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Solvatochromism of Distyrylbenzene Pairs Bound Together by [2.2]Paracyclophane: Evidence for a Polarizable "Through-Space" Delocalized State

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Abstract: A series of compounds were designed and synthesized to examine how through-space and through-bond electron delocalization respond to solvent effects. The general strategy involves the study of "dimers" of the distyrylbenzene chromophore held in close proximity by the [2.2]paracyclophane core and a systematic dissection of the chromophore into components with through-space and through-bond electronic delocalization. Steady state and time-resolved fluorescence spectroscopy in a range of solvents reveals a red-shift in emission and an increase in the intrinsic fluorescence lifetime for the emitting state in polar solvents when donor substituents are absent. We propose that through-space delocalization across the [2.2]paracyclophane core is more polarizable in the excited state, relative to the through-bond (distyrylbenzene based) excited state. When strong donors are attached to the distyrylbenzene chromophore, the charge transfer character of the distyrylbenzene-based excited state dominates fluorescence properties.

Introduction

Complex noncovalent assemblies of organic chromophores provide a challenge to chemical synthesis, the control of supramolecular arrangements, and our understanding of electronic coupling in collections of optical units. These assemblies are important in biology and in the function of organic semiconducting materials. A classic example of a well-defined self-organized array of optical units can be found in photosynthetic systems such as that of purple bacteria, where light absorption by antennae units, followed by energy migration between donor and acceptor groups, leads to charge separation and the conversion to chemical energy.[1] Electron and hole transport along duplex DNA, thought to proceed through π-stacked base pairs, is of interest due to the connection between charge recombination in oxidative damage and repair mechanisms in DNA[2] and constitutes an area of substantial debate.[3]

In amorphous organic semiconductors, structure/property correlations can be more difficult to understand because the collective response often rests on an arrangement of optical units with no long-range order. Defects often dominate emission, since facile fluorescence resonance energy transfer (FRET)[4] channels excitations to low-energy sites,[5] which may be poorly defined or too low in concentration to be fully characterized.[6] The history of conjugated polymers is replete with examples that show how interchain orientation depends on solvent history and how this spatial disposition influences bulk performance in light-emitting diodes[7−9] and thin film transistors.[10] The role of interchromophore orientation is also well appreciated in chromophore aggregates.[11,12] For example, H- and J-aggregates have been known for a long time,[13] have different optical properties, and

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differ with respect to the orientation of the molecular dipole moments.[14−16]

Ambiguities in the local structure within bulk materials and the importance of correlating geometry with optical properties for gauging the theoretical description of dipole−dipole coupling and/or electron exchange[17] has prompted efforts toward controlling the assembly of chromophores by techniques such as Langmuir−Blodgett monolayer deposition,[18] solvent-dependent dimerization,[19] DNA-assisted spatial control,[20] and incorporation into functionalized phospholipids,[21] among others.[22] Another approach involves the synthesis of molecules that constitute precisely defined chromophore pairs. Characterization of these molecules and comparison against the monomeric building blocks yield information on pairwise electronic communication, which may be extrapolated to larger multichromophoric systems. One example involves molecules with the general structure naphthalene−bridge−naphthalene, where the pairs of naphthalene chromophores are set in place by a rigid linker of variable length.[23]

In connection with the synthesis and spectroscopy of well-defined chromophore pairs with “though-space” delocalization,[24] a number of molecules that contain the [2.2]paracyclophane core[25] have been reported. The parent core may be viewed as a pair of strongly interacting benzene rings and displays spectroscopic features that have been described as analogous to those of a benzene excimer.[26] Synthetic elaboration allows examination of more complex chromophores and how molecular composition influences the transannular delocalization.[27] Some of these structures are designed to mimic interchain delocalization in conjugated polymers, such as poly(phenylenevinylene),[28,29] and are used to give insight into how the orientation, conjugation length, and contact site determine the lowest energy state for the pair of chromophores. Chromophores containing the paracyclophane core have also been designed to probe intramolecular charge transfer (ICT) across the transannular gap[30] and thus the properties of donor/acceptor groups separated through space.[31] Multiple substitution on the 4,7,12,15-sites[32] provides for nonlinear chromophores with a strong octupolar component.[33,34] It is also possible to incorporate [2.2]paracyclophane structures within the backbone of polymers to yield structures with both π- and through-space- conjugation.[35]

The unique structure and optical properties of paracyclophane molecules with prebuilt interchromophore delocalization suggested that this molecular platform could be useful for designing water-soluble optical reporters with decreased sensitivity to optical perturbations brought about by aggregation phenomena.[36] For example, the water-soluble compound octa(tetrabutylammonium) 4,7,12,15-tetrakis(3′,5′-bis(butoxysulfonate))styryl-[2.2]paracyclophane (**pCp-O-**, shown in Scheme 1) shows decreased perturbation with the addition of surfactant, relative to linear anionic polymers and oligomers with phenylenevinylene repeat units.[37] This decreased sensitivity to changes by the environment was attributed to a reduced tendency for

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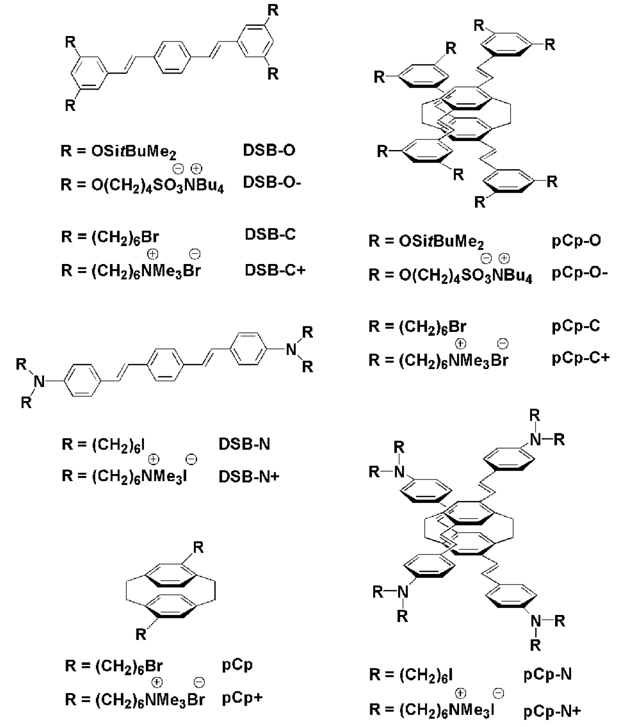
Scheme 1. Molecular Structures and Abbreviations Used in Previous and Current Studies



aggregation in water and to the intramolecular delocalization, which diminishes perturbations by adjacent molecules in the aggregate.

