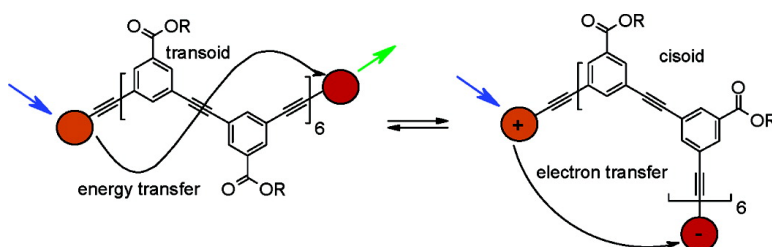


Supramolecular Control over Donor–Acceptor Photoinduced Charge Separation

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Supramolecular Control over Donor–Acceptor Photoinduced Charge Separation

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Abstract: A novel donor-bridge-acceptor system has been synthesized by covalently linking a *p*-phenylene vinylene oligomer (OPV) and a perylene diimid (PERY) at opposite ends of a *m*-phenylene ethynylene oligomer (FOLD) of twelve phenyl rings, containing nonpolar (*S*)-3,7-dimethyl-1-octanoxo side chains. For comparison, model compounds have been prepared in which either the donor or acceptor is absent. In chloroform, the oligomeric bridge is in a random coil conformation. Upon addition of an apolar solvent (heptane) the oligomeric bridge first folds into a helical stack and subsequently intermolecular self-assembly of the stacks into columnar architectures occurs. Photoexcitation in the random coil conformation, where the interaction between the donor and acceptor chromophores is small, results only in long-range intramolecular energy transfer in which the OPV singlet-excited state is transformed into the PERY singlet-excited state. In the folded conformation of the bridge, donor and acceptor are closer and their enhanced interaction favors the formation the OPV⁺-FOLD-PERY⁻ charge-separated state upon photoexcitation. As a result, the extent of photoinduced charge separation depends on the degree of folding of the bridge between donor and acceptor and therefore on the apolar nature of the medium. As a consequence, and contrary to conventional photoinduced charge separation processes, the formation of the OPV⁺-FOLD-PERY⁻ charge-separated state is more favored in apolar media.

Introduction

It is well established that electron-transfer processes occurring in peptides, proteins, or DNA depend on the specific structural features of the backbone that control the electronic coupling between the donor (D) and acceptor (A).^{1,2} For peptides, these not only include the distance, folding, and orientation,³ but also the dipole moments existing in helical peptides⁴ and the presence of hydrogen bonds.⁵ Changes in the secondary structure of the peptide interchromophoric bridge, induced by varying the solvent or temperature, are known to modulate the electronic interaction between donor and acceptor units.^{6,7} In nonbiological connected D–A dyads, modification of the conformation of a flexible bridge and the rate of electron transfer has been achieved

via metal coordination⁸ or photoisomerization.⁹ In recent years, there has been a considerable interest in foldamers, chain molecules that adopt a specific conformation in solution,

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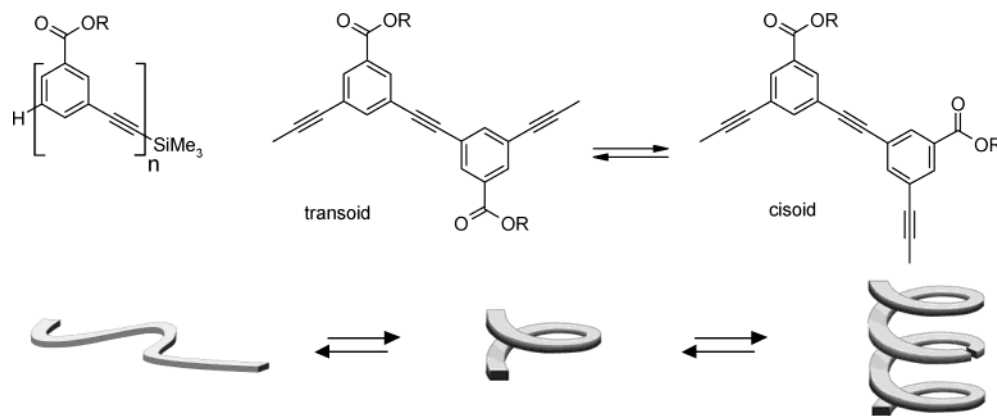


Figure 1. Transoid–cisoid equilibrium of oligo(*m*-phenylene ethynylene)s and schematic representations of the conformations of the FOLD oligomer upon increasing the volume percentage of poor solvent in good solvent (from left to right) as result of shifting the equilibrium to the right.

stabilized by noncovalent interactions.¹⁰ The unique control over the conformation of such foldamers by solvent, temperature, or via recognition and complexation of guest molecules makes these interesting candidates to use as bridges in D–A dyads that are sensitive to external stimuli.

Moore et al. have recently described that *m*-phenylene ethynylene oligomers (Figure 1) undergo a cooperative conformational transition in solution from a random state to a helical structure that involves π -stacking of aromatic residues in the backbone.^{11–16} This type of foldamer can go through conformational changes in solution by varying the polarity of the medium or the temperature, when it is of sufficient length ($n > 10$, n being the number of phenyl rings). This behavior arises from the difference in polarity between the aromatic hydrocarbon backbone and the side chains. Various techniques such as UV–vis, fluorescence, NMR, and ESR spectroscopy have

been used to study the solvophobic driven folding in solution in detail.¹¹ In a good solvent, the oligomer adopts a random coil conformation in which both transoid and cisoid conformations are present (Figure 1). When a poor solvent (for the backbone) is added, the oligomer folds into a helical stack by changing from transoid to cisoid conformations, keeping the side chains exposed to the solution and enabling stacking of the π -conjugated segments. This phenomenon has been found for oligomers with polar¹¹ and apolar¹⁵ side chains. Various strategies have been used to bias the helical twist sense of these foldamers, e.g., the use of chiral tethers in the oligomer chain,¹² diastereoselective complexation of chiral guests,¹³ and the use of side chains that contain a stereocenter by introduction of a methyl group.^{14,15} Even such small perturbation is enough to bias the helical twist. The folded state of these chiral oligomers often exhibits circular dichroism (CD) in the electronic absorption corresponding to the π system of the backbone. By increasing the solvophobic conditions, self-assembly of the helical *m*-phenylene ethynylene oligomers into larger stacks can occur (Figure 1).^{14b} Actually, for apolar side chain oligomers, the twist sense bias was only expressed when intermolecular aggregation of the stacks into columnar architectures takes place.¹⁵ The side chain chirality and the associated CD effect allow to monitor the supramolecular organization of these oligomers in solution and discriminate between the various stages of intra- and intermolecular self-assembly. X-ray diffraction (XRD) and transmission electron microscopy (TEM) have shown that in the solid state the foldamers can be present in two extreme packing motifs. A fully extended all-transoid conformation that packs into a lamellar structure or an all-cisoid structure that gives a hexagonally packed helical structure.¹⁶

We recently demonstrated that covalent and supramolecular dyads of oligo(*p*-phenylene vinylene) (OPV) donors and perylene diimide (PERY) acceptors exhibit photoinduced energy or electron transfer, depending on the extent of the electronic interaction between the D and A chromophores.^{17–20} Photoinduced charge separation is much more sensitive to the distance

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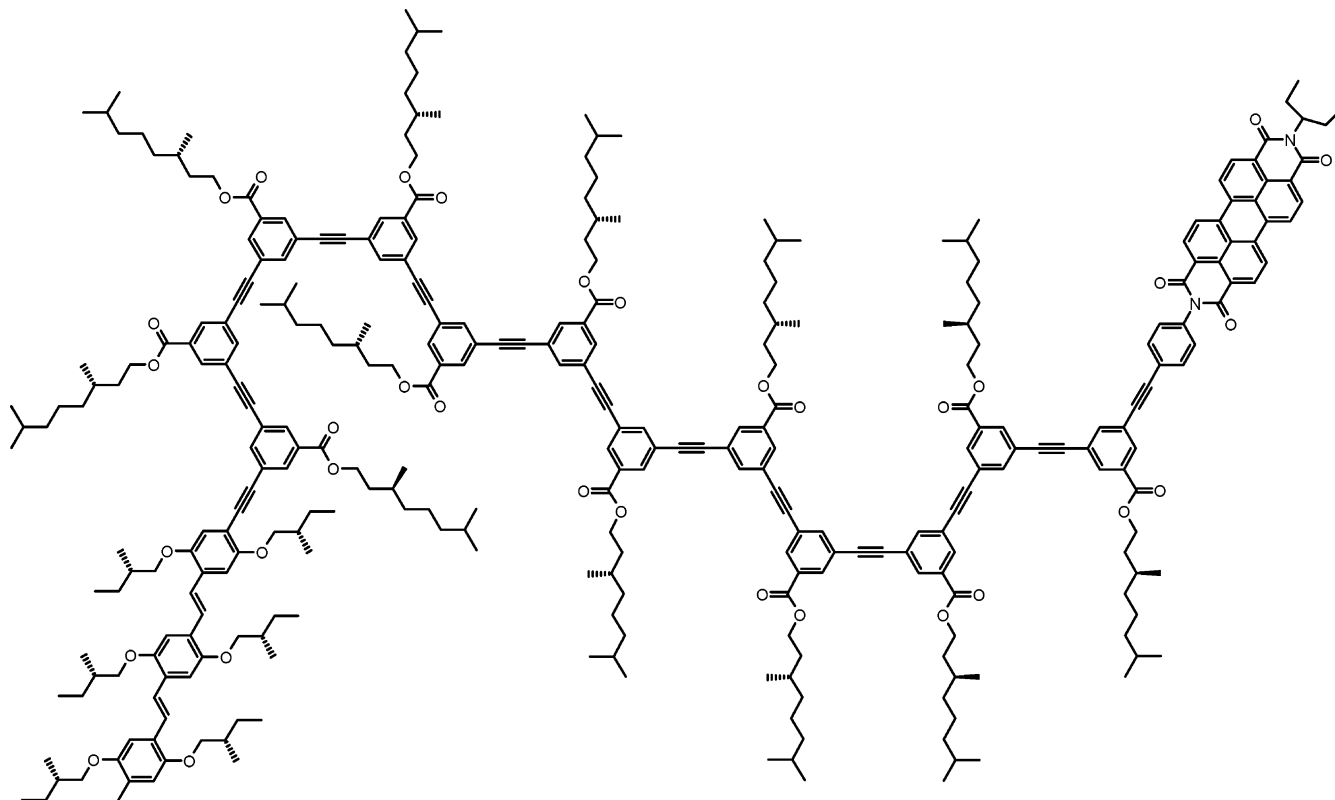


Figure 2. Structure of the OPV-FOLD-PERY dyad in a random coil conformation.

between the chromophores than long-range Förster singlet-energy transfer. In an attempt to direct and control the intramolecular photophysical process by a change in conformation only, we placed OPV and PERY chromophores at the termini of a *m*-phenylene ethynylene foldamer that consists of twelve phenyl rings carrying nonpolar chiral (*S*)-3,7-dimethyl-1-octanoyloxy side chains (OPV-FOLD-PERY, Figure 2). We compare the properties of the OPV-FOLD-PERY dyad, to model compounds in which either the donor or acceptor are missing, i.e. OPV-FOLD and FOLD-PERY. The conformational changes of FOLD bridge, induced by changing the polarity of the solvent, are monitored with UV-vis and CD spectroscopy to identify conditions of folded oligomers in solution. Photoluminescence studies of the different conformational states provide a measure of the interaction between donor and acceptor in the excited state and the discrimination between energy and electron transfer. We demonstrate that OPV-FOLD-PERY exhibits intramolecular long-range singlet-energy transfer in a random coil conformation and electron transfer in the folded state.

