the basis of the likely localization of the triplet exciton on a single porphyrin ring (see below), the triplet energy, ${}^3E_{00}$, was taken from reported values.¹²

TDCP Measurements. All measurements were performed with instrumentation described previously.^{4b,c} The experimental protocol was nearly identical to that for the previously reported transient dc photocurrent spectroscopy studies done in displacement current mode.^{13,14} A 1000 V potential was applied across a 0.25 mm gap between two electrodes. The samples were excited at 420–430 nm with an Oportek Vibrant OPO laser pumped with the third harmonic of a Quantel Brilliant Nd:YAG laser (10 Hz, ~ 2 ns fwhm). Laser beam profiles were collected with a 25 GHz Si photodiode (ET-2000 from Electro-Optics Technology, Inc.). Typical absorbed laser energies were ca. 20–40 μJ per pulse. Solution optical densities were between 0.8 and 1.0 at the excitation wavelength. Care was taken to minimize exposure to light. Solutions were purged with N_2 for 15–20 min before excitation. Reported values are averages from two to four energy-corrected data sets. A typical data set comprised 10–20 measurements, each of them an average of either 64 or 128 shots.

TDCP Analysis. The methodology of TDCP data analysis has been fully detailed elsewhere^{3a,b,15} and is only briefly

summarized here. The analysis has been developed for permanent dipole moments. We have simply adapted it assuming that the signals observed are due only to the polarizability change (induced dipole effects). The transient voltage, $v(t)$, which is measured across the load resistor R in the circuit described in Scheme 1, results from the displacement current, dQ/dt (where Q is charge), i.e., $v(t) = R dQ/dt$. The equation for time variation in the system is as follows^{3a,b,15}

$$v(t) + \tau_{RC} \frac{dv(t)}{dt} = RS \frac{dP}{dt} \propto \frac{dn_e}{dt} \quad (3)$$

where P is the polarization of solute (in nonpolar solvents), which is proportional to the excited-state population n_e , τ_{RC} is the RC time constant, and S is the surface area of the parallel measuring plates in the capacitance cell. It is instructive to consider the time evolution of the signal in a simplified two-state case (ground and excited states) where we only consider the polarizability change. For the porphyrin oligomer, the evolving transient voltage, $v(t)$, in response to laser excitation in an electric field can be expressed as^{3b}

$$v(t) + \tau_{RC} \frac{dv(t)}{dt} = H\Delta\alpha \left[\frac{e^{-t/\tau_{\text{eff}}}}{\tau_{\text{eff}}} - \frac{e^{-t/\tau_F}}{\tau_F} \right] \quad (4)$$

In eq 4, H is a constant experimental factor detailing the contributions of solvent and E in the experiment, τ_F is defined as the excited-state lifetime which is the observed fluorescence lifetime (τ_0) in the case of two states. τ_{eff}^{-1} equals $\tau_F^{-1} + \tau_r^{-1}$ where τ_r is the time constant for chromophore rotation. The solution for eq 4 is^{3b}

$$v(t) = H\Delta\alpha \left(\frac{e^{-t/\tau_{\text{res}}}}{\tau_{\text{res}}} - \frac{e^{-t/\tau_F}}{\tau_F} \right) \quad (5)$$

where τ_{res} takes the larger value of τ_r and τ_{RC} . A plot of eq 5 resembles the first derivative of a peak. The RC time constant used was 1.4 ns—a value obtained by first using a four-point contact measurement to obtain the capacitance of the cell. The value was tested and corroborated via fits of experimental TDCP measurements of 4-(dimethylamino)-4-nitrostilbene (DMANS) in toluene as a standard, according to previously published work.^{3a}

In the case of a three-state model with ground state (G), singlet excited state (S), and triplet excited state (T), a more complicated solution was used (see Supporting Information). Here τ_F is defined as the excited-state lifetime in absence of intersystem crossings, i.e., $\tau_F = 1/(k_f + k_{ic})$, where k_f and k_{ic} are the rate constants of fluorescence and the $S_1 \rightarrow S_0$ internal conversion, respectively. S and T components of the polarizability volume change were dissected in this solution. Analysis of the TDCP signal was aided by a fitting program kindly provided by Professor Sergei Smirnov. Up to three states (G, S, and T) were treated in the program.