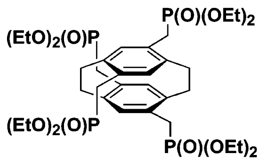
During studies of **pCp-O-**, it was noted that the natural lifetime of **pCp-O-** (26 ns) in water was considerably longer than that of the neutral precursor 4,7,12,15-tetrakis(3′,5′-bis(*tert*-butyldimethylsiloxy)styryl)-[2.2]paracyclophane, **pCp-O**, in organic solvents such as toluene (4 ns). Furthermore, the parent water-soluble distyrylbenzene chromophore **DSB-O-** shows a lifetime that is similar to those of previously characterized distyrylbenzene chromophores.[38] These differences suggested that the energy of the though-space state is influenced more strongly by the solvent.

In this contribution we detail the synthesis and optical studies of [2.2]paracyclophane molecules that are specifically designed to examine how the solvent perturbs the photophysics of pairs of distyrylbenzene molecules (Scheme 1). Specifically, the molecules prepared and studied are 4,7,12,15-(*N*,*N*-bis(6″-iodohexyl-4′-aminostyryl)-[2.2]paracyclophane (**pCp-N**), 4,7,-12,15-tetra(*N*,*N*-bis(6″-(*N*,*N*,*N*-trimethylammonium)hexyl)-4′-aminostyryl)-[2.2]paracyclophane octaiodide (**pCp-N+**), 4,7,12,15-tetra(3′,5′-bis(6″-bromohexyl)styryl)-[2.2]paracyclophane (**pCp-C**), and 4,7,12,15-tetra(3′,5′-bis(6″-(*N*,*N*,*N*-trimethylammonium)hexyl)styryl)-[2.2]paracyclophane octabromide (**pCp-C+**), where **C**/**N** corresponds to the substituents at the termini of the chromophores (**C** for alkyl and **N** for dialkylamine) and **C**/**C+** or **N**/**N+** stands for the chromophores in their neutral or charged states.

We also include in these studies distyrylbenzene and [2.2]-paracyclophane derivatives that correspond to the building blocks of the dimer structures. Compounds 1,4-bis(4′-(*N*,*N*-bis-(6″-iodohexyl)amino)styryl)benzene (**DSB-N**), 1,4-bis(4′-(*N*,*N*-bis(6″-(*N*,*N*,*N*-trimethylammonium)hexyl)amino)styryl)-benzene tetraiodide (**DSB-N+**), 1,4-bis(3′,5′-bis(6″-bromohexyl)-styryl)benzene (**DSB-C**), and 1,4-bis(3′,5′-bis(6″-(*N*,*N*,*N*-trimethylammonium)hexyl)styryl)benzene tetrabromide (**DSB-C+**) are the neutral and charged chromophore building blocks (Scheme 1). Pseudo-*p*-bis(6-bromohexyl)-[2.2]paracyclophane (**pCp**) and pseudo-*p*-bis(6-(*N*,*N*,*N*-trimethylammonium)hexyl)-[2.2]paracyclophane dibromide (**pCp+**) provide derivatives of [2.2]paracyclophane soluble in organic solvents and water, respectively.

Results

Synthesis. Two important building blocks for the synthesis of the target compounds are 4,7,12,15-tetra(diethylphosphonatemethyl)[2.2]paracyclophane (**1**) and 1,4-bis(diethylphosphonatemethyl)benzene (**2**).[33a,39] Reaction of **1** or **2** with the appropriately substituted benzaldehydes via the Horner−Emmons−Wittig reaction yields the **DSB** and **pCp** molecules in Scheme 1. The synthesis of **1** is available in the literature.[33] Briefly, it involves tetrabromomethylation of [2.2]paracyclophane under ultrasonic conditions, followed by treatment with triethyl phosphite. The overall yield of **1** from [2.2]paracyclophane is approximately 20%.



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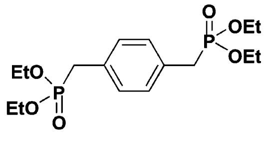

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The synthetic routes to the benzaldehyde intermediates are shown in Scheme 2. 3,5-Bis(6′-bromohexyl)benzaldehyde was synthesized in two steps, starting from 3,5-dibromobenzaldehyde. After protection with pinacol, the resulting 2-(3′,5′-dibromophenyl)-4,4,5,5-tetramethyl-[1.2]dioxolane (**3**) underwent two consecutive steps involving a lithium−halogen exchange achieved with *t*-BuLi and quenching with an excess of anhydrous 1,6-dibromohexane in THF. Deprotection via stirring at 60 °C in 10% HBr in a 2:1 mixture of water and THF affords 3,5-bis(6′-bromohexyl)benzaldehyde (**4**) in 60% yield. Attempts to use *n*-BuLi in the dual lithium−halogen exchange procedure proved unsuccessful and led to a mixture of products. The synthesis of *N*,*N*-bis(6′-iodohexyl)-4-aminobenzaldehyde (**7**) starts with the reaction of aniline with 6-chlorohexanol in butanol, which provides *N*,*N*-dihexanolaniline (**5**) in 70% yield. Treatment of **5** with phosphorus oxychloride in DMF produces *N*,*N*-bis(6′-chlorohexyl)-4-aminobenzaldehyde (**6**) in 75% yield. Chloride/iodide exchange via Finkelstein exchange under refluxing conditions in dry acetone affords **7** in 85% yield. The aldehyde products **4**, **6**, and **7** were purified by chromatography using a silica column, and the structures were confirmed by HR-MS and NMR spectroscopy.