Results and Discussion

Synthesis. The bridged donor-acceptor system OPV-FOLD-PERY dyad **10** and the model compounds FOLD-PERY **7** and OPV-FOLD **9** have been synthesized according to the route depicted in Scheme 1 utilizing the synthetic approach previously developed for *m*-phenylene ethynylene (FOLD) oligomers.²¹ This synthesis of the FOLD bridge uses a doubly protected oligo(*m*-phenylene ethynylene)s [I-(Ar-C≡C)_{*n*}-H] as the key intermediate. The ethynylene is protected as the corresponding trimethylsilyl (-TMS) derivative and the aryl iodide as a

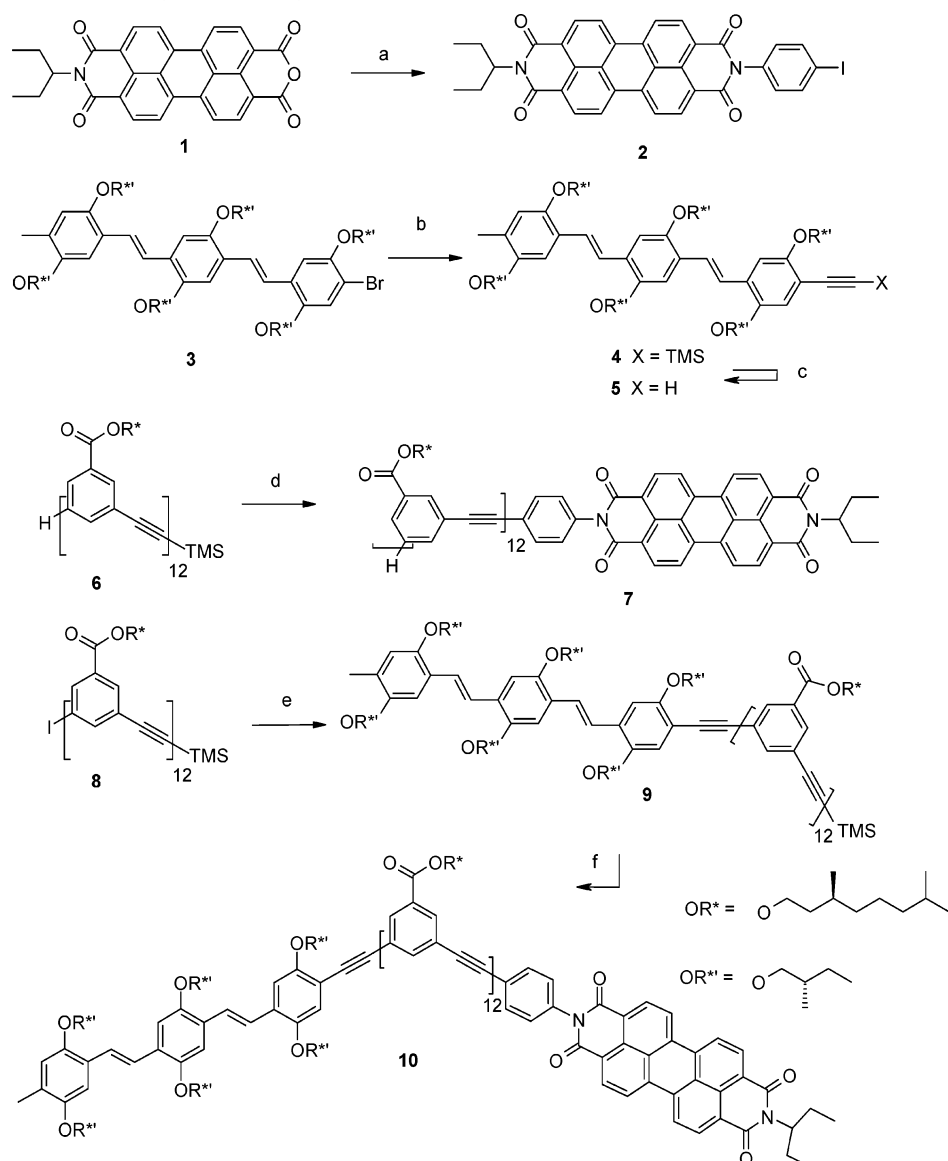
diethyltriazene (-N=N-NEt₂). This doubly protected [Et₂N₃-(Ar-C≡C)_{*n*}-TMS] oligomer can be selectively deprotected to the corresponding terminal acetylene (Et₂N₃-(Ar-C≡C)_{*n*}-H) with tetrabutylammonium fluoride (TBAF) or to the aryl iodide (I-(Ar-C≡C)_{*n*}-TMS) with methyl iodide. Coupling of these two products in a palladium-catalyzed Sonogashira coupling affords Et₂N₃-(Ar-C≡C)_{2*n*}-TMS, which is double in length but has exactly the same end group functionalities as the starting oligomer. By repetition, this double protecting group strategy enables a divergent growth of the folding oligomer. The actual synthesis of the chiral trimethylsilyl end-capped *m*-phenylene ethynylene dodecamer **6** (Ar-C≡C)₁₂-TMS and the corresponding iodinated dodecamer **8** I-(Ar-C≡C)₁₂-TMS that are used in this study has been described in detail in ref 15.

The functionalized model compounds (FOLD-PERY and OPV-FOLD) were obtained by coupling either a PERY or an OPV moiety to one of the bridge oligomers. Selective coupling of PERY and OPV at either side of the bridge yielded the OPV-FOLD-PERY dyad. To enable the linking of donor and acceptor chromophores to the foldamer via the palladium-catalyzed cross-coupling reaction, the OPV and the PERY chromophores were functionalized with ethynyl and iodine, respectively. As starting compounds we prepared perylene monoanhydride monoimide **1**²² and OPV **3**²³ as described previously. Iodine-functionalized perylene diimide **2** was obtained after reaction of 4-iodoaniline with perylene monoanhydride monoimide **1**. Coupling of trimethylsilylacetylene with OPV-bromide **3** and subsequent deprotection with tetrabutylammonium fluoride (TBAF) afforded the ethynyl end-capped OPV **4**. Model compound **7** (FOLD-

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Scheme 1. Synthesis of OPV-FOLD, FOLD-PERY, and OPV-FOLD-PERY^a

PERY) was obtained by coupling of iodoperylene diimide **2** with dodecamer **6**, in a Sonogashira reaction with in situ deprotection of the ethynyl functional group.²⁴ Reaction of **2** with previously deprotected dodecamer **6** resulted only in low yields due to the occurrence of a considerable amount of homocoupled **6**. Model compound **9** (OPV-FOLD) was obtained via reaction of ethynyl OPV **5** with the iodine functionalized foldamer **8**. An aliquot of OPV-FOLD **9** was further reacted with **2** (under similar conditions used to obtain PERY-FOLD **7**) to afford the OPV-FOLD-PERY bridged dyad **10** in low (9%) yield.

All compounds used in the photophysical investigations were characterized using ¹H NMR spectroscopy, mass spectrometry, and size exclusion chromatography. MALDI-TOF mass spectrometry established the correct mass of the compounds, together with less intense peaks corresponding to extra methylene groups

(M+12 and M+24, see Supporting Information, Figure S1).²⁵ For each of the compounds a single, symmetrical peak was obtained by size exclusion chromatography, revealing the absence of starting material or undesired longer adducts and that the compounds are highly monodisperse.

Absorption Spectroscopy. The UV–Vis absorption spectra of OPV-FOLD-PERY, OPV-FOLD, and FOLD-PERY in chloroform solution (Figure 3a) show the characteristic transitions of the FOLD bridge¹² at 288 and 304 nm, of the OPV donor at 432 nm, and of the PERY acceptor at 459, 489, and 527 nm. The spectrum of OPV-FOLD-PERY is a near superposition of the spectra of the individual OPV, FOLD, and PERY chromophores (Figure 3b). However, the para connectivity between the OPV and the FOLD bridge results in the extension of the conjugation length of the OPV moiety to the first phenyl

(25) The additional signals are due to the limited purity of (*S*)-3,7-dimethyl-1-octanol used for synthesizing the *m*-phenylene ethynylene bridge. The starting alcohol contained unintentionally a homologous impurity with an extra methylene group.