Semiempirical Calculations. An AM1 geometry optimization and single point ZINDO-1 calculations were performed using Hyperchem Pro 6.0. Ground-state molecular polarizabilities and volumes were calculated using the QSAR package in the software.

TABLE 1: Intersystem Crossing Yields (ϕ_{isc}) and Times (τ_{isc}), Singlet and Triplet Energies (${}^1E_{00}$, ${}^3E_{00}$), Fluorescence Lifetimes (τ_0), Quantum Yields (ϕ_f), and Excited-State Lifetimes in Absence of Intersystem Crossings (τ_F) for 1–7

compound	ϕ_{isc}	τ_{isc} (ns)	ϕ_f	${}^1E_{00}$	${}^3E_{00}$	τ_0 (ns)	τ_F (ns)
1	0.72	3.8	0.11	2.00	1.48	2.7	9.6
2	0.46	2.8	0.20	1.75	1.40	1.3	2.4
3	0.36	3.6	0.24	1.65	1.35	1.3	2.0
4	0.21	5.2	0.078	1.61	1.32	1.1	1.4
5 ^a	0.46	2.8	0.20	1.75	1.40	1.3	2.4
6 ^b	0.36	3.6	0.24	1.65	1.35	1.3	2.0
7	0.67	4.0	0.048	1.65	1.15	2.7	8.2

^a Assumed to be the same as that for 2. ^b Assumed to be the same as that for 3.

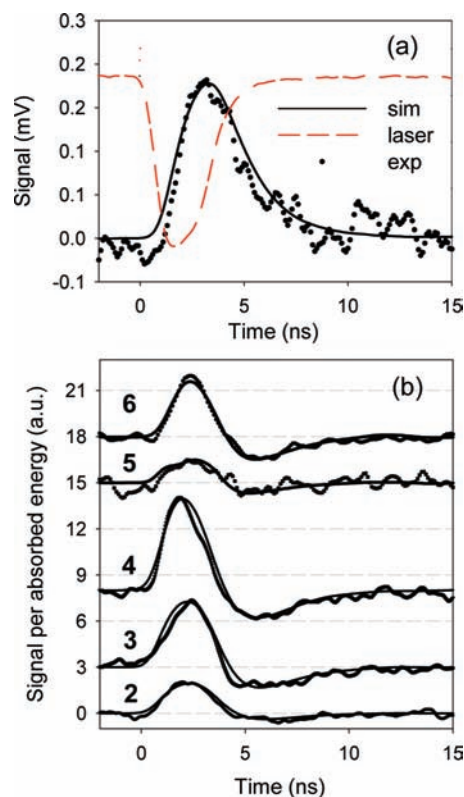


Figure 1. TDCP signals for (a) 1 and (b) 2–6 dissolved in toluene. In (a), dots are experimental data, the solid line is a fit, and the dash line is the laser pulse. In (b), the signals are normalized to correspond to the same absorbed energy and then are arbitrarily vertically offset for clarity. Noisy lines are experimental data; smooth solid lines are fits.

Results and Discussion

Table 1 summarizes photophysical data needed to interpret TDCP responses from 1–7 (i.e., singlet-to-triplet intersystem crossing yields (ϕ_{isc}) and times (τ_{isc}), singlet and triplet excited-state emission energies (${}^1E_{00}$, ${}^3E_{00}$), observed fluorescence lifetimes ($\tau_0 = 1/(k_f + k_{ic} + k_{isc})$, k_{ic} is the $S_1 \rightarrow S_0$ internal conversion rate constant), and quantum yields (ϕ_f)). Excited-state lifetimes ($\tau_F = 1/(k_f + k_{ic})$) in absence of intersystem crossings are also calculated and listed in order to fit TDCP responses using a three-state-model.^{3b}

Figure 1 shows TDCP signals for 1–6 dissolved in toluene. From eqs 3 and 4, the shapes of the signals (amplitude vs time) should closely approximate plots of the rate of change of the excited-state population (dn_e/dt) versus time. For an excited state that is long-lived (submicrosecond or longer) relative to the laser pulse, the signal's time profile resembles the pulse shape itself.