Compounds **1**, **2**, **4**, **6**, and **7** provide for a modular preparation of the compounds in Scheme 1 which contain distyrylbenzene fragments (Scheme 3). For example, Horner−Emmons−Wittig coupling between **1** and excess **4** using potassium *tert*-butoxide

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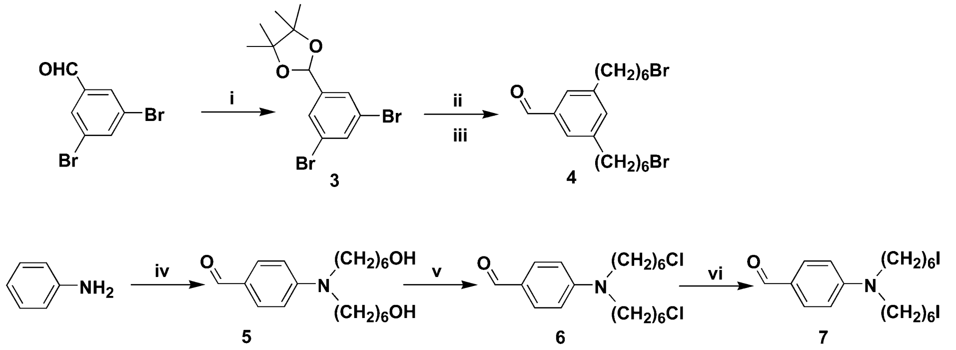
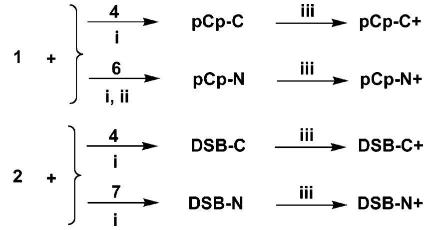
Scheme 2. Synthesis of 3,5-Bis(6′-bromohexyl)benzaldehyde (**4**), *N,N*-Bis(6′-chlorohexyl)-4-aminobenzaldehyde (**6**), and *N,N*-Bis(6′-iodohexyl)-4-aminobenzaldehyde (**7**)[a]



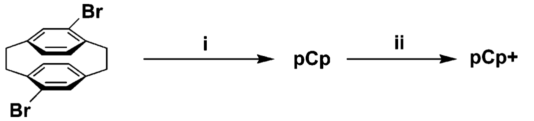
[a] Reaction conditions: (i) pinacol, trace TsOH, benzene, 48 h; (ii) *t*-BuLi, 1,6-dibromohexane, −78 °C to room temperature, 24 h; (iii) HBr, THF/H_2O, 60 °C, 24 h; (iv) 6-chloro-1-hexanol, *n*-butanol, K_2CO_3, reflux, 4 days; (v) $POCl_3$, DMF, 100 °C, 2 h; (vi) NaI, dry acetone, reflux, 2 days.

Scheme 3. Synthesis of **PCp-C**, **PCp-C+**, **PCp-N**, **PCp-N+**, **DSB-C**, **DSB-C+**, **DSB-N**, and **DSB-N+**[a]



[a] Reaction conditions: (i) *t*-BuOK, dry THF, 0 °C, 6 h; (ii) NaI, dry acetone, reflux; (iii) $N(CH_3)_3$, THF/H_2O, RT, 24 h.

Scheme 4. Synthesis of **PCp** and **PCp+**[a]



[a] Reaction conditions: (i) *t*-BuLi, 1,6-dibromohexane, −78 °C to room temperature, 24 h; (ii) $N(CH_3)_3$, THF/H_2O, RT, 24 h.

in THF at 0 °C provides **pCp-C** in 67% yield. Formation of the ionic water-soluble **pCp-C+** is achieved via quaternization with trimethylamine in a mixed solvent of THF and water with a yield of 91%. The analogous procedures for **pCp-N**, **pCp-N+**, **DSB-C**, **DSB-C+**, **DSB-N**, and **DSB-N+** are shown in Scheme 3. Full details can be found in the Supporting Information.

The synthesis of the “core-only” derivatives **pCp** and **pCp+** begins with the pseudo-*para* derivative 4,16-dibromoparacyclophane.[40] As shown in Scheme 4, two-fold lithium−halogen exchange of 4,16-dibromoparacyclophane using *t*-BuLi, followed by quenching with a large excess of 1,6-dibromohexane, provides **pCp** in 16% yield. Treatment of **pCp** with excess trimethylamine in THF/H_2O provides **pCp+**.

Table 1. Summary of Spectroscopic Data for **DSB** and **pCp**-Based Chromophores in Different Solvents

compd/solvent	λ_{abs} (nm, eV)	λ_{PL} (nm, eV)	τ_{meas} (ns)	Φ^a	τ_{int} (ns)
DSB-C/toluene	361, 3.43	389, 3.19[b]	0.9	0.70	1.3
DSB-C/DMSO	365, 3.40	393, 3.16[b]	1.3	0.69	1.8
DSB-C+/DMSO	364, 3.41	391, 3.17[b]	1.3	0.60	2.1
DSB-C+/water	356, 3.48	387, 3.20[b]	1.6	0.70	2.3
DSB-N/toluene	410, 3.02	450, 2.76	1.1	0.93	1.2
DSB-N/THF	410, 3.02	461, 2.69	1.2	0.77	1.5
DSB-N/DMSO	420, 2.95	506, 2.45	1.5	0.63	2.4
DSB-N+/DMSO	420, 2.95	506, 2.45	1.5	0.87	1.8
DSB-N+/water	408, 3.04	561, 2.21	1.7	0.24	6.9
pCp-C/toluene	396, 3.13	454, 2.73	2.2	0.75	2.9
pCp-C/THF	394, 3.15	458, 2.71	3.1	0.77	4.0
pCp-C/DMSO	399, 3.11	473, 2.62	4.9	0.50	9.8
pCp-C+/DMSO	397, 3.12	471, 2.63	4.9	0.60	8.2
pCp-C+/water	392, 3.16	496, 2.50	12.2	0.52	23.5
pCp-N/toluene	434, 2.86	486, 2.55	1.7	0.75	2.3
pCp-N/THF	436, 2.84	495, 2.51	2.2	0.67	3.3
pCp-N/DMSO	445, 2.79	536, 2.31	3.8	0.57	6.7
pCp-N+/DMSO	445, 2.79	535, 2.32	3.8	0.58	6.6
pCp-N+/water	435, 2.85	553, 2.24	0.5	0.04	12.5
pCp/hexanes	200, 6.20	345, 3.59	*c*	0.03	
pCp+/water	200, 6.20	352, 3.52	*c*	0.02	

[a] The quantum yield was measured using fluorescein and 9,10-diphenylanthracene as the references, with an estimated error of ±5%. [b] The first vibronic peak is reported rather than λ_{max}. [c] Laser source not available for the fluorescence lifetime measurement.