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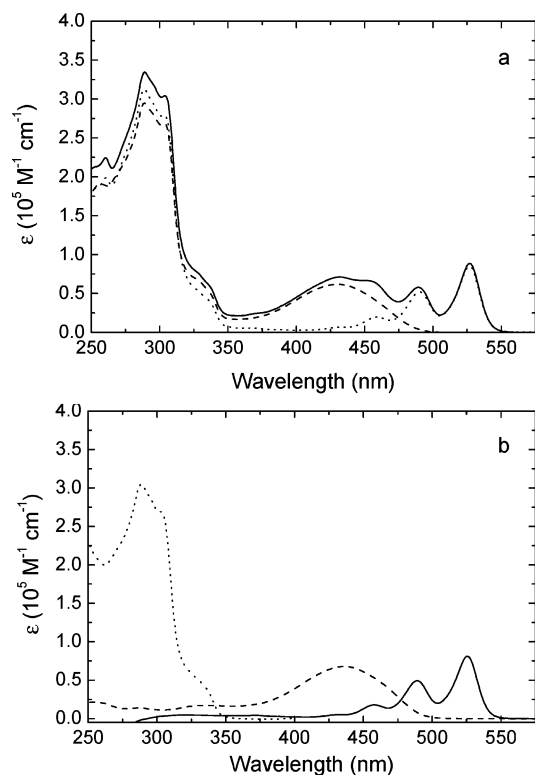


Figure 3. UV-vis absorption spectra of (a) OPV-FOLD-PERY (solid line), OPV-FOLD (dashed line), and FOLD-PERY (dotted line) in chloroform solution, and of (b) Model compounds *N,N'*-bis(1-ethylpropyl)perylene diimide (solid line, $\lambda_{\max} = 526$ nm, $\epsilon = 80\,900$ M $^{-1}$ cm $^{-1}$), methyl-end capped OPV (dashed line, $\lambda_{\max} = 436$ nm, $\epsilon = 68\,000$ M $^{-1}$ cm $^{-1}$),²⁶ and 12-FOLD bridge (**6**) (dotted line, ($\lambda_{\max} = 288$ nm, $\epsilon = 304\,500$ M $^{-1}$ cm $^{-1}$).

ring of the bridge. The meta linkage to the next ethynylene-phenylene segment disrupts further conjugation. As a result, the OPV absorption band of OPV-FOLD-PERY resembles closely that of an OPV oligomer with three vinylene bonds having $\lambda_{\max} = 436$ nm although the OPV moiety of OPV-FOLD-PERY only contains two vinylene bonds.²⁶ The transitions of FOLD bridge are identical to those previously published for the pure foldamers ($\lambda_{\max} = 288$ and 303 nm).¹⁵ Also the PERY chromophore is very much preserved after being connected to the bridge. The absorption spectrum is virtually identical to a perylene diimide dye carrying two 1-ethylpropyl substituents ($\lambda_{\max} = 458$, 489, and 526 nm).

The absorption spectrum of the FOLD bridge exhibits a shoulder at 304 and a peak at 288 nm in chloroform solution. Moore et al. have shown that the ratio of the absorbance of the shoulder (A_s) and the peak (A_p) is highly characteristic for the conformational state of the *m*-phenylene ethynylene foldamers, and supported this conclusion with results from fluorescence spectroscopy, NMR, ESR, XRD, and TEM studies.^{11–16} From these studies it is now well established that transoidal conformations result in a high A_s/A_p ratio, whereas cisoidal conformations lower the A_s/A_p ratio. The random-coil conformation, in which transoidal conformations persist, is therefore characterized by a high A_s/A_p ratio, whereas cisoidal conformations account for the formation of helices and a significant lower A_s/A_p ratio.^{11,15} The high A_s/A_p absorption ratio observed in chloroform solution indicates that in the FOLD bridge transoidal conformations

dominate for OPV-FOLD, FOLD-PERY, and OPV-FOLD-PERY and that the bridge is in a random coil conformation (Figure 4, state A).¹²

Folding in Chloroform/Heptane Mixtures. To establish the conditions at which the bridge folds, solutions of OPV-FOLD-PERY were prepared in chloroform/heptane mixtures of different composition and studied by means of UV-vis absorption and CD spectroscopy. With increasing amount of heptane in chloroform a decrease of the A_s/A_p ratio of OPV-FOLD-PERY (Figure 5) is observed, characteristic of folding of the bridge into a helically folded state (State B in Figure 4).¹² In addition, the shoulder at 304 nm and the peak at 288 nm observed in chloroform, undergo small shifts with increasing the heptane content. Starting at 80% heptane, a Cotton effect is observed in the UV region of the CD spectrum (Figure 5, inset) giving evidence of a bias in the twist sense of the helices. The appearance of optical activity is accompanied by a small blue shift of the FOLD absorption band. The fact that the CD effects are split into a positive and negative signal is consistent with exciton coupling as the source of chirality. Because the absorption spectra reveal essentially no conjugation of these *m*-phenylene ethynylene oligomers with increasing length,¹⁵ the simplest unit (phenyl-ethynyl-phenyl) can be considered as the excitonic unit. The CD effect can then be explained by the twisting of the dihedral angle of two ethyl-phenyl units at a central phenylene ring. In this view, the bias in the twist of the helices is induced by the chiral center on the side chains that will interact upon formation of a well-defined helical conformation and thereby transfer their chirality to the backbone. Nevertheless, the twist sense bias of these helices usually lags behind the initial folding of the oligomer, i.e., requires a larger fraction of the poor solvent to be added.^{14,15} In this view, the bias of the twist may be due to the highly apolar conditions, i.e., a “tightening” of the helix at higher heptane concentrations. However, the CD effect seems to occur simultaneously with the formation of intermolecular aggregation into columnar stacks, as inferred from absorption and fluorescence lifetime measurements (vide infra). The self-assembly of folded *m*-phenylene ethynylene oligomers into such helical columns exhibiting a CD effect has been described previously.^{14b,15} These columns have been identified as an intermediate architecture between helices in solutions and hexagonally packed columns of *m*-phenylene ethynylenes in the solid state.^{16b,c} Hence, we favor an interpretation of the CD effect at 80–90% heptane in terms of stacking of helices into columnar architectures (Figure 4, state C).

When the relative amount of heptane is increased beyond 90%, the overall FOLD absorption becomes less intense (hypochromicity), while the CD effect grows (Figure 5a). A similar hypochromicity has been observed for *m*-phenylene ethynylene oligomers with polar side chains in a polar solvent when the chromophores interact with one another in a stacked conformation.^{11h,13d,14b} Above 95% heptane, an unexpected inversion of the chirality in the region of the FOLD bridge occurs for the two compounds bearing a PERY chromophore (i.e., OPV-FOLD-PERY and FOLD-PERY). In the absorption spectrum of these two compounds, the FOLD chromophore now features a red-shifted broader absorption band and a sudden small increase of the A_s/A_p ratio is observed (Figure 5b). The inversion of chirality together with the loss of the isodichroic

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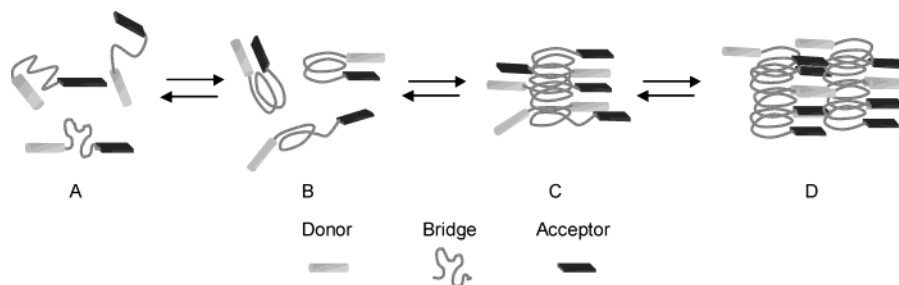


Figure 4. Schematic representation of the different conformational states of OPV-FOLD-PERY with decreasing polarity of the medium (from A to D). A: random coil; B: folded (helical) conformation; C: columnar stacks; D: interacting columns.

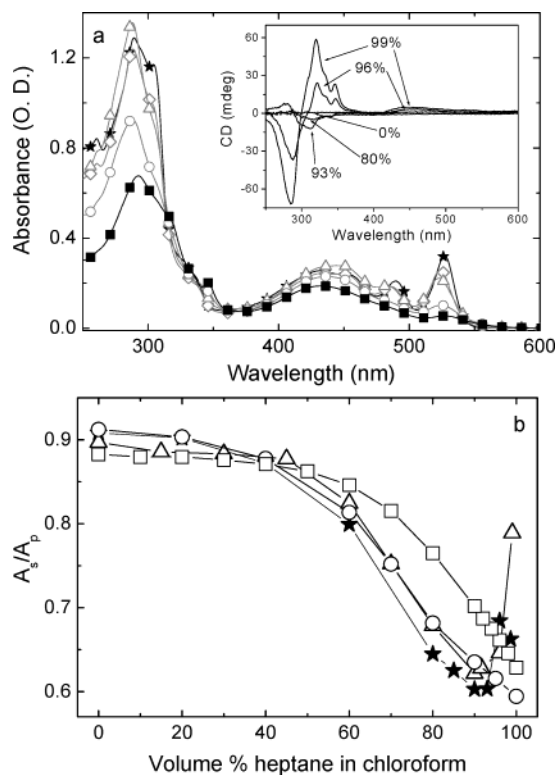


Figure 5. (a) UV/Visible spectra of OPV-FOLD-PERY (3.9×10^{-6} M) in 0% (solid star), 60% (diamond), 80% (triangle), 96% (circle) and 99% (solid square) volume heptane in chloroform. Inset: CD spectra of OPV-FOLD-PERY in heptane/chloroform solutions of different composition (the numbers denote volume percentage heptane in chloroform). (b) A_s/A_p ratios of OPV-FOLD-PERY (solid star), FOLD-PERY (open triangle), OPV-FOLD (open circle) and FOLD (open square) in chloroform/heptane solutions of different composition.

points observed for OPV-FOLD-PERY (Figure 4a, inset) and FOLD-PERY (See: Supporting Information, Fig. S2), at a high percentage of heptane, suggests that the helical columns start to interact with each other laterally, resulting in multi-columnar architectures with an opposite overall CD effect (Figure 4, state D).^{14b} Such interacting columns are known to exist in the solid state of *m*-phenylene ethynylenes, where they can pack in a hexagonal arrangement.¹⁶ In our view, the formation of this highly collapsed state is driven in part by the high tendency of perylene diimide chromophores to aggregate.²⁷ Actually, precipitation of OPV-FOLD-PERY occurs after standing 1–2 h at this very high percentage of heptane, whereas in all other solvents used in this study the compounds are fully soluble in the concentration ranges used.²⁸ Not surprisingly, the absorption

bands associated with the PERY chromophore of OPV-FOLD-PERY also undergo changes upon the addition of heptane, occurring at the same heptane concentrations were the CD effect of the FOLD appears. Above 80% heptane content, the optical density of the lowest energy PERY absorption band decreases considerably for the OPV-FOLD-PERY dyad. The same occurs for the FOLD-PERY model compound, whereas the OPV absorption of the OPV-FOLD-PERY and OPV-FOLD undergo much smaller changes (see Supporting Information, Figures S2–S4). This confirms that aggregation of the PERY chromophores under these conditions occurs and possibly drives the formation of multi-columnar aggregates as inferred from the CD spectra above.

The A_s/A_p ratios of the OPV-FOLD-PERY dyad, the OPV-FOLD and FOLD-PERY model compounds, and the unsubstituted FOLD bridge show an almost identical decrease with decreasing polarity of the medium indicative of a similar folding behavior up to a heptane content of 95%, where the compounds with a PERY chromophore start to deviate because of aggregation (Figure 5b). The CD spectra are most pronounced for the foldamers that bear a PERY chromophore, consistent with the PERY as a driving force for aggregation. In contrast, the OPV-FOLD model shows only a very small CD signal, even in almost pure heptane (see: Supporting Information, Fig. S3).

