Acc. Chem. Res. **2001,** *34,* 30−39

Bichromophoric Paracyclophanes: Models for Interchromophore Delocalization

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Received June 8, 2000

ABSTRACT
The electronic delocalization between chromophores in the solid is an important parameter to optimize when designing organic materials for optoelectronic applications. The [2.2]paracyclophane framework allows for the synthesis of well-defined, nonfluxional molecules that bring together two chromophores into close proximity. From the photophysical properties of these molecules we can examine how the chromophore conjugation length, their relative orientation, and the regiochemistry of contact affects the electronic delocalization between the two subunits.

Introduction

A critical consideration for designing and optimizing organic materials relevant for optoelectronic technologies concerns the electronic communication between individual chromophoric subunits. It is well known that the relative orientation and distance between individual molecules in the solid affects electronic delocalization and therefore important bulk properties. For example, organic transistors with molecules properly aligned over long distances display better transport properties and lower operating voltages.[1] In polymer-based light-emitting diodes, ordered regions lead to excimer sites that lower the electroluminescence quantum yield.[2,3] Understanding and ultimately controlling the electronic delocalization between organic subunits remains a fundamental challenge for creating molecular electronic devices[4,5] capable of electronic switching by electric fields,[6] electromechanical forces,[7] or photoactive/photochromic[6,8] response. Advances in these phenomena, known collectively as molecular “nanotechnology”,[9] depend on an improved understanding of the interplay between orientation of molecules relative to one another, the photophysics of the individual chromophore, and the resulting electronic motion in the bulk.[10]

Typical applications of organic materials as device components involve amorphous thin films in which the molecular subunits experience a range of environments and which have poorly defined morphological irregularities.[11] Furthermore, because intermolecular energy migration is facile in the bulk, the optical properties under study may be dominated by only a small fraction of the sample.[12] These complications prevent us from examining how the environment surrounding a given chromophore affects the properties of interest. Even in solution, interchromophore collisions are trajectory-dependent events from which orientational factors are not obtained. The fate of photoexcitations in polymer chains, molecular solids, and aggregates remains an outstanding problem in photophysics. Well-defined model compounds that bring together optical fragments in a defined manner provide important insight into the nature of “through-space” delocalization.[13] We define “through-space” interactions as perturbations in molecular electronic structure caused by another chromophore via Dexter and/or Förster mechanism(s).[14,15]

A better understanding of interchromophore delocalization would make an impact beyond the confines of materials chemistry. The electronic communication between antennae and reaction centers in photosynthesis is a subject of intense research.[16] 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[17] and constitutes an area of substantial debate.[18]

These considerations have led to substantial efforts in confining chromophores within supramolecular structures that predetermine their spatial relationships. One approach connects oligonucleotides via stilbene dicarboxamide linkers. Formation of complementary sequences forces the close proximity of stilbene units.[19] Derivatization of stilbenes and other chromophores such that strong hydrogen-bonding synthons assemble “tapes” of close-proximity ensembles enables examination of aromatic−aromatic interactions.[20] Supramolecular assemblies of fatty acid monolayers also provide chromophore aggregates with well-defined structures.[21]

In this Account, we provide an overview of our work concerning well-defined paracyclophane molecules made to model interchromophore interactions in polymers and organic solids. This work was motivated by our studies on the photophysics of block copolymers containing polychromophores or conjugated polymer segments. The polymer work is reviewed briefly first. Subsequently, we examine the synthesis, optical characterization and theoretical description of paracyclophane molecules that are designed to connect a pair of chromophores within a rigid and precise structure.

Born in upstate New York, Glenn P. Bartholomew pursued a career in the field of photography before attending college. After five years at Eastman Kodak in Rochester, NY, he began studying chemistry. He received his B.S. in chemistry from the State University of New York at Geneseo in 1998. Now at the University of California, Santa Barbara, he is pursuing his Ph.D. in the group of Professor G. C. Bazan. His current research focuses on the organization of organic materials in the solid state and designing paracyclophane-based nonlinear optical materials.

Guillermo C. Bazan received a B.Sc. from the University of Ottawa in 1986 and a Ph.D. from MIT in 1990. After spending two years as a postdoctoral fellow at Caltech, he became as Assistent Professor of Chemistry at the University of Rochester. In 1998 he moved to the University of California, Santa Barbara, where he is Professor of Chemistry, Professor of Materials Science, and Director of the Center for Polymers and Organic Solids. His research interests concern the study of photophysical processes in organic materials and the design and synthesis of new organometallic complexes that catalyze polymerization reactions.

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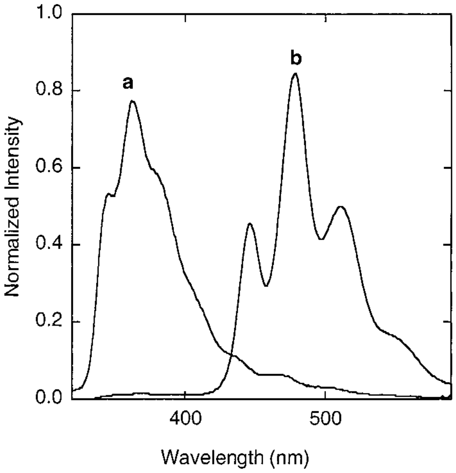
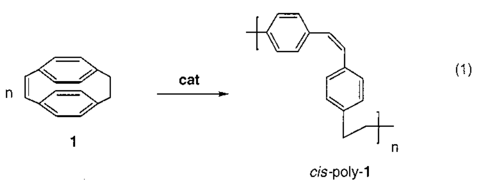


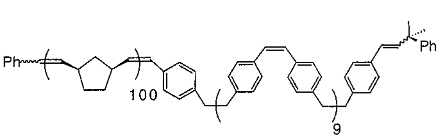
FIGURE 1. Normalized fluorescence spectra ($\lambda_{excitation}$ = 330 nm) of (a) random copolymer of NBE and **1** and (b) poly$\mathbf{1}_{12}$-*block*-polyNBE$_{200}$.