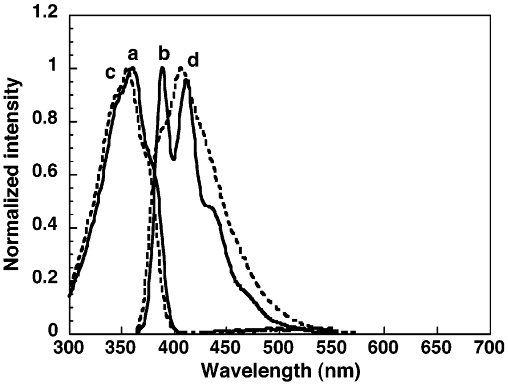


Figure 1. Normalized absorption (a) and PL (b) for **DSB-C** in toluene (solid lines) and absorption (c) and PL (d) for **DSB-C+** in water (dashed lines). All fluorescence spectra were obtained by excitation at λ_{abs}.

Absorption and Fluorescence Spectroscopy. Table 1 summarizes the spectroscopic data obtained for the compounds in this study. *We note that for the remainder of the paper the spectra of neutral compounds are reported in toluene, while those of the charged compounds are reported in water, unless otherwise stated.* The absorption and photoluminescence (PL) spectra of **DSB-C** and **pCp-C** are shown in Figures 1 and 2, respectively. The absorption maximum (λ_{abs}) of **DSB-C** is 361 nm and the PL maximum (λ_{PL}) is 389 nm. The PL of **DSB-C** contains vibronic structure and displays a Stokes shift characteristic of distyrylbenzene chromophores in nonpolar solvents.[41] The most prominent differences in the absorbance of **DSB-C**

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(40) Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3527.

(41) Renak, M. L.; Bartholomew, G. P.; Wang, S.; Ricatto, P. J.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 7787.

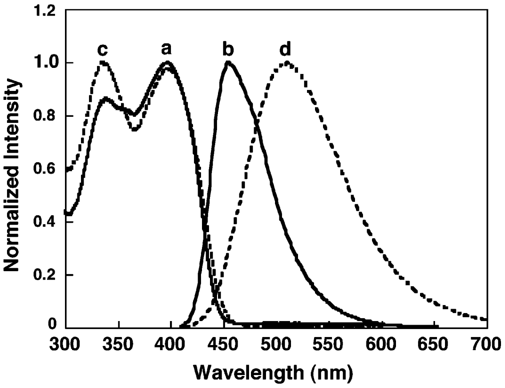

Figure 2. Normalized absorption (a) and PL (b) for **pCp-C** in toluene (solid lines) and absorption (c) and PL (d) for **pCp-C+** in water (dashed lines). All fluorescence spectra were obtained by excitation at λ_{abs}.

versus **pCp-C** is the red-shifted λ_{abs} of **pCp-C** (396 nm) and the "double hump" appearance of the absorption for **pCp-C** in the 300−450 nm range, which reflect the through-space electronic exchange between the two **DSB** fragments.[29] For a 1×10^{-6} M solution, the vibronic structure in the PL spectra is better defined in **DSB-C** than in **pCp-C**, which is consistent with the monomeric versus dimeric nature of the two structures. The photoluminescence quantum efficiencies for **DSB-C** (70%) and **pCp-C** (75%) are similar.

Figures 1 and 2 also contain the absorption and PL of **DSB-C+** and **pCp-C+**. The spectra of **DSB-C+** are similar to those of **DSB-C**, except for a broadening of the PL, which blurs the vibronic fine structure (Gaussian peak shape analysis reveals the first vibronic peak of **DSB-C** in toluene and **DSB-C+** in water to be 390 and 384 nm, respectively; see Supporting Information). In the case of the **pCp-C**/**pCp-C+** pair, there is a negligible change in absorption; however a substantial red-shift in PL is observed for **pCp-C+**. That the λ_{PL} of **pCp-C+** is 42 nm (0.23 eV) red-shifted relative to **pCp-C** is the first indication that the through-space, or "phane", state localized primarily on the [2.2]paracyclophane core shows a stronger solvatochromic effect, relative to the distyrylbenzene excited state.

As described previously,[37] the structurally related pairs **DSB-O**/**DSB-O-** and **pCp-O**/**pCp-O-** show similar trends to those described for their **DSB-C**/**DSB-C+** and **pCp-C**/**pCp-C+** counterparts, indicating that the alkoxy substitution pattern at the meta positions of the aromatic ring does not influence greatly the ground state and excited state energies. Additionally, possible interactions between the oxygen atoms and solvents, such as hydrogen bonding, do not obviously perturb the optical properties of the "**O**" series. For both the "**C**" series and the "**O**" series, there are no dramatic changes in quantum efficiencies with variations of solvent polarity.

The PL of **pCp-C** and **pCp-C+** are identical in DMSO with $\lambda_{PL} = 472 \pm 1$ nm (Figure 3). This solvent is of intermediate polarity, between water and toluene, and can dissolve both the neutral and charged molecules. Similar PL spectra in DMSO (and DMF) were observed for each neutral/charged pair of structures, i.e., **DSB-C**/**DSB-C+**, **DSB-N**/**DSB-N+,** and **pCp-N/pCp-N+**. On the basis of this information, we attribute changes in the PL spectra of structurally related chromophore pairs (which differ only in the charge of the pendant groups) to the interactions of the conjugated organic fragments with the solvent medium. In other words, the charged ionic groups on the periphery of the molecular structure necessary for solubility in water do not perturb the excited state energies.[42]

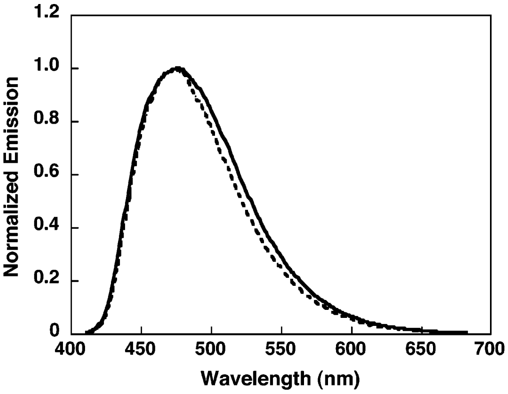

Figure 3. Normalized PL spectra for **pCp-C** (dashed line) and **pCp-C+** (solid line) in DMSO. All fluorescence spectra were obtained by excitation at λ_{abs}.