In summary, absorption and CD spectroscopy show that OPV-FOLD-PERY adopts different conformational states depending on the volume percentage of heptane (Figure 5). In pure chloroform, the OPV-FOLD-PERY dyad is in a random coil conformation (state A). The absorption spectrum in chloroform is independent of the concentration in the range studied (from 3×10^{-7} to 3×10^{-5} M, see Supporting Information, Figure S5) indicating that folding or aggregation does not occur in chloroform at these concentrations. Only upon the addition of heptane the OPV-FOLD-PERY foldamer collapses into a folded state (state B). Above 80% heptane, the appearance of a CD effect and the change in intensity of the FOLD and PERY absorptions give evidence of the intermolecular self-assembly of the molecular helices into columnar architectures (state C). Under highly apolar conditions (>95% heptane), further aggregation seems to occur and the columns start to interact with each other laterally, giving a state (state D) that resembles the solid state but still is soluble. Under conditions where aggregation occurs, it is likely that the extent of the intermolecular interaction depends on the concentration and temperature. Although relevant, this has not been studied in detail as we will focus the photophysical experiments (*vide infra*) at conditions

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(28) Shaking the solution suffices to redissolve the precipitates, measurements were only performed on clear solutions.

Table 1. A_s/A_p Absorption Ratios Observed for OPV-FOLD, FOLD-PERY, and OPV-FOLD-PERY Dissolved in Solvents of Different E_T^N

solvent	E_T^N	A_s/A_p		
		OPV-FOLD	FOLD-PERY	OPV-FOLD-PERY
heptane:chloroform (99:1)	0.006	0.62	0.78 ^a	0.66 ^a
cyclohexane	0.006	0.61	0.59	0.61
carbon tetrachloride	0.052	0.78	0.77	0.76
dioxane	0.164	0.73	0.77	0.74
tetrahydrofuran	0.207	0.83	0.83	0.83
chloroform	0.259	0.91	0.90	0.91

^a Minimum value for the A_s/A_p ratio for FOLD-PERY is 0.62 and for OPV-FOLD-PERY is 0.60 in a 90:10 heptane:chloroform mixture. The higher ratios in the 99:1 mixtures are due to the intercolumnar interaction (state D, Figure 4).

were folding does occur but aggregation is still absent. These conditions are met in chloroform containing less than 80% heptane.

Folding in Other Solvents. The number of solvents in which the bridge can fold is rather high.^{11h} The A_s/A_p ratios (Table 1) for OPV-FOLD-PERY, OPV-FOLD, and FOLD-PERY indicate that the three foldamers are folded to a similar extent when they are in the same solvent, but that the degree of folding varies with the nature of solvent. The lowest A_s/A_p ratio is observed for the most apolar solvents, heptane and cyclohexane. Only in these two solvents a Cotton effect is observed (see Supporting Information, Figures S6–S8). The A_s/A_p ratio for OPV-FOLD-PERY and FOLD-PERY in heptane is somewhat higher than that of OPV-FOLD because of intercolumnar interactions (Figure 4, state D). Aggregation in heptane results in a rise of the A_s/A_p ratio and in fact lower values are observed in mixtures of heptane with 10% chloroform (Figure 5b and footnote Table 1). Reichardt's E_T^N index has found acceptance in the literature as a reliable and convenient parameter for solvatochromic effects in solvents of different polarity.²⁹ Table 1 shows that the A_s/A_p ratio generally increases with E_T^N index, although the relation is not perfect. In a more extensive study on the formation of helices of *m*-phenylene ethynylene oligomers carrying polar side chains in a wide range of solvents, a similar general relation of A_s/A_p with E_T^N index was established, although (like in the present case) some exceptions remained.^{11h} The absence of optical activity together with a low A_s/A_p absorption ratio in solvents such as tetrahydrofuran, dioxane, and carbon tetrachloride (also at higher concentrations, see Supporting Information, Figure S9), indicates that the conformation of the bridge in solvents of medium polarity is restricted to random coil or helical conformations of the bridge, and that no intermolecular interactions occur (only conformational states A and B are present).

Electronic Properties And Energetic Considerations. To establish the conditions for photoinduced energy or electron transfer between FOLD, OPV, and PERY chromophores, it is of interest to determine the energy of the various electronic states. Fluorescence spectroscopy in combination with cyclic voltammetry has been used to establish the energetics of these processes.

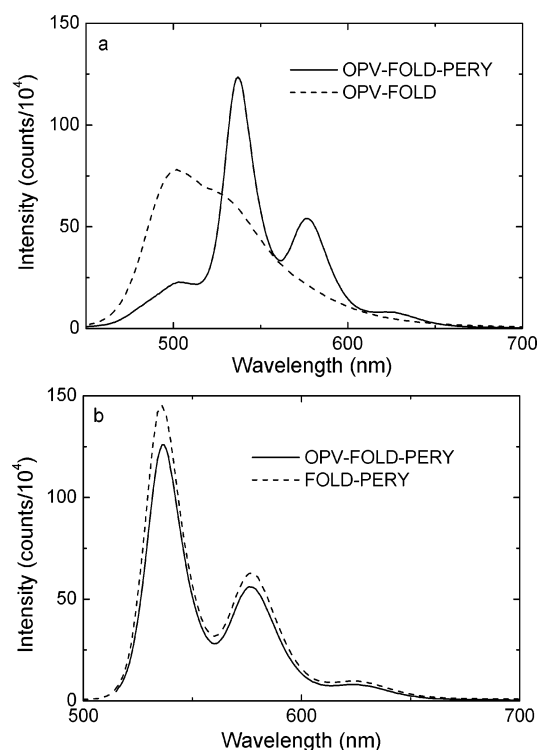


Figure 6. (a) Photoluminescence spectra of OPV-FOLD-PERY and OPV-FOLD in chloroform solution after selective photoexcitation of the OPV moiety at 380 nm. (b) Photoluminescence spectra of OPV-FOLD-PERY and FOLD-PERY in chloroform solution after selective photoexcitation of the PERY moiety at 512 nm. The concentration of the solutions was [OPV-FOLD] = 3.5×10^{-6} M, [FOLD-PERY] = 3.4×10^{-6} M, and [OPV-FOLD-PERY] = 2.9×10^{-6} M; spectra were corrected for the optical density at the excitation wavelength.

Fluorescence Spectroscopy. The fluorescence spectra of the donor and acceptor moieties have been measured in chloroform solution after selective excitation of the OPV (at 380 nm) and PERY (at 512 nm) chromophores in the OPV-FOLD and FOLD-PERY model compounds, respectively (Figure 6). The emission of the OPV chromophore maximizes at 502 nm and exhibits an additional shoulder due to an unresolved vibrational progression at ~ 530 nm.²⁶ The fluorescence quantum yield of OPV-FOLD is $\phi = 0.84$. The fluorescence of the PERY chromophore of FOLD-PERY has a quantum yield of $\phi = 0.80$ and the emission consists of a band with a maximum intensity at 535 nm and two additional vibronic bands at 577 and 622 nm. The fluorescence data reveal that in OPV-FOLD-PERY the energy of the singlet-excited state decreases from being localized on the FOLD bridge (4.55 eV), via OPV (2.47 eV), to the PERY (2.32 eV) chromophore. As a consequence singlet-energy transfer may occur in the series: ${}^1\text{FOLD}^* \rightarrow {}^1\text{OPV}^* \rightarrow {}^1\text{PERY}^*$.

Cyclic Voltammetry. The oxidation and reduction potentials of the redox centers have been measured for the donor OPV-FOLD and acceptor FOLD-PERY reference compounds and are assumed to be identical in the OPV-FOLD-PERY dyad. The cyclic voltammogram of OPV-FOLD exhibits two reversible oxidation waves with half-wave potentials at +0.83 and +1.05 V, while for FOLD-PERY two reversible reduction waves are found at half-wave potentials of -0.60 and -0.82 V (potentials are given vs SCE, recorded in dichloromethane with 0.1 M TBAPF₆) (see Supporting Information, Fig. S10). In the -1.0 to $+1.0$ V range no redox reactions occur that are associated with the FOLD bridge. The first oxidation potential of OPV–

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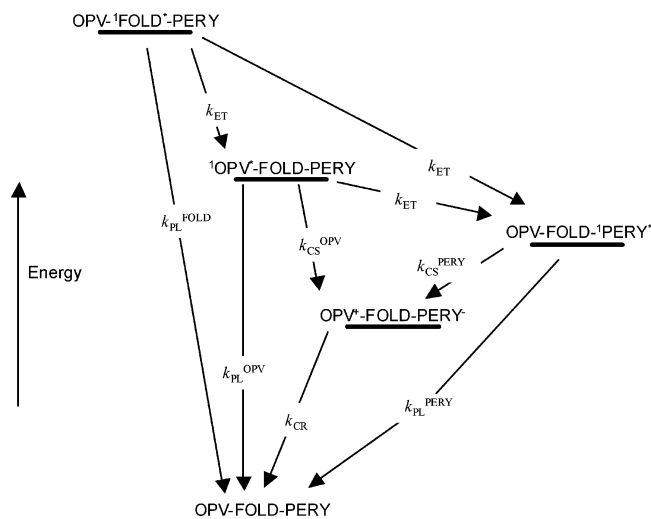


Figure 7. Schematic diagram describing the energy levels of the singlet and charge-separated states of OPV-FOLD-PERY.

FOLD is close to the values of +0.80 and +0.75 V found for the first oxidation waves of methyl end-capped OPV oligomers with two and three vinylene bonds, respectively.³⁰ Likewise, the first reduction potential of −0.60 V of PERY–FOLD is fits nicely between the values for a bisalkyl and bisaryl substituted perylene diimides of −0.65 and −0.55 V, respectively.^{17,18} This shows that the redox potentials of the chromophores are not significantly perturbed by conjugation to the bridge.

Energetic Considerations of the Photophysics. The most probable photophysical processes after photoexcitation of either donor or acceptor in dyad OPV-FOLD-PERY are schematically represented in the energy diagram in Figure 7. Photoinduced electron transfer from the OPV donor to the PERY acceptor can only occur when the $\text{OPV}^{*+}\text{-FOLD-PERY}^{*-}$ charge-separated state is lower in energy than the PERY singlet-excited state ($\text{OPV-FOLD-}^1\text{PERY}^*$) and competes with the intrinsic relaxation processes (mainly fluorescence) of the $^1\text{PERY}^*$ state. Contributions of the FOLD bridge in charge transfer processes, either in the random coil or helical stacked conformations, are not likely because of the high redox potentials of the FOLD segment.