Polyparacyclophenes

The ring-opening metathesis polymerization of [2.2]-paracyclopan-1-ene (**1** in eq 1) affords *cis*-poly-**1**.[22] Poly-**1**



may be viewed as a stereoregular polychromophore made up of *cis*-stilbene components interconnected via ethylene linkages. These chromophores are oriented in the same direction with a strict configurational arrangement, and the percentage weight of polymer which is photoactive is higher than for typical all-organic polychromophores.[23] The living characteristics of the polymerization sequence make it possible to prepare block copolymers with norbornene and **1** by sequential addition of the two monomers (i.e., poly-$\mathbf{1}_{10}$-*block*-poly-NBE$_{100}$). When NBE (100 equiv) and **1** (10 equiv) are added



poly-$\mathbf{1}_{10}$-*block*-poly-NBE$_{100}$

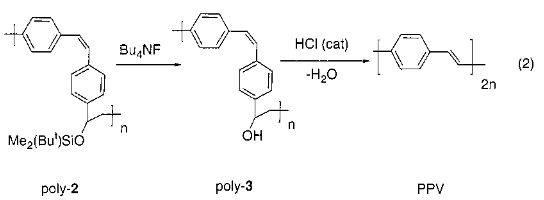
simultaneously, a polymer is obtained with a statistical distribution of stilbene fragments along a polynorbornene backbone.

A comparison of the fluorescence spectra from solutions of poly-$\mathbf{1}_{12}$-*block*-poly-NBE$_{200}$ and a random copolymer of NBE and **1** highlights the effect of chromophore close proximity within a polymer chain (Figure 1). Emission from the random copolymer is similar to that of *trans*-stilbene (Figure 1a). For poly-$\mathbf{1}_{12}$-*block*-poly-NBE$_{200}$, the frequency of emission is significantly red shifted and reminiscent of stilbene aggregates (Figure 1b).[21,24,25]

From an examination of optical properties versus polymer structure, it was determined that interchromophore delocalization along the polymer backbone is responsible for the low-energy emission. Aggregation is discouraged by attaching side groups to the polyparacyclophene segment. That both the *all-trans* and *all-cis* structures fail to show aggregate emission indicates the importance of secondary structure. Furthermore, a critical number of stilbene units in sequence is required. In the random copolymer of NBE and **1**, the greater separation between stilbene units prevents cooperativity.[23]

Extension to Conjugated Polymers

Polyparacyclophenes can be used to obtain defect-free and size-specific block copolymers of poly(*p*-phenylenevinylene) (PPV).[26] Polymerization of 9-[(*tert*-butyldimethylsilyl)oxy][2.2]paracyclophan-1-ene (**2**) leads to a material (poly-**2** in eq 2**)** that can be converted to PPV under mild conditions after deprotection to poly(9-hydroxy[2.2]-paracyclophan-1-ene) (poly-**3**). While there are various



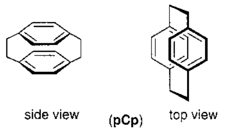
routes to conjugated PPVs,[27] there are two aspects that make the paracyclophene approach unique. First, the polymerization is living, which affords a narrow polydispersity and enables the synthesis of block copolymers. Second, dehydration from poly-**3** to the conjugated structure can be achieved under mild conditions. These features make poly-**2** a useful photoresist material for patterning PPV by using microlithographic techniques.[28]

Block copolymers containing a soluble poly-NBE segment attached to specific chain lengths of the typically insoluble PPV (i.e., PPV$_x$-*block*-poly-NBE$_{100}$, $x = 5-30$) can be studied spectroscopically in solution and allow for fluorescence quantum yield studies as a function of PPV units.[29] Most relevant to the discussion here is that increasing the concentration results in a decrease in emission quantum yield (Φ_f).[30]

These self-quenching results with poly-**2** provide an interesting contrast to the work with poly-**1**-*block*-poly-NBE. For poly-**1**, aggregation causes an increase in fluorescence quantum yield and a red shift in the emission relative to the stilbene components. Only changes in Φ_f occur for PPV$_x$-*block*-poly-NBE$_{200}$. These differences in photophysical response for structurally related polymer backbones led us to consider the problem of chromophore–chromophore delocalization.

Stilbenoid Dimers: Effect of Conjugation Length and Relative Chromophore Orientation

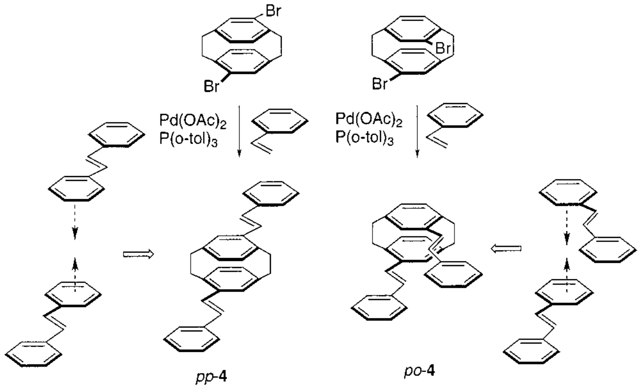
Conceptually, our goal was to generate a family of structurally well-defined, nonfluxional molecules which bring two photoactive units into close proximity. A molecule of this type would allow us to examine the perturbation on the optical properties of the components as a function of their spatial relationship and their chemical structure. The [2.2]paracyclophane[31–33] bridge was chosen to serve as the locus of interchromophore contact[34,35] since it enforces cofacial overlap of two phenyl rings, minimizes intramolecular motion, and has proven useful for the study of $\pi-\pi$ electron delocalization and ring strain in organic compounds.[31] For example, [2.2]paracyclophane (**pCp**) itself behaves as a pair of strongly interacting benzene rings and displays spectroscopic features that have been described as analogous to those of a benzene excimer.[36] More recent work on **pCp**[37] has detailed with greater precision the energy levels and electronic relaxation processes. Although the molecule is drawn as flat here for clarity, ring strain distorts the phenyl rings in the paracyclophane core. The distance between bridgehead carbons on opposing rings is $\sim$2.78 Å, while the distance between rings measured from the nonbridging carbon–carbon bonds is $\sim$3.09 Å.[33]