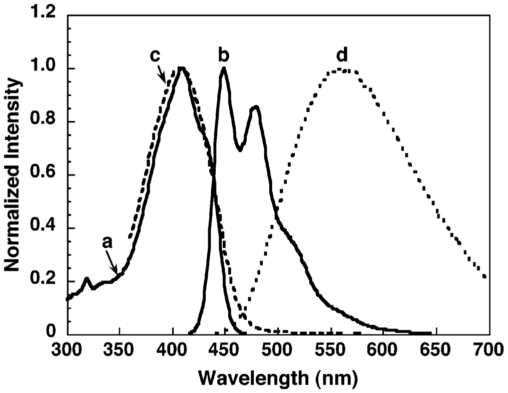

Figure 4. Normalized absorption (a) and PL (b) for **DSB-N** in toluene (solid lines) and absorption (c) and PL (d) for **DSB-N+** in water (dashed lines). All fluorescence spectra were obtained by excitation at λ_{abs}.

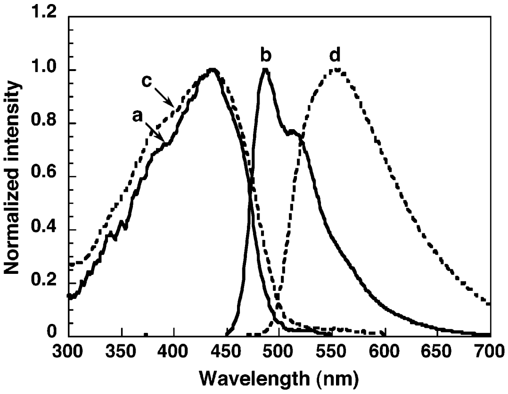

Figure 5. Normalized absorption (a) and PL (b) for **pCp-N** in toluene (solid lines) and absorption (c) and PL (d) for **pCp-N+** in water (dashed lines). All fluorescence spectra were obtained by excitation at λ_{abs}.

Figures 4 and 5 show the absorption and PL spectra of **DSB-N** and **pCp-N**. For **DSB-N**, $\lambda_{abs} = 410$ nm and the emission displays vibronic structure with $\lambda_{PL} = 450$ nm. It is immediately obvious that both the absorption and PL of **DSB-N** are red-shifted relative to **DSB-C**. This difference is attributed to the strong electron-donating properties of the amino group.[43] For

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(42) Pond, S. J. K.; Tsutsumi, O.; Rumi, M.; Kwon, O.; Zojer, E.; Brédas, J.-L.; Marder, S. R.; Perry, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 9291.

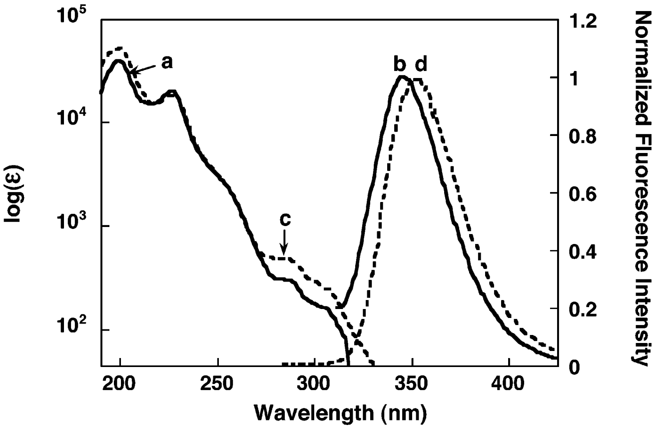

Figure 6. Log-scale absorption (a) and normalized PL spectra (b) for **pCp** in hexanes and log-scale absorption (c) and normalized PL (d) for **pCp+** in water. The PL spectra were obtained by excitation at 240 nm.

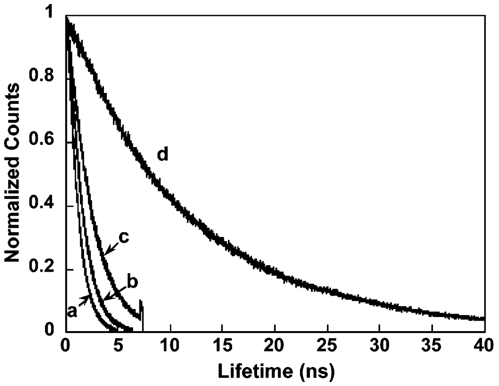

Figure 7. Fluorescence intensity decays of (a) **DSB-C** in toluene, (b) **DSB-C+** in water, (c) **pCp-C** in toluene, and (d) **pCp-C+** in water.

DSB-N, there is a progressive red-shift in λ_{PL} and decrease in quantum yields with increased solvent polarity (Table 1). For example, on going from toluene to DMSO, λ_{PL} shifts from 450 to 506 nm and the corresponding quantum efficiencies drop from 93% to 63%. Absorption maxima are less sensitive to solvent polarity, indicating that the solute−solvent interactions are of lesser importance in the ground state. This behavior is well known and can be attributed to a solvent stabilization of an excited state with charge transfer character.[44,45]

The absorption maximum of **pCp-N** is 24 nm red-shifted relative to **DSB-N** and does not change to an appreciable extent when measured in different solvents (Table 1).[33a] The PL of **pCp-N** ($\lambda_{PL} = 486$ nm) is noticeably red-shifted from that of the parent **DSB-N** ($\lambda_{PL} = 450$ nm), and the PL red-shifts for both compounds with increasing solvent polarity. This trend is different relative to **pCp-C/DSB-C**. As will be discussed later, these data provide evidence that the excited state in **pCp-N** is most likely localized on the distyrylbenzene arm.

Figures 4 and 5 also contain the absorption and PL of **DSB-N+** and **pCp-N+**. The absorption of **DSB-N+** is similar to that of **DSB-N**. However, there is a red-shift of 111 nm in the PL for **DSB-N+** ($\lambda_{PL} = 561$ nm) and a lower quantum efficiency (24%) as compared to **DSB-N** (93%). Similar to the **DSB-N+/DSB-N** pair, a red-shift of 67 nm is observed in the λ_{PL} of **pCp-N+**, as compared to **pCp-N**. The quantum efficiency changes from 75% for **pCp-N** to 4% for **pCp-N+**. It is interesting to note that both **DSB-N+** and **pCp-N+** have structureless emission and very similar λ_{PL}. The more pronounced sensitivity of **pCp-N+** relative to **pCp-C+** suggests that the **pCp-N+** excited state contains more charge transfer character or that it is substantially more sensitive to solvent polarity and polarizability.

The absorption and PL spectra of **pCp** in hexanes and **pCp+** in water are shown in Figure 6. Larger oscillator strengths denote allowed transitions, and both **pCp** and **pCp+** show allowed electronic transitions at 200 and 227 nm, a weakly allowed transition at 255 nm, and forbidden transitions at 287 and 306 nm. These data are in good agreement with previously observed spectra[25,26c] and theoretical analysis[26b] for the absorption spectra of [2.2]paracyclophane.