Folding experiments of the bridge in OPV-FOLD-PERY have been performed by the addition of heptane to a chloroform solution of the dyad. Two parameters with opposite effects on the charge separation reaction change as the amount of heptane is increased. On one hand, at high volume percentages of heptane, folding of the bridge occurs which reduces the distance between donor and acceptor and, thereby, favors charge transfer. On the other hand, the low polarity of heptane compared to chloroform, makes this solvent less effective in screening the photogenerated charges and thereby will increase the energy of the $\text{OPV}^{*+}\text{-FOLD-PERY}^{*-}$ charge-separated state. An estimate of the change in Gibbs free energy for photoinduced electron transfer in solution for the OPV-FOLD-PERY dyad can be obtained from the Weller equation³¹

$$\Delta G_{\text{CS}} = e(E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A})) - E_{00} - \frac{e^2}{4\pi\epsilon_0\epsilon_s R_{\text{cc}}} - \frac{e^2}{8\pi\epsilon_0} \left(\frac{1}{r^+} + \frac{1}{r^-} \right) \left(\frac{1}{\epsilon_{\text{ref}}} - \frac{1}{\epsilon_s} \right) \quad (1)$$

Table 2. Change in Gibbs Free Energy Change for Intermolecular Electron Transfer (ΔG_{CS}) in OPV-FOLD-PERY in Chloroform and Heptane, the Total Reorganization Energy (λ), and the Barrier for Electron Transfer (ΔG^\ddagger)

solvent	ϵ_s	R_{cc} (Å)	ΔG_{CS} OPV (eV) ^a	ΔG_{CS} PERY (eV) ^b	λ (eV) ^c	ΔG^\ddagger (eV) ^d
heptane	1.902	106	0.03	0.18	0.30	0.19
		30	−0.15	0.00	0.30	0.08
		10	−0.65	−0.50	0.30	0.03
chloroform	4.806	106	−0.79	−0.64	1.06	0.04
		30	−0.86	−0.71	0.97	0.02
		10	−1.06	−0.91	0.71	0.01

^a From eq 1 with E_{00} (OPV) = 2.53 eV in heptane and 2.47 eV in chloroform. ^b From eq 1 with E_{00} (PERY) = 2.38 eV in heptane and 2.32 eV in chloroform. ^c Determined from $\lambda = \lambda_i + \lambda_s$, with $\lambda_i = 0.30$ eV, and λ_s from the Hush relation $\lambda_s = (e^2/4\pi\epsilon_0)(1/(2r^+) + 1/(2r^-) - (1/R_{\text{cc}}))(1/n^2 - 1/\epsilon_s)$.³³ ^d Determined from the Marcus relation assuming that transfer occurs from the PERY S_1 state $\Delta G^\ddagger = (\Delta G_{\text{CS}} + \lambda)^2/4\lambda$.³²

In this equation, $E_{\text{ox}}(\text{D})$ and $E_{\text{red}}(\text{A})$, are the oxidation and reduction potentials of the donor and acceptor molecules or moieties respectively measured in a solvent with relative permittivity ϵ_{ref} (8.93 for CH_2Cl_2), E_{00} is the energy of the excited state from which the electron transfer occurs (OPV or PERY singlet-excited state), and R_{cc} is the center-to-center distance of the positive and negative charges in the charge-separated state. The radii of the positive and negative ions are given by r^+ and r^- and ϵ_s is the relative permittivity of the solvent, $-e$ is the elemental charge, and ϵ_0 is the vacuum permittivity. At close proximity (e.g., $R_{\text{cc}} = 10$ Å), charge separation between the OPV donor and the PERY acceptor is exergonic in heptane as calculated from eq 1 using $E_{\text{ox}}(\text{D}) = +0.83$ V, $E_{\text{red}}(\text{A}) = -0.60$ V (vide supra) and setting the ionic radii to $r^- = 4.7$ Å¹⁸ and $r^+ = 5.1$ Å,³⁰ while assuming that the process occurs from the lowest singlet excited state of the PERY chromophore (Table 2). In heptane, the limiting distance at which charge separation becomes no longer exergonic is ~ 30 Å (Table 2). Larger distances will result in an $\text{OPV}^{*+}\text{-FOLD-PERY}^{*-}$ charge-separated state that is less stable than the PERY singlet excited state. In the more polar solvent chloroform, charge separation is in principle feasible ($\Delta G_{\text{CS}} < 0$) even when the molecule is in a completely extended configuration (distance ~ 106 Å). However at such large distances, kinetic factors will impede the intramolecular charge transfer, because the electronic coupling between donor and acceptor in the excited state is negligible at this distance.

The occurrence of photoinduced electron transfer not only depends on the change in free energy ΔG_{CS} as given in Table 2 (which should be negative), but also on the barrier ΔG^\ddagger for this process. The barrier for electron transfer can be estimated from ΔG_{CS} and the reorganization energy λ using the Marcus equation.³² The reorganization energy λ expresses the energy that is necessary to bring the system from its equilibrium geometry in the excited state to the charge-separated state. The reorganization energy is the sum of internal (λ_i) and solvent (λ_s) contributions. For conjugated systems such as OPV and PERY λ_i is on the order of 0.3 eV,¹⁸ while λ_s can be estimated from the Hush equation.³³ The corresponding values for the

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barrier are collected in Table 2, and show that in chloroform and in heptane the barrier is small in the folded state ($\Delta G^\ddagger \leq 0.03$ eV for $R_{cc} = 10$ Å) and similar to the thermal energy at room temperature (~ 0.026 eV). This analysis demonstrates that electron transfer is exergonic and occurs with a small barrier in the folded state in both solvents

It is important to mention that the UV–vis and CD spectra indicate that at high heptane concentrations aggregation of helices into columns occurs. Such aggregation would give rise to intermolecular electron transfer pathways between favorably oriented donor and acceptor chromophores. This is not considered in the discussion above, as solvent molecules are no longer dissolving the chromophores. In the following, we will give special attention to establish the conditions where aggregation does not yet occur and only folding enables the photoinduced electron transfer.

Photoinduced Energy and Electron Transfer in Different Conformational States of the Bridge. The interaction between donor and acceptor in the excited state can be investigated with photoluminescence and photoinduced absorption spectroscopy. Quenching of either donor or acceptor fluorescence indicates an energy or charge-transfer process. Photoinduced absorption spectroscopy (PIA) can be used to monitor the formation and decay of the OPV⁺-FOLD-PERY⁻ charge-separated state. In the following sections, the donor acceptor interaction in the excited state is first described for a random coil conformation followed by the results for folded conformations.

Photophysics with the Bridge in a Random Coil Conformation. In chloroform, the bridge is in a random-coil conformation. Hence, the relative orientation of donor and acceptor chromophores for OPV-FOLD-PERY is not well defined and probably numerous conformers exist. Photoluminescence spectroscopy reveals that, in chloroform, the two chromophores interact in the excited state. Selective photoexcitation of the OPV unit in OPV-FOLD-PERY at 380 nm results in emission of the PERY part ($\lambda_{em,max} = 537$ nm), concomitant with a reduction of the fluorescence intensity of the OPV chromophore ($\lambda_{em,max} = 504$ nm) compared with the fluorescence of the OPV-FOLD compound (Figure 6a). In contrast, the quantum yield of the PERY emission, after selective photoexcitation of the PERY moiety in OPV-FOLD-PERY at 512 nm, approaches that of the FOLD-PERY reference compound (Figure 6b). According to the energy diagram in Figure 7, a quenching of the PERY emission would be expected to occur upon formation of the OPV⁺-FOLD-PERY⁻ charge-separated state. Because the PERY emission is not significantly quenched, photoinduced charge separation is negligible in chloroform. In a random coil conformation, the OPV-FOLD-PERY dyad resembles D-bridge-A systems with a saturated hydrocarbon chain as a bridge, albeit with less conformational freedom. Out of all possible conformations in chloroform, barely a few will provide sufficient proximity and interaction between the OPV donor and the PERY acceptor to allow for charge transfer.

The excitation spectrum of the PERY emission nearly coincides with the absorption spectrum of OPV-FOLD-PERY (Figure 8). The overlap is particularly good in the region of the PERY and OPV absorption. This implies that singlet-energy transfer to the PERY chromophore occurs after photoexcitation of OPV chromophore, and to a considerable extent also after exciting the FOLD (processes indicated with k_{ET} in Figure 7).

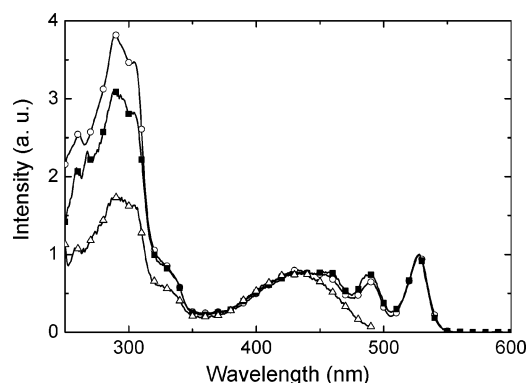


Figure 8. Excitation spectra of the 496 nm (open triangles) and 535 nm (solid squares) emission, and absorption spectrum of OPV-FOLD-PERY (open circles), in chloroform. Concentration is 2.85×10^{-7} M.

However, there is a small mismatch between the absorption and excitation spectra in the region of the FOLD absorption, indicating that energy transfer from the bridge is not complete. The excitation spectrum of the OPV emission also reveals that energy transfer occurs from the FOLD bridge onto the OPV chromophore. The difference between the absorption and excitation spectra is larger for the OPV moiety. This indicates that some, but not all, photoexcitations of the FOLD oligomer transfer their excited-state energy first to the OPV chromophore, before ending up at the PERY moiety.