(**pCp**)

Pseudo-para- and pseudo-ortho isomers of distyryl[2.2]paracyclophane (*pp*-**4** and *po*-**4**, respectively, in Scheme 1) are obtained in good yield by treatment of the corresponding pseudo-ortho or pseudo-para dibromoparacyclophane[38] with styrene under Heck coupling conditions.[39] Compounds *pp*-**4** and *po*-**4** are configurational isomers, differing in the relative orientation of the pendant groups (i.e., 180° vs 60°). Each represents a dimer of stilbene with a different spatial arrangement between the two subunits.

Scheme 1



A protocol similar to that in Scheme 1, using 4,4′-*tert*-butylvinylstilbene instead of styrene, provides the pseudo-para and pseudo-ortho isomers of bis[4-(4′-*tert*-butylstyryl)styryl][2.2]paracyclophane (*pp*-**5** and *po*-**5**). These two molecules correspond to dimers of distyrylbenzene, a material which represents a small oligomeric unit from a PPV chain and which has found utility in device fabrication.[40]

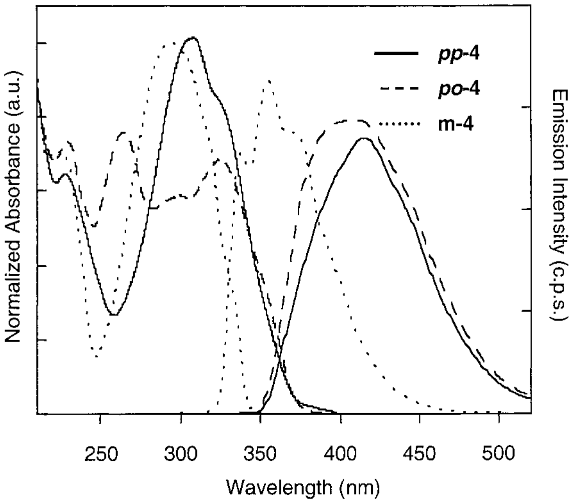
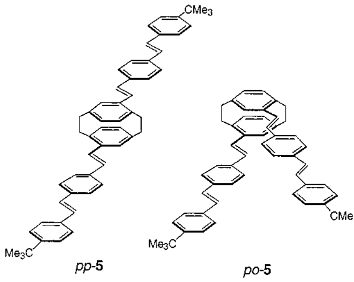
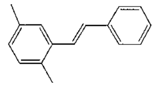


FIGURE 2. UV–vis absorption and normalized fluorescence spectra of *m*-**4**, *pp*-**4**, and *po*-**4**. Emission spectra were measured by exciting at the absorption maximum.



pp-**5** *po*-**5**

Figure 2 shows the absorption and emission spectra of *pp*-**4**, *po*-**4**, and the parent monomeric chromophore 2,5-dimethylstilbene (*m*-**4**). A slight red shift of 13 nm is observed in the absorbance spectrum of *pp*-**4** relative to that of *m*-**4**. More pronounced differences are evident in their respective emission spectra ($\lambda_{\max\,(\mathrm{em})}$(*pp*-**4**) = 412 nm vs $\lambda_{\max\,(\mathrm{em})}$(*m*-**4**) = 355 nm). Whereas *m*-**4** reveals vibronic definition, the broad band shape (which is maintained down to 77 K) and larger Stokes shift for *pp*-**4** mimic those of excimers.[36] The emission spectra of *po*-**4** and *pp*-**4** are similar. However, the close proximity of the two alkene units in *po*-**4** results in an apparent splitting of the absorbance band (λ_{abs} = 264 and 325 nm). Unlike an excimer, there is evidence for a ground-state electronic interaction between the subunits of *po*-**4**.[37]



m-**4**

Figure 3 shows the spectra for *pp*-**5**, *po*-**5**, and 4-(2,5-dimethylstyryl)-4′-*tert*-butylstilbene (*m*-**5**). The absorbance and emission spectra of *m*-**5** are characteristic of the distyrylbenzene chromophore. A red shift of ca. 15 nm is observed in the absorbance of the "dimers" *pp*-**5** and *po*-**5** relative to *m*-**5**. Note that unlike *pp*-**4** and *po*-**4**, the

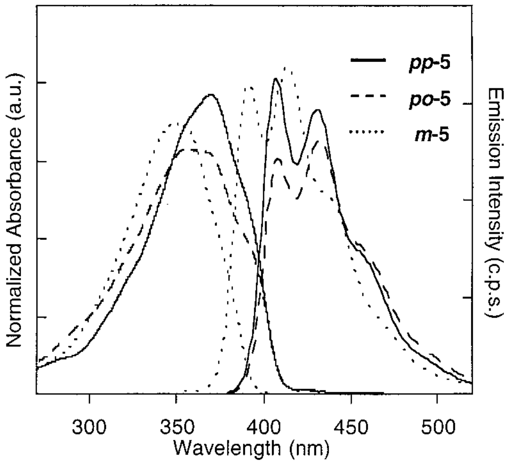
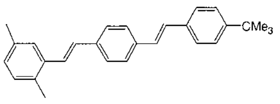