Comparison of the absorption spectra of **pCp/pCp+** shows that the peaks are fairly insensitive to the solvent, indicating that the electronic description of the ground states is similar. However, for **pCp** in hexanes, $\lambda_{PL} = 345$ nm, while in water, the λ_{PL} for **pCp+** occurs at 352 nm. The lower energy PL frequency for the paracyclophane core in more polar media provides further evidence of the solvatochromism of the “through-space” state.

Fluorescence Lifetime Measurements. Fluorescence intensity decay measurements provide information complementary to the steady state data and give insight into excited state dynamics.[4] In this section, we compare the fluorescence decay properties of the **pCp** derivatives with those of their parent **DSB** counterparts in different solvents.

The emission intensity decays of **DSB-C** and **DSB-C+**, as measured using single photon counting techniques, are shown in Figure 7. Table 1 contains both the lifetime obtained from decay measurements (τ_{meas}) and the intrinsic, or natural, lifetime (τ_{int}) for each chromophore. The τ_{int} is calculated using the formula $\tau_{int} = \tau_{meas}/\Phi$, where Φ is the quantum yield of the chromophore. **DSB-C** has τ_{int} of 1.3 ± 0.2 ns, while $\tau_{int} = 2.3 \pm 0.2$ ns for **DSB-C+**. The difference for a distyrylbenzene chromophore without strong acceptor or donor groups as a function of solvent is therefore small. Fluorescence intensity decay curves for **pCp-C** and **pCp-C+** are also shown in Figure 7. Similar to **DSB-C**, **pCp-C** also has a relatively short τ_{int} of 2.9 ± 0.3 ns. However, **pCp-C+** has a τ_{int} of 24 ± 2 ns. This longer lifetime can be used to infer that the through-space state, which has a low oscillator strength,[28] participates more strongly in the description of the excited state.

The τ_{int}s of **DSB-N**, **pCp-N**, **DSB-N+,** and **pCp-N+** follow a different trend. The τ_{int} value (1.2 ± 0.1 ns) of **DSB-N** is similar to that of **DSB-C**, while **DSB-N+** has a $\tau_{int} = 6.9 \pm 0.7$ ns. Similar to **pCp-C**, **pCp-N** displays a relatively short τ_{int} (2.3 ± 0.2 ns). However, **pCp-N+** has a natural lifetime of $\tau_{int} = 12 \pm 1$ ns, which is considerably shorter than that of **pCp-C+**. In the Discussion section we show that these differences in τ_{int} values for the different chromophores can be used to gauge the relative contributions of through-bond and through-space states in the description of the emissive state.

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(43) (a) Rumi, M.; Ehrlich, J. E.; Heikal, A. A.; Perry, J. W.; Barlow, S.; Hu, Z.; McCord-Maughon, D.; Parker, T. C.; Röckel, H.; Thayumanavan, S.; Marder, S. R.; Beljonne, D.; Brédas, J.-L. *J. Am. Chem. Soc.* **2000**, *122*, 9500. (b) 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.

(44) Sarker, A. M.; Strehmel, B.; Neckers, D. C. *Macromolecules* **1999**, *32*, 7409.

(45) Strehmel, B.; Sarker, A. M.; Malpert, J. H.; Strehmel, V.; Seifert, H.; Neckers, D. C. *J. Am. Chem. Soc.* **1999**, *121*, 1226.

From Table 1, it can be seen that for each pair of related structures **pCp-C/pCp-C+** and **pCp-N/pCp-N+**, there is a clear progression toward longer τ_{int} values with increasing solvent polarity, with the “carbon only” **pCp-C/pCp-C+** molecules being more sensitive.

Discussion

Schemes 3 and 4 provide a straightforward modular access to [2.2]paracyclophane derivatives that contain distyrylbenzene chromophores on the top and bottom “decks” of the core structure and that are soluble in solvents ranging from alkanes to water. The key steps are the Horner−Emmons−Wittig reaction of **1** with benzaldehydes **4** and **6**, which ultimately yield **pCp-C** and **pCp-N**. Ionic versions **pCp-C+** and **pCp-N+** are produced in near quantitative yields by treatment of **pCp-C** and **pCp-N** with excess trimethylamine. Removal of unreacted trimethylamine does not pose a problem because of its low boiling point. Modification of these steps, starting with **2**, provides for the parent distyrylbenzene chromophores. Compound **pCp** is generated via double lithiation of 4,16-dibromo-[2.2]paracyclophane, followed by quenching with 1,6-dibromohexane. Finally, trimethylamine and **pCp** provide **pCp+**.

From a structural point of view, the **pCp-X** (where **X** = **O**, **C**, **N**) molecular series can be thought of as two **DSB-X** chromophores held in close proximity by virtue of the [2.2]-paracyclophane core.[28] Differences in optical properties between structurally related monomers and dimers stem from the through-space electronic delocalization, or electron exchange, across the center ring of the **DSB-X** structure.[29] As shown in Figure 3 and Table 1, we find that there are no measurable differences in the absorption or fluorescence spectra when one compares the neutral version of a molecule to its charged counterpart (i.e., **pCp-C** vs. **pCp-C+**), in the same solvent. The cationic quaternary groups and anionic sulfonate functionalities, together with their corresponding counterions, do not play an important role in determining the energies of the excited states.

DSB-C and **DSB-C+** are the most basic distyrylbenzene structures in this study. Their PL maxima (λ_{PL}) are not influenced by the properties of the solvent. The absence of a solvatochromic effect is consistent with the similar charge distribution of the ground state and the emitting state.[41] The values calculated for the intrinsic lifetimes (τ_{int}) are also quite similar (1.3 ns for **DSB-C** and 2.3 ns for **DSB-C+**). In contrast, for **pCp-C** and **pCp-C+**, the spectra change as a function of solvent. On going from toluene to water the λ_{PL} red-shifts by approximately 42 nm (0.23 eV) and the τ_{int} increases from ~3 to ~24 ns. Therefore, by creating the possibility of delocalization across the [2.2]paracyclophane bridge, one observes an emitting state that is more sensitive to solvent polarity[46] and has a lower oscillator strength.