Because the excitation spectrum of OPV-FOLD-PERY coincides with the absorption spectrum above 350 nm, the quenching of the OPV fluorescence is mainly due to an intramolecular photoinduced singlet-energy transfer from the ¹OPV* state to form the more stable ¹PERY* singlet-excited state (Figure 8). The quenching of the OPV emission can be used to estimate an average distance between the donor and acceptor using the Förster model for energy transfer.³⁴ This model, which is based on a dipole–dipole interaction mechanism, provides an expression for the rate for the energy transfer, k_{ET}^F , via

$$k_{ET}^F = \frac{1}{\tau} \left(\frac{R_c}{d} \right)^6 \quad (2)$$

In this equation, τ is the lifetime of the donor chromophore, R_c is the critical transfer radius and d the center-to-center distance between the redox centers, the parameter that we wish to determine. Using the experimental OPV fluorescence quenching ($Q = 4.16$) and the experimental fluorescence lifetime of the OPV segment in OPV-FOLD-PERY ($\tau = 1.41$ ns), the rate constant for energy transfer can be estimated by using the relation

$$k_{ET} = \frac{Q - 1}{\tau} \quad (3)$$

This provides $k_{ET} = 2 \text{ ns}^{-1}$ as an estimate for the rate constant. R_c can be calculated using the Förster equations

$$R_c^6 = \frac{9000 \ln(10) \frac{2}{3} \phi J_F}{128 \pi^5 N n^4} \quad (4)$$

$$J_F = \frac{\int f(\nu) \frac{\epsilon(\nu)}{\nu^4} d\nu}{\int f(\nu) d\nu} \quad (5)$$

In eqs 4 and 5, ϕ is the luminescence quantum yield of the donor ($\phi = 0.84$, for OPV-FOLD), N the Avogadro constant, and n the refractive index of the solvent (1.444). J_F is the overlap integral of the luminescence spectrum of the donor ($f(\nu)$ of OPV) on an energy scale (cm^{-1}) and the absorption spectrum of the acceptor ($\epsilon(\nu)$ of PERY). For OPV-FOLD-PERY the overlap integral is $J_F = 2.5 \times 10^{-13} \text{ cm}^6/\text{mol}$. The average distance between the chromophores is then $d = 5.5 \text{ nm}$. This implies that the foldamer does not adopt an extended configuration, in which the center-to-center distance is of roughly 10 nm, but as expected, a random conformation. Although the data appear to be suitably described by the Förster model, it has been recently shown that *m*-phenylene ethynylene segments can have a strong coupling between chromophores in the excited state, which may offer an alternative pathway for the energy transfer.³⁵

Photophysics with the Bridge in a Folded Conformation in Heptane/Chloroform: Photoluminescence Spectroscopy.

To study the influence of the decreasing polarity and the associated folding and intermolecular aggregation of the FOLD on the emission of the individual chromophores, experiments were performed on the OPV-FOLD and FOLD-PERY model compounds in solvents with different heptane/chloroform content. The fluorescence intensity of OPV-FOLD slightly increases upon addition of heptane (see Supporting Information, Figure S11). The absence of any quenching in OPV-FOLD with decreasing polarity excludes that of OPV–OPV aggregates are formed in any heptane/chloroform mixture. Quite on the contrary, the fluorescence of the acceptor chromophore in FOLD-PERY undergoes a dramatic quenching, starting from 80% of heptane in chloroform (Figure 9a, and inset therein). This quenching coincides with a decreased intensity of the lowest energy PERY absorption band (Figure 5) and is consistent with aggregation of the PERY chromophores and hence with intermolecular aggregation of the helices (state C) above 80% heptane. Moreover, at high heptane contents, the fluorescence spectra of FOLD-PERY feature an additional emission centered at approximately 630 nm, associated with perylene diimide excimers.³⁶ Fluorescence lifetime measurements of the PERY fluorescence of FOLD-PERY were performed by monitoring the emission at 600 nm. At this wavelength, both the PERY chromophores of the random coil foldamers (with molecularly dissolved PERY chromophores) and those of the aggregated state (PERY excimers) contribute to the emission. Hence, the lifetime traces recorded at 600 nm will reveal any change in the relative contributions of the two emissions. The data collected in Figure 9b show that the perylene aggregates (with an excited-state lifetime of $\tau = 30 \text{ ns}$ vs. $\sim 4 \text{ ns}$ of molecularly dissolved PERY chromophores) start to appear already at 70 volume percent heptane and become the predominant species in almost pure heptane. The observed fluorescence quenching supports the proposed conformational exchanges in FOLD-PERY inferred from absorption and CD spectroscopy.

For OPV-FOLD-PERY, an increase of the percentage of heptane results in a quenching of the PERY emission, regardless

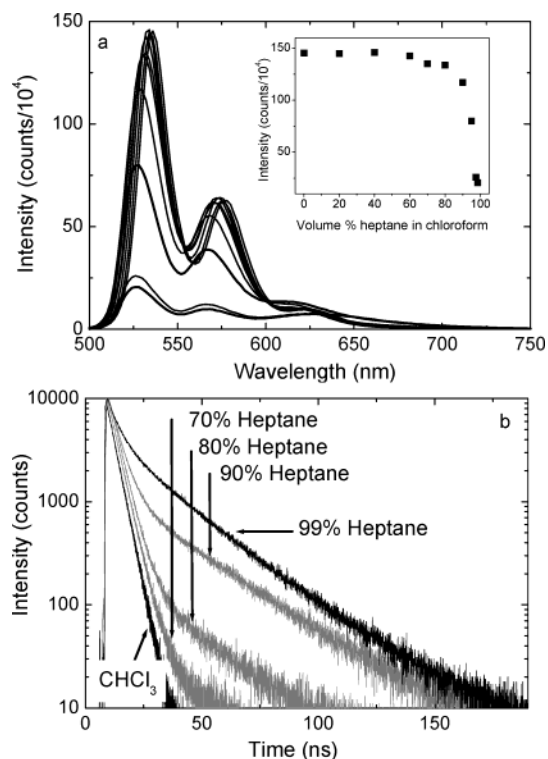


Figure 9. (a) Steady-state photoluminescence spectra of FOLD-PERY model compound in solutions of chloroform/heptane mixtures of different composition. Inset: Maximum fluorescence intensity of FOLD-PERY in chloroform/heptane mixtures of different composition (The fluorescence intensities have been corrected for small deviations from O. D. = 0.1 at the excitation wavelength). (b) Time profiles of the fluorescence at 600 nm of FOLD-PERY model compound in solutions of chloroform/heptane mixtures of different composition. Concentration is $4.45 \times 10^{-6} \text{ M}$.

which of the two chromophores is excited (Figure 10). In more apolar environments, the folding of the bridge (state B) and the formation of intermolecular stacks (states C and D) decreases the distance between donor and acceptor. When the two chromophores are in close proximity, charge separation may occur in the excited state. The lack of excimer emission at 630 nm for OPV-FOLD-PERY at all chloroform/heptane ratios, indicates the absence of perylene diimide excimers and leaves charge separation as the most likely fluorescence quenching process (Figure 7). The absence of a red-shifted emission also implies that donor and acceptor do not form an emissive exciplex prior to electron transfer.

Time-resolved fluorescence of OPV-FOLD-PERY measured at 600 nm revealed that the lifetime of the PERY emissions is $\sim 4 \text{ ns}$ up to 80% heptane, while above 80% slightly shorter lifetimes are observed (Figure 10c). The absence of a longer-lived (30 ns) lifetime component in the fluorescence decay curves upon the addition of heptane supports the absence of perylene diimide excimers in the intermolecular assembled states in OPV-FOLD-PERY (states C to D, Figure 4). On the other hand, the absence of a reduction of the lifetime above 80% heptane is surprising. This suggests that the electron transfer reaction that causes the PL quenching is so fast in state B that that the corresponding lifetime is shorter than the time resolution of the experimental set up and is not detected by time-resolved photoluminescence. Such a fast formation of the charge-separated state is rarely observed in solution, unless donor and acceptor are directly connected¹⁷ or in a face-to-face orienta-

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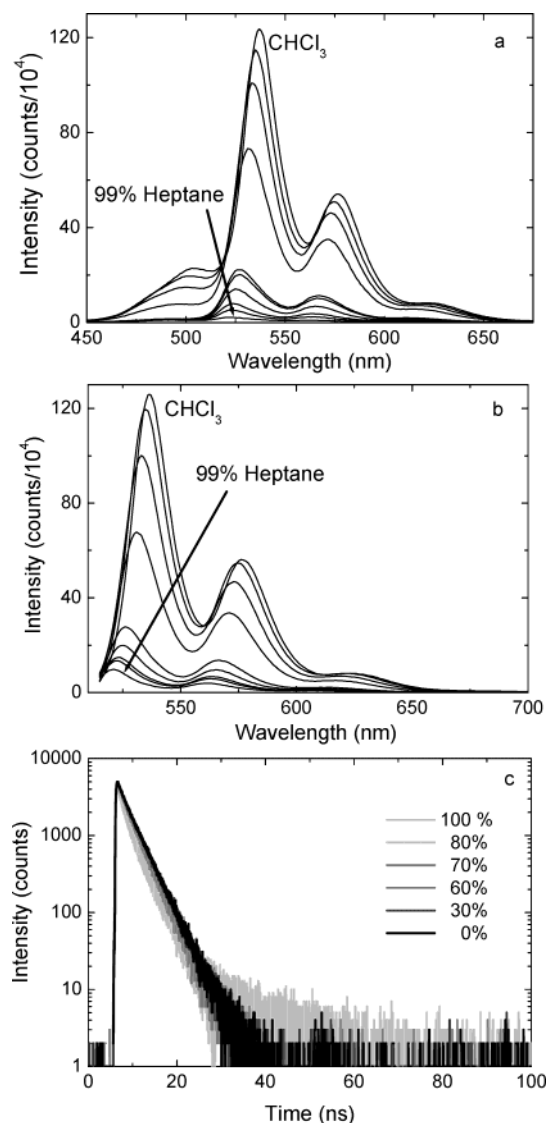


Figure 10. Steady-state photoluminescence spectra of OPV-FOLD-PERY in chloroform/heptane solutions of different composition after selective excitation of the OPV at 380 nm (a) and the PERY at 510 nm (b). Concentration is 3.61×10^{-6} M. (c) Time-resolved photoluminescence spectra of OPV-FOLD-PERY in chloroform/heptane solutions of different composition with excitation at 400 nm. Numbers give the vol % of heptane.

tion.³⁷ Hence, within the folded state (state B) only in conformations where donor and acceptor are placed in a face-to-face orientation, charge transfer may take place as a predominant decay route, whereas for less favorably folded conformers, radiative decay of ¹PERY* will occur. In the region above 80% heptane, where intermolecular and intercolumnar aggregation occurs (states C and D, Figure 4), more donor and acceptors are brought in close proximity and intermolecular charge separation can occur in addition to the intramolecular process.