FIGURE 3. UV–vis absorption and normalized fluorescence spectra of *m*-**5**, *pp*-**5**, and *po*-**5**. Emission spectra were measured by exciting at the absorption maximum for each compound.

absorption spectra of *pp*-**5** and *po*-**5** are similar. Likewise, the emission data from *pp*-**5** and *po*-**5** are similar to those of *m*-**5** (~16 nm red shifted).



m-**5**

Qualitatively, these observations imply that, for *pp*-**4** and *po*-**4**, the electronic communication across the transannular gap leads to an excited state that is more stable than that of the isolated stilbene component. Holding two of the larger distyrylbenzene chromophores in close proximity results in negligible ground state interactions and in emission that closely resembles that of the parent chromophore. Note that these results are consistent with observations made with the block copolymers discussed above. Close contacts for stilbene result in red-shifted emission, while no aggregate emission is observed for the PPV blocks in PPV$_x$-*block*-poly-NBE$_{200}$.

Theoretical Analysis of Stilbenoid Dimers

To explore the electronic origin for the different optical responses, a collaborative effort with the chemical theory research group of Professor Shaul Mukamel at the University of Rochester was initiated. Mukamel's collective electronic oscillator (CEO) approach[41] has proven successful for describing the optical response of chromophore aggregates in real space and is ideally suited for analyzing the electronic structure of the paracyclophane dimers *pp*-**4**, *po*-**4**, *pp*-**5**, and *po*-**5**. This technique computes molecular vertical excitation energies and their oscillator strengths (which allows one to infer linear absorption spectra). In addition, the transition density matrices, or electronic modes, are calculated for each excited state. These matrices show relevant electronic motion when the molecule interacts with light in real space.[41]

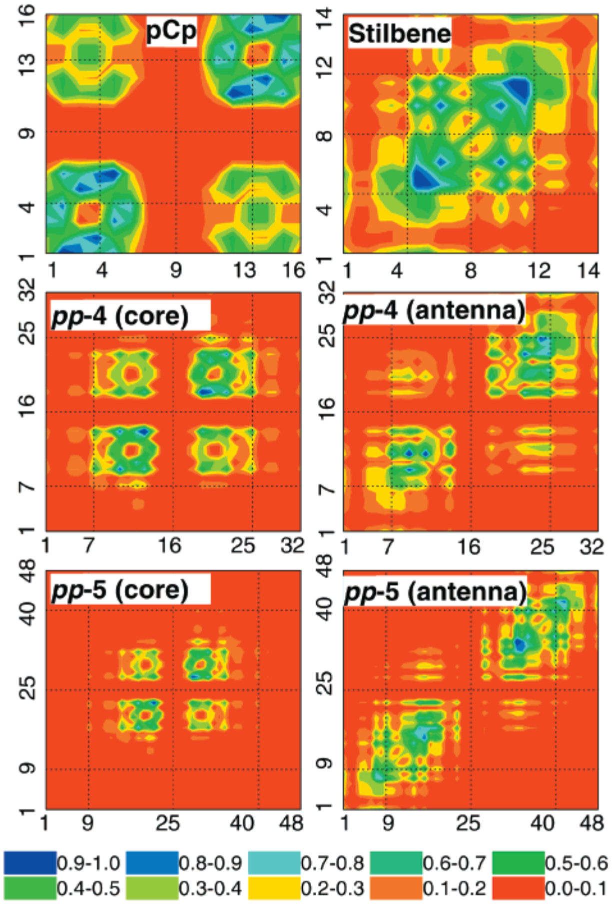
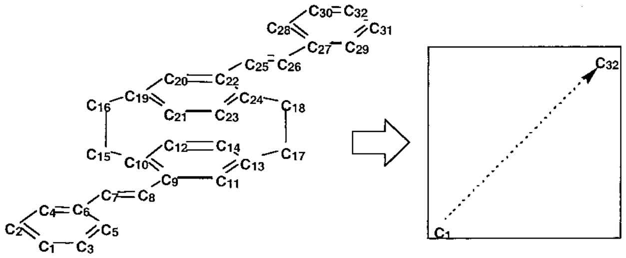


FIGURE 4. Contour plot of the density matrices calculated for **pCp**, stilbene, *pp*-**4**, and *pp*-**5** by the CEO method. The *x* and *y* axes correspond to the atom numbering scheme for each compound, which roughly follows the length of the molecule (see Scheme 2 for a representative numbering scheme of *pp*-**4**). The color scheme indicates the amplitude of probability for a change in charge density on each atom (*x* and *y* = *i*) or between atoms (off-diagonal elements) when going from the ground state to that excited state. The transitions correspond to the following frequencies: **pCp**, 3.95 eV; stilbene, 4.12 eV; ***pp*-4** (core), 2.91 eV; ***pp*-4** (antenna), 3.69 eV; ***pp*-5** (core), 2.91 eV; ***pp*-5** (antenna), 3.29 eV.