Figure 6 shows that the PL spectra of **pCp** and **pCp+**, which are essentially alkyl-substituted [2.2]paracyclophane cores, display a solvatochromic effect. Like **pCp-C** and **pCp-C+**, neither **pCp** nor **pCp+** has functionalities available for hydrogen bonding, which strongly suggests dependence on the solvent polarity. Since the λ_{PL} of **pCp+** in water is 7 nm (0.07 eV) red-shifted relative to **pCp** in hexanes, we infer a more pronounced polarization or charge transfer component in the emitting state relative to the ground state.

There is a strong similarity between the solvent effects on **pCp-C** and **pCp-C+**, and the solvatochromism of the pyrene and naphthalene excimers, which has been studied in detail.[47] For these excimers in nonpolar solvents, different solvation energies have been attributed primarily to dispersion interactions, which result from fluctuations in the instantaneous dipole moments of the solvent and the solute molecules, and the solute transition dipole moment contribution. In polar solvents one needs to also consider the solvent Stark effect, which describes the motion of solvent dipoles around the emissive molecules.[48] The solvent dependence of the emission frequency, in conjunction with the fact that excimers are nonpolar,[49] indicates that the spectral shifts result from differences in polarizability between the excimer and the dissociative ground state.

Extension of the results from naphthalene and pyrene excimer studies to the solvatochromism of **pCp** implies that the excited state of **pCp** is more polarizable than the ground state (which is not dissociative by virtue of its covalent structure). Similarly, for **DSB-C**, the absence of measurable solvent dependence of the fluorescence spectra implies that the ground and emissive states have similar polarizabilities. We also note that the solvent stabilization energy as determined by the energy difference in the λ_{PL} of **pCp** and **pCp+** in hexanes and water, respectively (0.07 eV), is smaller than that observed in **pCp-C**/**pCp-C+** (0.23 eV), which suggests that the polarizability of **pCp-C**/**pCp-C+** is further enhanced through its more extended π-conjugated system. For **pCp-O** and **pCp-O-**, a similar explanation may be offered.

A qualitative summary of the electronic structure of bichromophoric [2.2]paracyclophane compounds, shown in Scheme 5, is necessary to understand the effect of solvent on τ_{int}.[28c,29a] In Scheme 5, the characteristics of the S_1 and S_2 electronic states of the dimer can be approximated and understood as a combination of two states: one that is similar to that of the parent chromophore (**TB**) and another which contains delocalization between the two monomers and is largely localized on the [2.2]paracyclophane core (**TS**). The **TB** abbreviation is used to highlight typical through-bond π conjugation, while **TS** refers to the through-space delocalization across the transannular gap.[50] Three different structural situations have been encountered and studied previously. Compound **A** contains two stilbene units in close proximity. The main absorption band corresponds to that of the stilbene framework. A lower energy state exists (S_1), which has a much weaker oscillator strength, is primarily located on the internal core, and has mostly **TS** character. Absorption, followed by internal conversion, populates the S_1 state.

In situation **B**, two distyrylbenzene chromophores are contacted via their *terminal* aromatic rings. Within this structure, the excited state is more stable when localized along the

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(46) The fluorescence spectrum of **pCp-C** in dodecane is identical to that measured in hexanes (see Supporting Information). Since the polarizability of dodecane is significantly larger (α = 22.8 Å^3) than that of hexanes (α = 11.8 Å^3), we propose that the dipole of the solvent plays the major role in the solvatochromic shifts. See: (a) Bosque, R.; Sales, J. *J. Chem. Inf. Comput. Sci.* **2002**, *42*, 1154. (b) Böttcher, C. J. F. *Theory of Electric Polarization*; Elsevier Scientific Publishing Co.: Amsterdam, 1973.

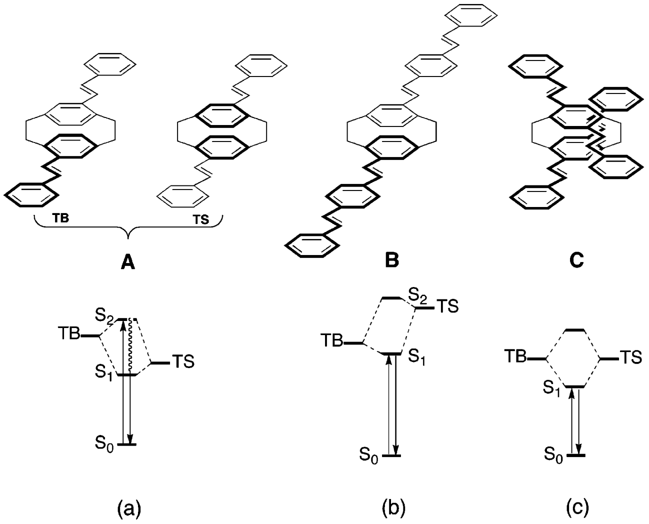
(47) (a) Castanheira, E. M. S.; Martinho, J. M. G. *Chem. Phys. Lett.* **1991**, *185*, 319. (b) Castanheira, E. M. S.; Martinho, J. M. G. *J. Photochem. Photobiol. A: Chem.* **1994**, *80*, 151.

(48) Suppan, P.; Ghoneim, N. *Solvatochromism*; The Royal Society of Chemistry: Cambridge, U.K., 1997.

(49) Barltrop, J. A.; Coyle, J. D. *Principles of Photochemistry*; John Wiley and Sons: Chichester, England, 1978.

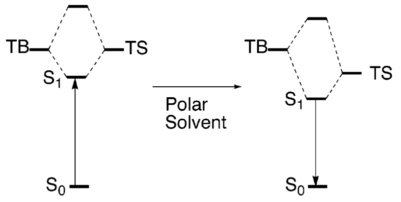
(50) The **TS** state localized on the [2.2]paracyclophane core contains a degree of $\pi-\sigma-\pi$ delocalization via the ethylene bridges; however it arises primarily due to cofacial $\pi-\pi$ delocalization. See refs 28c and 29a.

Scheme 5. Qualitative Electronic Description of Bichromophoric [2.2]Paracyclophane Molecules[a]



[a] (a) In **A**, absorption occurs via the stilbene fragment, as shown by excitation from S_0 to S_2. Internal conversion populates S_1, which is primarily **TS**, and emission occurs from there. (b) In **B**, **TB** (chromophore) is of lower energy, relative to **TS**. (c) The regiochemistry of the interchromophore contact in **C** results in an S_1 state with substantial mixing of **TB** and **TS**.