TABLE 2: Calculated Photoinduced Polarizability Volume Changes, the Calculated Molecular Volume, and Molecular Polarizability of the Ground State for 1–7

compound	τ_r (ns) ^a	$^1\Delta\alpha_V$ (Å ³) ^a	$^3\Delta\alpha_V$ (Å ³) ^a	V (Å ³) ^b	α_{GS} (Å ³) ^b
1	0.3	60 ± 20	60 ± 20	2200	90
2	0.65	430 ± 40	100 ± 50	3800	170
3	0.8	650 ± 110	110 ± 40	5300	240
4	1.0	950 ± 150	170 ± 30	6900	320
5	0.8	410 ± 100	80 ± 40		
6	1.0	640 ± 150	120 ± 60		
7	0.3	<70	<50	7200	230

^a The rotational lifetime (τ_r), singlet change in polarizability volume ($^1\Delta\alpha_V$), and the triplet change in polarizability volume ($^3\Delta\alpha_V$) were determined from the fitting of the TDCP measurements. ^b Molecular volume (V) and molecular polarizability of the ground state (α_{GS}) were calculated using Hyperchem Pro 6.0.

For **1**, the intersystem crossing yield is high so that a large triplet-excited-state population is built up; see Figure 1a. Consistent with this behavior, the TDCP signal can be fit by considering only the long-lived triplet excited state. From the fit, the excess polarizability volume $\Delta\alpha_V$ is about 60 Å³.

For an excited state that is short-lived and comparable to the laser pulse, n_e will be proportional to the instantaneous pulse intensity, and dn_e/dt versus t will resemble the first derivative of the laser pulse shape. Compound **4**, which suffers much less intersystem crossing, approximately satisfies this condition and indeed does display a derivative-like signal shape. The observed deviation (i.e., attenuation of the negative-going lobe) is largely a consequence of finite rotational dynamics; see Figure 1b. From the fit, the excess polarizability volume is ~ 950 Å³. For **2**, **3**, **5**, and **6**, the difference in signal shape and magnitude can be explained in terms of those two limiting cases.

Photoexcitation of **1–4** yields populations of both singlet and triplet excited states. The corresponding TDCP responses of **2–4** while dominated by singlet contributions are better fit by including the triplet contribution. As illustrated in Figure 1 for **1**, one consequence of triplet formation is an attenuation of the negative-going lobe of the TDCP signal. The amount of triplet contribution used in the TDCP fitting was determined by calculating the intersystem quantum yield from experimental parameters nearly identical to the conditions in the TDCP experiment. Photoacoustic calorimetry data, estimates of the singlet and triplet energy levels, and fluorescence quantum yields were used for this purpose; see summary in Table 2. With the determination of the rate of intersystem crossing and measurement of the singlet lifetime, $\Delta\alpha_V$ (Å³) can be separated into the singlet contribution ($^1\Delta\alpha_V$) and the triplet contribution ($^3\Delta\alpha_V$). As shown in Table 2, $^1\Delta\alpha_V$ of the singlet excited states of ethynyl-functionalized monomer, dimer, trimer, and tetramer species **1–4** dramatically increase with increasing chromophore size, while $^3\Delta\alpha_V$ exhibits much less change with chromophore size. This points to delocalization of the singlet exciton along the entire molecule and localization of the triplet exciton in a much smaller region.

From perturbation theory, the ground-state molecular polarizability depends on both the transition dipole moments ($\langle M_{nm} \rangle$) (m and n are the initial and final states, respectively) and the energy differences (ΔE) between the ground and excited states¹⁶

$$\alpha \propto \sum \frac{M_{nm}^2}{\Delta E} \quad (6)$$

Similarly, the excited-state molecular polarizability depends on transition-dipole moments for excitation to higher states and

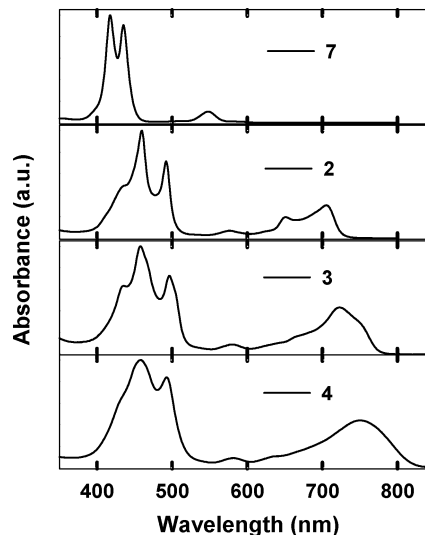


Figure 2. UV-vis spectra of **7**, **2**, **3**, and **4** in toluene, showing red shifting of Q-bands upon extending and/or enhancing porphyrin/porphyrin electronic conjugation.