Indeed, by use of the CEO method all of the features in the absorption and emission spectra are faithfully replicated. The contour plots of the density matrices in Figure 4 have *x* and *y* axis labels representing each individual atom. Scheme 2 gives a representative numbering scheme along the length of the molecule for *pp*-**4**. For reference, this analysis was performed for both **pCp** and stilbene, and the results are shown as the top two panels in Figure 4. The intensity scale of the color scheme shown

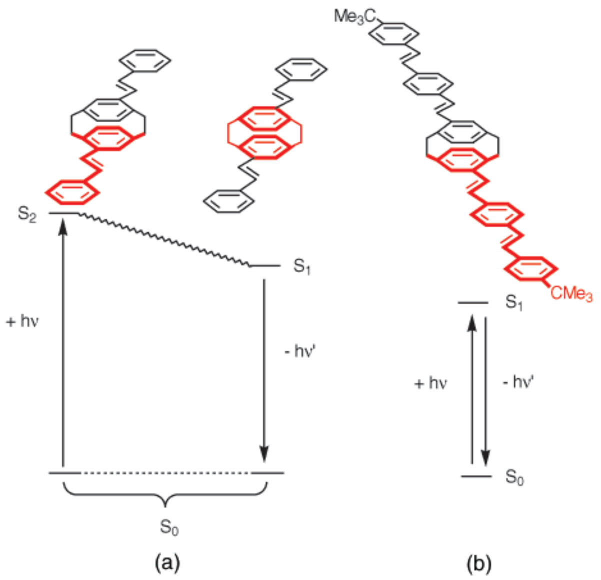
Scheme 2



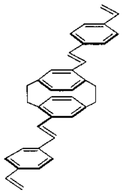
highlights the participation strength. From the diagonal element (*i*,*i*) one obtains the change in electron density at carbon *i* when going from the ground state to that excited state. The off-diagonal component (*i*,*j*) depicts the amplitude of probability for charge exchange between carbon *i* and carbon *j*. For *pp*-**4**, there are two possible excited states that roughly correspond to the isolated **pCp** moiety (labeled "core") and the chromophore (labeled "antenna") that is "dimerized" via the **pCp** bridge. The lowest frequency electronic mode corresponding to the lowest excited state in *pp*-**4** is the "core" state. Additionally, this mode has a vanishing oscillator strength. The first allowed mode corresponds to the antenna. Two excited states that can be segregated into modes localized on the **pCp** framework and the distyrylbenzene chromophore exist for the dimer *pp*-**5** as well. However, the fluorescence is dominated by the antenna mode, which is allowed and which has a lower energy.

Altogether, these results lead to the qualitative energy diagram for photoexcitation dynamics shown in Scheme 3. In all cases the most significant absorption is attributed to the "monomer" chromophore antenna, i.e., stilbene in the case of *pp*-**4** or distyrylbenzene in the case of *pp*-**5**. There is a second excited state to consider, namely one which mainly involves the **pCp** core. This state will be referred to as the "phane" state and contains the through-space delocalization.[35] Emission from this state is broad and featureless. Two situations may be encountered after photon absorption. For *pp*-**4**, the energy of the localized excitation is higher than that of the state containing the **pCp** core (a in Scheme 3). Internal conversion transfers the excitation from the localized "monomer", and emission takes place from the "phane" state. In analogy to interchromophore contacts in the bulk, this process mimics energy migration from an individual molecule to the "aggregated" site. Furthermore, the extinction coefficient for direct excitation from the ground state is weak. Population of the "phane" state should result in a relatively long-lived excited state, which is observed experimentally.[35] It is noteworthy that longer lifetimes also characterize the aggregate emission of poly-$\mathbf{1}_{10}$-*block*-poly-NBE$_{100}$ and conjugated polymers.[23,2a]

Scheme 3



The second situation arises when the energy of the "monomer" is lower than that of the corresponding "phane" state (b in Scheme 3). This is the case for vinylstilbene (i.e., **6**) and distyrylbenzene (i.e., **7** or *pp*-**5**/*po*-**5**). Under these circumstances, there is no driving force for "energy migration", the excitation remains localized, and there is therefore negligible difference between the spectra of the parent compound **5** and the dimers *pp*-**5** and *po*-**5**.



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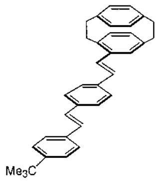

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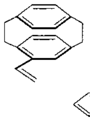
"Phane" State Delocalization

A series of molecules with limited conjugated lengths were prepared to examine the extent to which the "phane" state is affected by exocyclic substituents. Molecules **8**–**10** were synthesized by modification of methods used in the synthesis of *pp*-**4** and *pp*-**5**.



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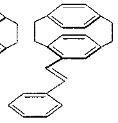

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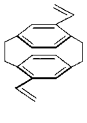

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Radiative relaxation from **8**–**10** in solution at room temperature shows the two characteristic features of the "phane" state, namely structureless emission and long fluorescence lifetime. Figure 5 collects the fluorescence spectra for a series of molecules that emit from this state. The progressive red shift in the emission maxima with increasing conjugation length and number of substituents

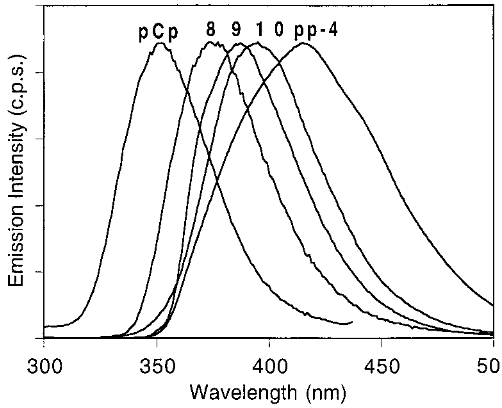


FIGURE 5. Collected emission data for compounds **pCp**, **8**, **9**, **10**, and *pp*-**4**.