A comparison of the steady-state photoluminescence of PERY-FOLD and OPV-FOLD-PERY gives an estimate of the extent of charge transfer in the dyad as a result of folding (Figure

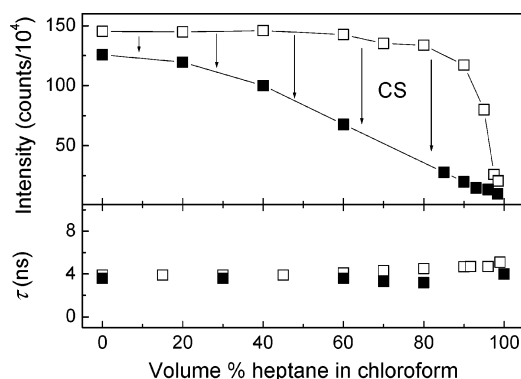


Figure 11. Photoluminescence intensities (above) and (short)-lifetime (below) of the PERY emission in OPV-FOLD-PERY (solid squares) and FOLD-PERY (open squares) in chloroform/heptane mixtures of different composition. The extent of charge separation can be estimated from the difference between the two emission intensities. The arrows denote the amount of the charge separation (CS). Concentrations: [FOLD-PERY] = 2.45×10^{-6} M, [OPV-FOLD-PERY] = 3.6×10^{-6} M.

11). The significant quenching of the PERY photoluminescence upon addition of heptane to chloroform solutions of OPV-FOLD-PERY compared to FOLD-PERY strongly suggests that charge separation occurs to yield the OPV^{•+}-FOLD-PERY^{•-} charge-separated state. For low amounts of heptane, the charge separation takes place only to a small extent but upon folding of OPV-FOLD-PERY the efficiency of the charge transfer process increases. It is important to note that up to 80% heptane no intermolecular self-assembly of OPV-FOLD-PERY occurs and hence the quenching of the PERY luminescence is due to an intramolecular photoinduced electron transfer in the folded state. The result that the efficiency for charge separation increases with decreasing polarity is opposite to the conventional behavior of a D-A dyad in the normal Marcus region ($-\Delta G_{CS} < \lambda$). Although this result is surprising it is not unique, there are various parallels in field of biological electron transfer.^{38,4ab,7,38} Above 80% heptane the comparison of the two intensities is no longer valid, because the excimer formation of FOLD-PERY results in a quenching of the fluorescence and that is not associated with charge separation.

The residual fluorescence of OPV-FOLD-PERY with excitation of the OPV chromophore (Figure 10a) shows that the relative contribution of the PERY emission increases compared that of the OPV emission by a factor of about three, going from pure chloroform to 80% hexane (see Supporting Information, Figure S12). This emission results from dyad molecules in which electron transfer is absent and that are, hence, not completely folded. The increase of the PERY/OPV fluorescence intensity ratio indicates a more efficient energy transfer under more apolar conditions. The factor of 3, relates to an increase of k_{ET} to ~ 8 ns⁻¹ and an average D-A distance of 4.4 nm, i.e., less than that in pure chloroform but larger than the range where electron transfer would occur. The decreased distance is consistent with the proposed folding mechanism. A control experiment in which OPV-FOLD and PERY are mixed in equimolar amounts in chloroform/heptane mixtures showed no evidence of intermolecular contributions to the energy or electron-transfer reactions under these conditions hexane (see Supporting Information, Figure S13).

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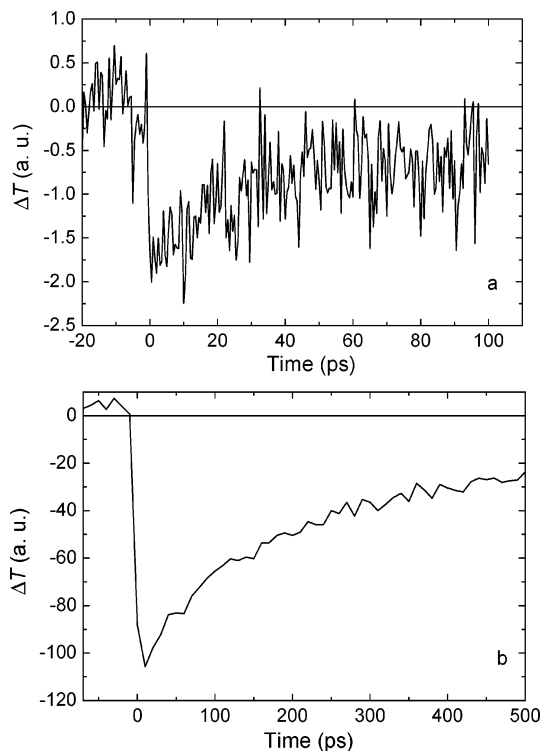


Figure 12. Differential transmission dynamics for OPV-FOLD-PERY in mixtures of chloroform/heptane of 60:40 (a) and 99:1 (b) at the radical cation absorption of OPV at 1450 nm with excitation of primarily OPV at 450 nm from -20 to 100 ps (a) and -100 to 500 ps (b). Concentration $\approx 10^{-5}$ M.

Photophysics with the Bridge in a Folded Conformation in Heptane/Chloroform: Pump–Probe Spectroscopy. The formation and decay of the photoinduced charges of OPV-FOLD-PERY have been followed by means of transient photoinduced absorption spectroscopy. In this experiment, the OPV chromophore is excited at 450 nm and the absorption at 1450 nm associated with the OPV^{•+} radical cation is monitored in time (Figure 12).¹⁸ At 60% heptane in chloroform, the differential transmission at 1450 nm is not very intense (Figure 12a). The small signal is in agreement with the low quenching of the PERY emission observed at 60% heptane ($Q \approx 2$, Figure 11). The time profile of the 1450 nm transient absorption indicates that the charges are formed within 1 ps. This rapid formation of the OPV^{•+}-FOLD-PERY^{•-} charge-separated state is consistent with the absence of short lifetimes in the time-resolved photoluminescence of the PERY chromophore and is attributed to occur for conformations of OPV-FOLD-PERY with a face-to-face orientation of donor and acceptor moieties. The decay of the signal cannot be fitted to a single-exponential function, suggesting that several charged species are involved in the measurement. A feasible explanation for this result could be the conformational heterogeneity of the system: in the folded conformation of the bridge (Figure 4, state B), the position between donor and acceptor is dynamic and not all conformers provide the face-to-face orientation between donor and acceptor required for immediate charge transfer. The fact that the signal is low suggests that few systems have the required face-to-face orientation, and the fact that the signal does not grow with time implies that the conformational changes are slow on the time scale of the experiment.

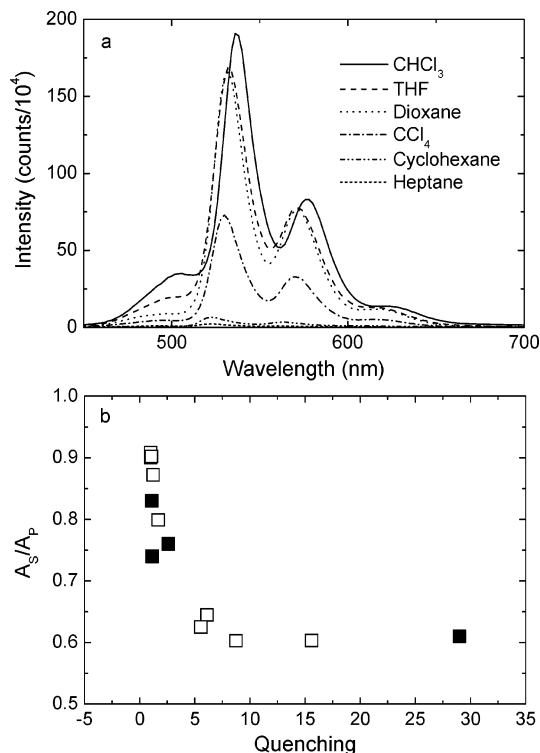


Figure 13. CD and PL spectra of OPV-FOLD-PERY in different solvents (left) and quenching ratio vs the A_s/A_p ratio in chloroform/heptane mixtures of different composition (open squares) and in pure solvents of different polarity (solid squares) (right).

At almost 100% volume heptane, the transient absorption is much more intense (Figure 12b). This is consistent with the much higher PL quenching and attributed to intermolecular photoinduced electron transfer in the aggregated state. The helical conformations have folded into columnar architectures, and likely several columns are interacting with each other (state D, Figure 4). More donor and acceptors are brought in close proximity and apart from *intramolecular* processes also *intermolecular* charge separation takes place. Under these conditions, the formation of the charges is immediate, even though the heptane content is the highest and the medium is strongly apolar. In strongly aggregated states the polarity of the solvent is less relevant, because charge transfer takes place, as it would do in a solid-state blend of the donor and acceptor. Paddon-Row et al. observed that in a face-to-face orientated donor–acceptor dyad, photoinduced electron-transfer took place within 1 ps, irrespective of the polarity of the medium.³⁹ Again the decay of the 1450 nm signal cannot be fitted to a single-exponential function. However, the charge-separated states are much longer lived at high percentage of heptane, than in 60% heptane. These results can be rationalized by migration of the charges to different parts of the aggregates.

Photophysics with the Bridge in a Folded Conformation in Other Solvents. The fluorescence spectra of OPV-FOLD-PERY are shown in Figure 13a for a variety of solvents of different polarity. Analogous to the behavior in different heptane/chloroform mixtures, a decrease of the solvent polarity results in an increased quenching of the PERY photoluminescence in OPV-FOLD-PERY. The quenching in these solvents

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is also attributed to photoinduced charge separation from the OPV to the PERY chromophore caused by the folding of the bridge. There seems to be an inverse relation between the A_s/A_p ratio and fluorescence quenching in these solvents (Figure 13b). The observed A_s/A_p ratio and the quenching of the PERY emission are similar in carbon tetrachloride and in a mixture of heptane/chloroform (60:40) (Figures 11 and 13a). These results show that the conformational folding of OPV-FOLD-PERY and the resulting enhancement of the photoinduced charge transfer is a general phenomenon that can be achieved and controlled by modifying the polarity of the medium, either in solvent mixtures or by varying the nature of the pure solvent. Again, it is important to point out that in carbon tetrachloride OPV-PERY-FOLD is mainly present in the helically folded state. Intermolecular stacked columns do not form in carbon tetrachloride and, hence, the quenching of the OPV and PERY luminescence gives strong evidence of an intramolecular photoinduced electron transfer occurring with a higher efficiency in the less polar carbon tetrachloride than in chloroform, THF, or dioxane (Figure 13a).

Conclusions

A novel donor-bridge-acceptor system has been synthesized by connecting OPV donor and PERY acceptor chromophores at the opposite ends of a long foldable cross-conjugated oligomer, FOLD. The conformation of this bridge can be controlled between random coil and helically folded states, by changing the polarity of the medium. In chloroform solution the bridge is in a random coil conformation. As a consequence most donor and acceptor chromophores are too far apart to undergo a photoinduced charge transfer reaction. Fluorescence spectroscopy revealed that under these conditions photoexcitation of the OPV moiety results in a singlet-energy transfer to the PERY chromophore. The average distance between OPV and PERY chromophores in chloroform, as estimated by the Förster equation for energy transfer, is 5.5 nm. This distance supports the idea that the FOLD oligomer adopts a random coil conformation in chloroform is not in a completely extended conformation (~10 nm).