on energy differences between the specific excited state and higher states. Interestingly, in the two-state limit (i.e., ground state and a single excited state) perturbation theory promises a *negative* value for the change in polarizability and, indeed, behavior of this kind is occasionally seen experimentally.¹³ Only when significant coupling to upper excited states is present does the excess polarizability become positive.

The striking increases in $^1\Delta\alpha_V$ upon oligomerization of the ethynyl-terminated porphyrin **2** are consistent with increases in transition dipole moments (especially in the Q-band region) due to delocalization of excitons over multiple porphyrins. They are also consistent with red shifts in the ground-state absorption spectrum and with broadening of the spectrum (due to additional transitions); see Figure 2 (electronic absorption spectra of **2**, **3**, **4**, and **7** in toluene). Replacement of the butadienyl linkages in **3** with phenyl linkage (**7**) diminishes the electronic coupling between porphyrin subunits, resulting in Q-band absorption energies and intensities that are similar to those of a single isolated porphyrin.¹ For chromophores **2**, **3**, and **4**, the Q-band red shifts as the length of the conjugated oligomer increases.

One of the interesting features of oligomers like **2–4** is their propensity to assemble into well-defined large structures in the presence of multitopic ligands.^{7a,8} Ladder structure **5** and prism structure **6** are two such assemblies. A question that arises with these structures is whether absorption produces excitons that span the full assembly or instead yields excitons that are confined, at least transiently, to a single oligomer. We reasoned that TDCP measurements could differentiate between the two possibilities by reporting on the excited-state excess polarizability volume. As shown in Table 2, we find that excitation of the ladder structure **5** yields a $\Delta\alpha_V$ value that is nearly identical to that for the isolated ladder rail, **2**.¹⁴ We conclude that the exciton is transiently confined to just one of the two available rails. Similarly, for **6**, we conclude that the exciton is transiently confined to just one of the three available panels of the prism.

Finally, we also have examined the phenyl-linked porphyrin trimer, **7**, featuring much less electronic coupling between porphyrin subunits. The TDCP signal of **7** is not shown in Figure 1 as it is too small to be distinguished from noise. The entries in Table 2 comprise upper limit estimates for **7** based on the magnitude of the noise and the absence of a discernible TDCP signal. Consistent with earlier reports,¹ we

conclude that phenyl linkages, which are rotated away from coplanarity with the porphyrins, are ineffective at facilitating exciton delocalization. The resulting $\Delta\alpha_V$ value is similar to (or less than) that for **1** and points to localization of the exciton on a single porphyrin. This conclusion agrees well with findings for closely related compounds based on transient ESR^{2b} and transient microwave conductivity measurements.^{2f,g}

Conclusions

Transient dc photoconductivity can be used to measure changes in molecular polarizability volume following electronic excitation. The excess polarizability volumes of the singlet excited states of ethynyl-functionalized monomer, dimer, trimer, tetramer, and phenyl-linked trimer species are 60, 430, 650, 950, and $<70 \text{ \AA}^3$, respectively, while the excess polarizability volume of the triplet excited states is much less sensitive to the chromophore size. The findings are consistent with the notion of delocalization of the singlet exciton along the whole molecule and localization of the triplet exciton in a much smaller region. These findings are consistent with earlier reports based on transient ESR and transient microwave conductivity studies of closely related systems. In a ladder assembly comprising two dimers and a prism assembly comprising three trimers, the excess polarizability volumes of the singlet excitons are 410 and 640 \AA^3 , respectively, indicating that the excitons are transiently confined to individual oligomers rather than being delocalized over entire assemblies.

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Supporting Information Available: Details of synthesis and characterization of **1–4** and **7**, the solution for a three-state-model with ground state (G), singlet excited state (S), and triplet excited state (T), dissecting the signal contributions into S and T components, and simulated TDCP signals with different percentages of intersystem crossing yields. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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