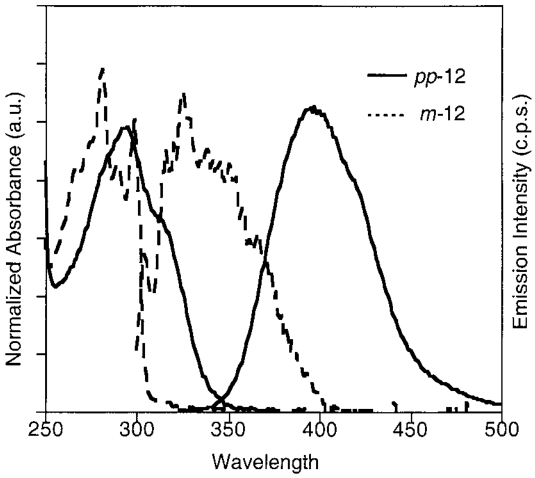
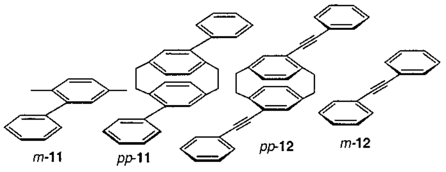


FIGURE 6. UV–vis absorption and normalized fluorescence emission data for *m*-**12** and *pp*-**12**.

on the paracyclophane core indicates that the effective conjugation length for the "phane" state includes partial delocalization onto the exocyclic substituents. As the conjugation length of the pendant chromophore increases, however, the electronic state localized on the attached chromophores becomes lower in energy, as seen in the case of *pp*-**5**.

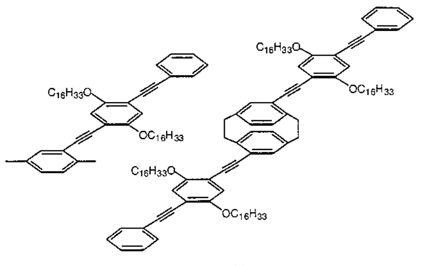
Other Chromophores

Scheme 3 serves as the basis to describe the optical properties of other chromophore dimers. Compounds *pp*-**11** and *pp*-**12** correspond to dimers of biphenyl and diphenylacetylene, respectively, and were prepared using standard coupling methods.[42] Both *pp*-**11** and *pp*-**12** show


m-**11** *pp*-**11** *pp*-**12** *m*-**12**

broad emission spectra that are considerably red shifted compared to their monomeric counterparts *m*-**11** and *m*-**12** ($\lambda_{\max\ (\mathrm{em})}$ for *m*-**11**, 325 nm; for *pp*-**11**, 390 nm; for *m*-**12**, 340 nm; for *pp*-**12**, 405 nm; see Figure 6 for pp-**12** vs *m*-**12**). These spectral signatures are consistent with absorption by the chromophore arms followed by internal conversion to the "phane" state.

Extension of the chromophore to model 1,4-bis(phenylethynyl)benzene (*m*-**13**) leads to results consistent with observations for *pp*-**5** and *m*-**5**. Figure 7 compares *pp*-**13** to the corresponding parent *m*-**13**. There is little difference in the emission of the "dimer" relative to the parent chromophore, demonstrating that the excitation remains localized on the absorbing fragment.



m-**13** *pp*-**13**

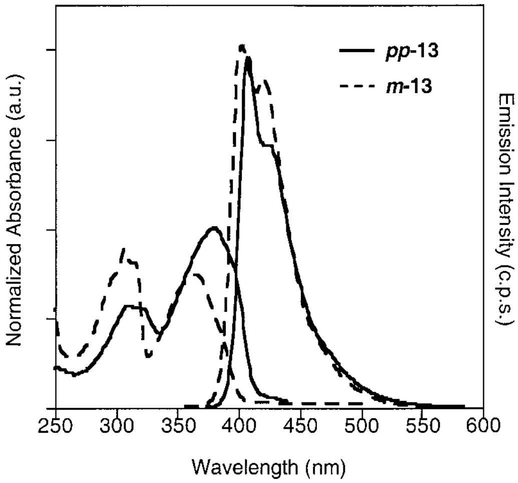
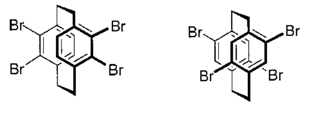


FIGURE 7. UV–vis absorption and normalized fluorescence emission data for *m*-**13** and *pp*-**13**. Emission spectra were measured by exciting at the absorption maximum for each compound.

Location of Interchromophore Contact

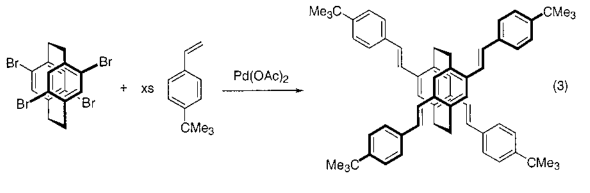
An important geometric parameter to consider when two chromophores approach each other is the location of contact. Until now, only contacts across the end rings of the chromophores have been considered. It was of interest to examine paracyclophane dimers that hold together oligophenylenevinylene chromophores via the central ring.[43] We will refer to this interaction as "criss-cross" delocalization to differentiate it from the "termini" contact probed by molecules *pp*-**4**, *po*-**4** and *pp*-**5**, *po*-**5**. These studies map the effect of contact regiochemistry on the photophysics of the pair.