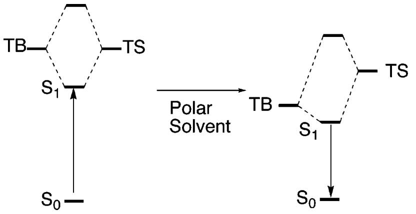
Scheme 6. Qualitative Description of the Effect of Polar Solvents on the **PCp-C**/**PCp-C+** Emissive State



distyrylbenzene framework, with **TS** being higher in energy. The properties of **B** are thus similar to those of the parent distyrylbenzene framework, with little perturbation of the emission frequency and fluorescence lifetimes. Finally, in situation **C**, two distyrylbenzene chromophores are contacted via their internal ring. This geometry causes mixing of **TB** and **TS** and gives rise to an electronic structure that is delocalized throughout the entire molecule.

On the basis of the solvatochromism observed in Figures 1−7, the previous characterization of solvent effects on aromatic excimers,[47] the insensitivity toward solvent polarizability,[46] and the electronic structures described in Scheme 5, it is possible to account for the dependence of τ_{int} of **pCp-C** and **pCp-C+** on solvent polarity, as shown in Scheme 6. In a nonpolar solvent, the description is similar to that in Scheme 5c, with the emitting S_1 state containing substantial **TB** and **TS** mixing. Increasing solvent polarity leaves **TB** relatively unperturbed (recall the lack of solvatochromism for **DSB-C**/**DSB-C+**), but lowers the **TS** energy level (as in the case of **pCp**/**pCp+**). As the energy difference of these states increases, the S_1 state becomes more **TS**-like and it acquires a smaller oscillator strength. Therefore, the longer τ_{int} value of **pCp-C+** in water, relative to **pCp-C** in toluene, is due to the stabilization of **TS** and its greater participation in the description of S_1. When going from a nonpolar to a polar solvent, the electronic structure of the molecule becomes more like situation **A** in Scheme 5a. Similar arguments can be put forth for **pCp-O**/**pCp-O-**.

Scheme 7. Qualitative Description of the Effect of Polar Solvents on the **PCp-N**/**PCp-N+** Emissive State



We now turn our attention to the nitrogen-containing compounds. For **DSB-N** and **DSB-N+**, there is a strong solvatochromic effect. The red-shifted PL with increased solvent polarity,[51] as well as the loss in fluorescence quantum yields, reflects the intramolecular charge transfer character of these compounds[52] due to the electron-rich terminal amino groups. That vibronic structure appears in the fluorescence spectra of both **DSB-N** and **pCp-N**, together with the fact that **DSB-N+** and **pCp-N+** have similar PL maxima and τ_{int}, indicates that S_1 is mainly described by **TB**, which is located on the donor-substituted distyrylbenzene fragment (Scheme 7).

Conclusion

The series of compounds **pCp-C**/**pCp-C+** and **pCp-N**/**pCp-N+** and the constituent structures **pCp**/**pCp+**, **DSB-C**/**DSB-C+**, and **DSB-N**/**DSB-N+** allow for a dissection of the problem of how solvents of different polarities influence through-space and through-bond delocalized fragments. We find that for a given neutral/charged pair, the PL properties are identical when in the same solvent, which implies that the ionic groups are not responsible for spectral differences. The **pCp-C** system shows a solvent-induced red-shift in PL and an increase in fluorescence lifetime, which do not occur in the parent **DSB-C** chromophore. That information, in conjunction with the solvatochromic effect in **pCp**/**pCp+**, indicates that the through-space state created by electron exchange across the [2.2]paracyclophane core is susceptible to solvent polarity.[46] Analogy to excimer solvatochromism suggests that this solvent effect is not due to a charge transfer component in the excited state, but rather to a more polarizable electronic structure. The solvent Stark effect is further enhanced with increased conjugation, which is known to increase polarizability. The lowering of the **TS** energy by water makes its participation in the S_1 description for **pCp-C+** more pronounced, which decreases the oscillator strength and increases the fluorescence lifetime. A more complete analysis for the reason of the increased polarizability awaits a formal theoretical treatment. Similar PL properties are observed for the **DSB-N/DSB-N+** and **pCp-N/pCp-N+** pairs, suggesting the solvatochromic behavior is dominated by the charge transfer component of the distyrylbenzene chromophore.

Experimental Section

Optical Properties. All spectroscopic measurements were performed using spectral grade solvents from Aldrich. UV−visible absorption spectra were recorded on a Shimadzu UV-2401 PC dual beam

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(51) The possible participation of solvent polarizability has not been evaluated at this point.

(52) (a) 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, C.; Webb, W. W.; Wu, X.-L.; Xu, C. *Science* **1998**, *281*, 1653. (b) de Souza, M. M.; Rumbles, G.; Samuel, I. D. W.; Moratti, S. C.; Holmes, A. B. *Synth. Met.* **1999**, *101*, 631.

spectrometer. Photoluminescence spectra were obtained on a PTI QuantaMaster fluorometer at a detection angle of 90° relative to the excitation source. The solutions had concentrations between 1×10^{-6} and 1×10^{-5} M. Quantum efficiencies were determined relative to 9,10-diphenylanthracene in cyclohexane[53] and freshly prepared fluorescein (in aqueous 0.1 M NaOH),[54] with quantum efficiencies of 91% and 92%, respectively. The error associated with this technique is estimated to be ±5%. Fluorescent lifetime measurements were performed using a time-correlated single-photon-counting technique (TCSPC).[55] The PL was excited by laser pulses with a duration of nearly 120 fs, produced via the second-harmonic generation process from the output of an ultrafast Ti:sapphire regenerative amplifier. The luminescence was dispersed in a spectrometer and detected by a micro channel-plate photomultiplier tube (MCP PMT; Hamamatsu R3809U-51). MCP PMT output and trigging signal from a fast photodiode were connected to a SPC-300 TCSPC board (Beker & Hickl), which performed the statistical analysis of the photon flux and restored the fluorescence transients. TCSPC data were filtered numerically to remove electrical ringing noise and were deconvoluted from the instrument response.

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Supporting Information Available: Detailed synthetic procedures and characterization for all compounds, along with the fluorescence spectra of **pCp-C** in dodecane and hexanes and Gaussian curve fitting of the fluorescence of **DSB-C** and **DSB-C+** in various solvents. This material is available free of charge via the Internet at http://pubs.acs.org.

JA044326+

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(54) Magde, D.; Wong, R.; Seybold, P. G. *Photochem. Photobiol.* **2002**, *75*, 327.
(55) O'Connor, D. V.; Phillips, D. *Time Correlated Single Photon Counting*; Academic Press: London, U.K., 1984.