Bromination of paracyclophane gives equal amounts of the isomeric tetrabromides 4,7,12,15-tetrabromo[2.2]paracyclophane (4,7,12,15-**Br$_4$pCp**) and 4,5,12,13-tetrabromo[2.2]paracyclophane (4,5,12,13-**Br$_4$pCp**). Separation by repeated crystallization in acetone affords the desired 4,7,12,15-**Br$_4$pCp** in 40% yield. The arms are constructed by Heck reaction under the phase-transfer conditions reported by Jeffrey.[44] For example, reaction of an excess of 4-*tert*-butylstyrene with 4,7,12,15-**Br$_4$pCp** in the presence of Pd(OAc)$_2$ for 4 days affords 4,7,12,15-tetra(*tert*-butylstyryl)[2.2]paracyclophane (*cc*-**14**; *cc* for criss-cross) in 55% yield (eq 3).[45]



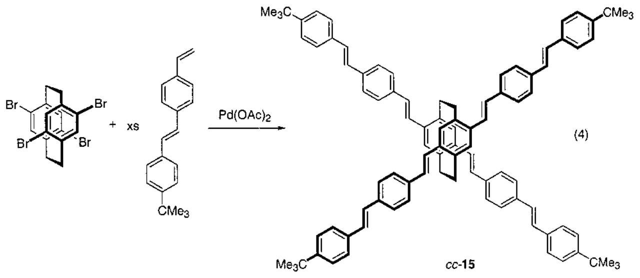
4,5,12,13-**Br$_4$pCp** 4,7,12,15-**Br$_4$pCp**

A similar approach starting with 4-(4-*tert*-butylstyryl)styrene provides the analogue of *cc*-**14** with increased conjugation length. Reaction of an excess of 4-(4-*tert*-

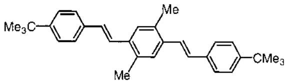


cc-**14**

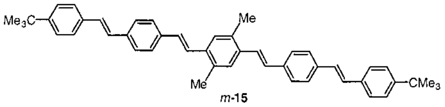
butylstyryl)styrene with 4,7,12,15-**Br$_4$pCp** in DMF using Pd(OAc)$_2$ invariably gave a mixture of coupling products in which the fourfold coupled product was the minor component. Twofold and threefold coupled intermediates precipitate out of solution because of their limited solubility in DMF. Improved yields are obtained using dimethylacetamide (DMA) under dilute conditions and 23 mol % of catalyst. Thus, reaction of 4-(4-*tert*-butylstyryl)styrene with 4,7,12,15-**Br$_4$pCp** in DMA affords 4,7,12,15-tetra(4-(4′-*tert*-butylstyryl)styryl)[2.2]paracyclophane (*cc*-**15** in eq 4) in 18% yield as a slightly soluble yellow powder.



The absorption and emission spectra of *cc*-**14** and *cc*-**15** are shown in Figures 8 and 9, respectively, together with the data corresponding to the monomeric components *m*-**14** and *m*-**15**.



m-**14**



m-**15**

Since both *cc*-**14** and *cc*-**15** exhibit similar optical properties, only those of *cc*-**15** will be discussed in detail. The absorption maximum for *cc*-**15**, appearing at 429 nm, is considerably red shifted from that of *m*-**15**, or even standard samples of PPV.[26] These observations are noticeably different from those corresponding to the termini dimers such as *pp*-**4** and *pp*-**5** and suggest considerable delocalization across the paracyclophane bridge.

Figure 10 shows the calculated electronic modes corresponding to the lowest excited states of *cc*-**15**. Most significant is the considerable delocalization across the entire molecule. In the termini contact pairs, the optical properties could be neatly explained in terms of excitations that migrated to the "phane" state (for short arms) or that remained localized in the chromophores (in the case of longer arms). Choosing a trajectory such that the inner rings are brought into close proximity prevents an analogous dissection of parts. The optical properties and electronic description of the criss-cross delocalized pairs indicate that the excitation is delocalized across the entire molecule. In a sense, there is strong mixing of the "phane" and the antenna or chromophore states.

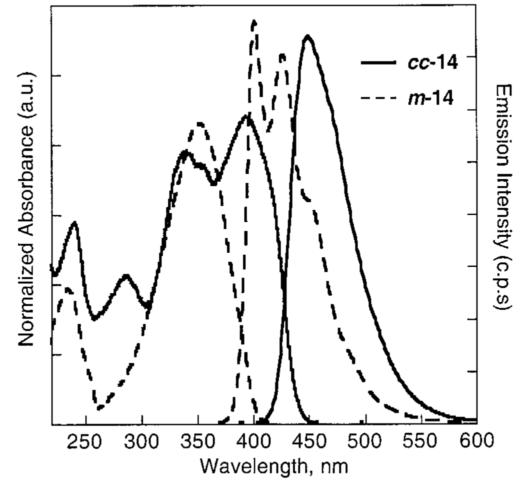


FIGURE 8. UV−vis absorption and normalized fluorescence emission data for *m*-**14** and *cc*-**14**. Emission spectra were measured by exciting at the absorption maximum for each compound.

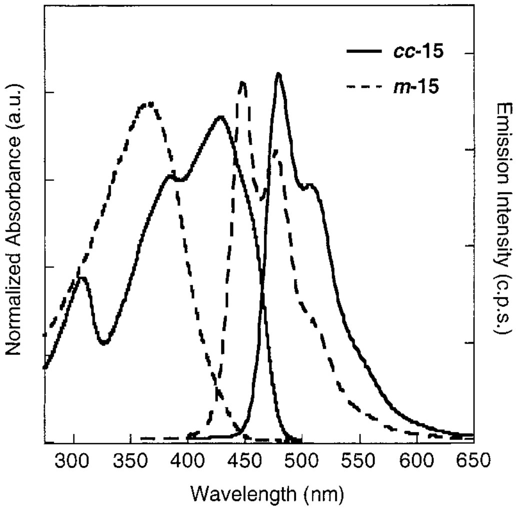


FIGURE 9. UV−vis absorption and normalized fluorescence emission data for *m*-**15** and *cc*-**15**. Emission spectra were measured by exciting at the absorption maximum for each compound.

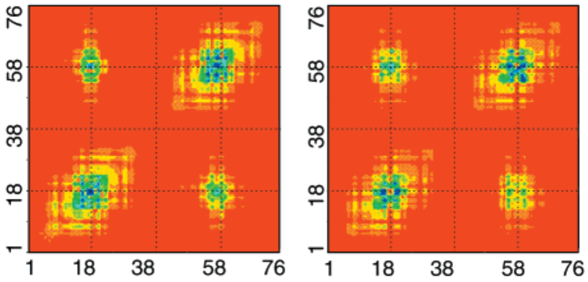


FIGURE 10. Contour plot of the density matrices calculated for the lowest states in *cc*-**15** by the CEO method. The transitions correspond to frequencies of 2.78 and 3.21 eV, left to right.

Insight into how the contact site leads to different levels of delocalization can be extracted from the atomic coef-

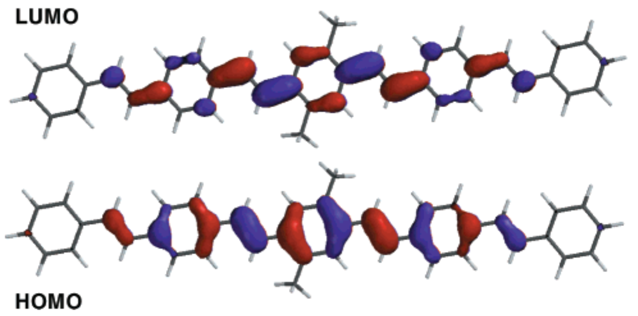


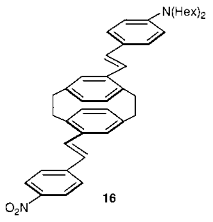
FIGURE 11. HOMO and LUMO density maps for an *m*-**15** analogue. The geometry was assumed to by fully planar, and single-point energies were calculated by the Hartree−Fock method with the 3-21G* basis set.

ficients of the HOMO and LUMO in the participating fragments.[46] As shown in Figure 11, both orbitals for *m*-**15** indicate strong participation of all carbon atoms in the central ring. The outer rings, however, contain nodes at the 3 and 5 positions, and less efficient electronic communication can be expected for the termini contact pairs. The criss-cross chromophores allow overlap of ring carbons that participate strongly in the HOMO and the LUMO.

Future Directions

The photophysics of the stilbene “dimers” (*pp*-**4**, *po*-**4**) make this molecular framework an interesting candidate for building quadratic nonlinear optical (NLO) chromophores. Typical organic NLO systems based on intramolecular charge transfer (ICT) from a donor toward an acceptor moiety through a π-system require a compromise in properties.[47,48] Most strategies to increase the degree of ICT require greater conjugation length. Although greater ICT typically leads to a greater nonlinearity in the optical response, the increased conjugation leads to a lower transparency in the spectral region of interest, limiting the potential usefulness of the material. Paracyclophane-based molecules may afford advantages in this tradeoff by generating a strong NLO response while providing a favorable displacement of the region of transparency.

Compound **16** was synthesized in an effort to examine the degree of ICT across the paracyclophane core with donor substitution at the terminal end of one stilbene unit and a terminal acceptor group on the other.[49] This molecule provides a unique opportunity to examine a well-defined “through-space” ICT system.



16

Hyperpolarizability measurements of **16** lead to a $\beta(0)$ static value that is 3 times higher than that for the parallel superposition of the two monosubstituted stilbenes. As expected, β-related properties are much more sensitive indicators of ICT than dipole moments or linear polarizability properties.[50] It appears that the paracyclophane core indeed leads to significant ICT while preserving transparency due to absorption attributable to the stilbene units rather than the larger system. These results suggest the possibility of extending the concept of ICT to multisubstituted systems whose quadratic NLO is derived in part from an octupolar design.[51] Our long-range goals are to utilize the paracyclophane core as a multidimensional tunneling barrier for applications such as NLO media and two-photon absorption. We also recognize the potential of the paracyclophane framework to build well-defined multidecker clusters of organic chromophores analogous to inorganic quantum-confined nanomaterials.

Summary

Paracyclophane derivatives that bring together conjugated organic fragments contain molecular features that mimic those of bichromophoric “aggregates”. The “phane” state derives stabilization from through-space delocalization between the top and bottom aromatic fragments. Depending on the conjugation length, and therefore the excited state energy, of the absorbing chromophore fragment, the excitation can stay localized on the absorbing fragment or migrate to the “phane” state. This internal conversion between the two states is analogous to energy migration from an isolated molecule to an aggregated site. Delocalization between fragments depends strongly on the regiochemistry of contact, and this dependence can be rationalized partly by examination of the molecular description of the participating fragments. It should be noted, however, that the electronic coupling between two chromophores connected by a paracyclophane core is stronger, relative to that between the two chromophores adjacent to each other in the bulk. Ring strain at the core brings the chromophores closer than van der Waals distances, thereby enabling stronger electronic communication. Initial examples indicate that intramolecular charge transfer across the paracylophane bridge could form the basis for designing new organic materials with enhanced nonlinear properties.

The authors are grateful to the NSF (DMR 9500627) and the ONR for financial support of this work and to Professor Shaul Mukamel (University of Rochester), Professor Joseph Zyss (Ecole Normale Supérieure de Cachan), and Dr. Sergei Tretiak (Los Alamos National Laboratories) for many useful discussions.

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AR9901568