Upon addition of heptane to chloroform solutions of OPV-FOLD-PERY, the bridge starts to fold up into a helix. With increasing amount of heptane, these helices self-assemble into columnar architectures and eventually into multi-columnar architectures. These intermolecular interactions only occur for OPV-FOLD-PERY and FOLD-PERY, but not for OPV-FOLD, suggesting that they originate from the tendency of the PERY chromophore to aggregate. In the folded state of OPV-FOLD-PERY, the OPV and PERY chromophores exhibit a photoinduced charge transfer, because of the decreased D–A distance. The folding of the bridge and the associated photoinduced electron transfer of OPV-FOLD-PERY not only occur in heptane/chloroform mixtures, but also in less polar pure solvents (e.g., carbon tetrachloride). While the ability to differentiate between energy and electron transfer by changing the polarity of the solvent is not unusual, the surprising result is that here, contrary to the traditional polarity dependence, electron transfer is enhanced in less polar solvents. This is a direct result of the specific conformational changes of the foldamer in apolar solvents that bring donor and acceptor in closer proximity. With this result the nonbiological *m*-phenylene ethynylene foldamers,

parallel the behavior observed for some oligopeptide bridges.^{3s,4ab,7,38}

Summarizing, we have shown that the bridge in OPV-FOLD-PERY provides a unique means to change the distance and orientation, and thereby the photophysical interaction between donor and acceptor. With OPV-FOLD-PERY a hierarchical build-up of a photoactive supramolecular D–A system has been obtained, starting from two semi-isolated chromophores showing only energy transfer, via intermediates capable of rendering electron transfer, into an aggregated state featuring, in addition to electron transfer, charge migration. This donor–foldamer–acceptor dyad can be considered as a first step toward the supramolecular construction of synthetic architectures that are able to perform complicated photophysical and photochemical processes, similar to those observed in the photosynthetic reaction center. Such appealing synthetic analogues may find future application in photocatalytic reactions and solar light energy conversion.

Experimental Section

General Methods. All reagents and solvents were used as received or purified using standard procedures. NMR spectra were recorded on a Varian Mercury Vx at frequencies of 400 and 100 MHz for ¹H and ¹³C nuclei, or Varian Gemini 2000 at frequencies of 300 and 75 MHz for ¹H and ¹³C nuclei, respectively. Tetramethylsilane (TMS) was used as an internal standard for ¹H NMR and CDCl₃ for ¹³C NMR. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed on a Perseptive DE PRO Voyager MALDI-TOF mass spectrometer using a dithranol matrix. A Shimadzu LC-10AT system combined with a Polymer Laboratories MIXED-D column (Particle size: 5 μm; Length/I. D. (mm):300 × 7.5) and UV detection (520 nm) was employed for size exclusion chromatography (SEC), using CHCl₃ as an eluent (1 mL/min). Spectroscopic studies were performed on solutions with concentrations in the order of 10⁻⁶ M, at room temperature. Samples were allowed to equilibrate for at least 12 h before the measurement.

Starting Materials. The synthetic procedures for the preparation of the chiral trimethylsilyl end-capped *m*-phenylene ethynylene dodecamer **6** [(Ar–C≡C)₁₂–TMS] and the corresponding iodinated dodecamer **8** [I–(Ar–C≡C)₁₂–TMS] used in this study has been described in detail in ref 15.

***N*-(1-Ethylpropyl)-*N'*-(4-iodophenyl) perylene diimide (**2**).** Perylene monoanhydride monoimide **1** (38.6 mg, 0.08 mmol), 4-iodoaniline (182 mg, 0.83 mmol), imidazole (0.53 g, 7.8 mmol), and catalytic amounts of Zn(AcO)₂ were mixed and stirred for 1 h at 160 °C. After cooling to room temperature the solid reaction mixture was extensively washed with methanol to yield 49 mg of **2** (92%) as a dark red powder. ¹H NMR (CDCl₃, 300 MHz): δ 8.66 (t, 4H), 8.56 (d, 4H), 7.90 (d, 2H), 7.12 (d, 2H), 5.11–5.00 (m, 1H), 2.35–2.17 (m, 2H), 2.03–1.89 (m, 2H), 0.95 (t, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 138.65, 135.17, 134.77, 134.09, 131.81, 131.38 (broad signal), 130.60, 129.72, 129.46, 126.57, 126.29, 123.32, 123.00, 94.66, 57.81, 25.01, 11.38. MALDI-TOF MS (*M*_w = 662.49) *m/z* = 662.19 [M]⁺.

(*E,E*)-4-{4-(4-Methyl-2,5-bis[(*S*)-2-methylbutoxy]styryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]-4-trimethylsilyl ethynylbenzene (4**).** Bromide **3** (0.2 g, 0.22

mmol), PdCl₂ (3.97 mg, 0.02 mmol), PPh₃ (17.6 mg, 0.07 mmol) and Cu(AcO)₂ (4.47 mg, 0.02 mmol) were dissolved in 5 mL anhydrous triethylamine. Argon was purged through the solution for 30 min after which (trimethylsilyl)acetylene (44 mg, 0.44 mmol) was added. The reaction mixture was heated at 80 °C for 16 h. The solvent was removed in vacuo, the residue dissolved in methylene chloride and washed with NH₄Cl, water and dried over MgSO₄. Purification by column chromatography (chloroform:pentane, 1:1, R_f = 0.2) afforded 92 mg (45%) of compound **4**. ¹H NMR (CDCl₃, 300 MHz): δ 7.52 (d, 1H), 7.50 (d, 1H), 7.45 (d, 1H), 7.44 (d, 1H), 7.18 (s, 1H), 7.16 (s, 1H); 7.12 (s, 1H), 7.10 (s, 1H), 6.94 (s, 1H), 6.72 (s, 1H), 3.92–3.67 (m, 12H), 2.22 (s, 3H), 2.00–1.84 (m, 6H), 1.70–1.55 (m, 6H), 1.40–1.25 (m, 6H), 1.11–1.02 (m, 18H), 1.02–0.95 (m, 18H), 0.27 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz): δ 154.91, 151.67, 151.20, 150.93, 150.46, 150.20, 129.03, 127.95, 127.62, 126.76, 125.15, 123.97, 123.20, 122.16, 121.64, 117.38, 116.28, 112.06, 110.14, 109.92, 109.60, 108.38, 101.79, 98.91, 74.66, 74.25, 74.14, 73.38, 35.10, 35.04, 35.01, 34.98, 34.95, 26.36, 26.32, 26.25, 26.14, 16.78, 16.70, 16.52, 16.40, 11.44, 11.36, 0.01. MALDI-TOF MS (*M*_w = 909.37) *m/z* = 908.35 [M]⁺.

(*E,E*)-4-{4-(4-Methyl-2,5-bis[(*S*)-2-methylbutoxy]styryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]-4-ethynylbenzene (5). To a solution of **4** (36.7 mg, 0.04 mmol) in dry THF was added 1 M tetrabutylammonium fluoride in THF (0.044 mL). The reaction mixture was stirred for 1 min and subsequently filtered over silica gel using chloroform as eluent. The solvent was removed in vacuo yielding 32 mg (95%) of a yellow solid which was used without further purification. ¹H NMR (CDCl₃, 300 MHz): δ 7.53 (d, 1H), 7.51 (d, 1H), 7.45 (d, 1H), 7.44 (d, 1H), 7.18 (s, 1H), 7.16 (s, 1H); 7.15 (s, 1H), 7.10 (s, 1H), 6.97 (s, 1H), 6.72 (s, 1H), 3.92–3.67 (m, 12H), 3.31 (s, 1H), 2.22 (s, 3H), 2.00–1.84 (m, 6H), 1.70–1.55 (m, 6H), 1.40–1.25 (m, 6H), 1.11–1.02 (m, 18H), 1.02–0.95 (m, 18H). MALDI-TOF MS (*M*_w = 837.25) *m/z* = 836.51 [M]⁺.

PERY–FOLD (7). A mixture of **2** (11 mg, 0.016 mmol), **6** (39.8 mg, 0.0014 mmol), Pd(PPh₃)₄ (1.06 mg, 0.0009 mmol) and potassium acetate (2 mg, 0.020 mmol) in dry toluene (1 mL) and *N,N*-dimethylformamide (1 mL) was heated to 100 °C for 24 h, and subsequently the solvent was evaporated in vacuo. The residue was triturated with water and extracted with methylene chloride. The methylene chloride extract was worked up to give crude products, which were purified by flash column chromatography (CH₂Cl₂/pentane to 9:1, R_f = 0.4) to yield 10 mg (22%) of **4** as a light red solid. ¹H NMR (CDCl₃, 400 MHz): δ 8.77–8.67 (m, 8H), 8.20–8.17 (m, 22 H), 8.03 (ddd, 1H), 7.92–7.87 (m, 11H), 7.75 (d, 2H), 7.70 (ddd, 1H), 7.45 (t, 1H), 7.38 (d, 2H), 5.10–5.02 (m, 1H), 4.50–4.32 (m, 24 H), 2.33–2.22 (m, 2H), 2.00–1.90 (m, 2H), 1.90–1.78, (m, 12 H), 1.70–1.47 (m, 36H), 1.40–1.12(m, 72 H), 1.00–0.90 (m, 42 H), 0.88–0.84 (m, 72H); ¹³C NMR (CDCl₃, 100 MHz): δ 165.23, 165.18, 165.12, 163.43, 138.24, 135.70, 135.34, 134.31, 132.74, 132.67, 132.42, 131.97, 131.44, 131.37, 130.95, 129.90, 129.71, 129.58, 128.93, 128.56, 126.77, 126.46, 124.06, 123.89, 123.58, 123.49, 123.42, 123.12, 122.99, 90.34, 89.18, 89.11, 89.02, 88.92, 64.30, 63.96, 57.76, 50.89, 39.18, 37.10, 35.51, 29.94, 29.70, 27.94, 25.01, 24.59, 22.69, 22.59, 19.66, 11.35. MALDI-TOF MS (*M*_w = 3949.19) *m/z* = 3948.18 [M]⁺ (See Supporting Information).

OPV–FOLD (9). A mixture of **8** (38.7 mg, 0.01 mmol), **5** (11.7 mg, 0.012 mmol), Pd₃(dba)₂ (2.4 mg, 0.003 mmol), PPh₃ (7 mg, 0.03 mmol), CuI (1 mg, 0.005 mmol) dissolved in dry triethylamine (1 mL) was purged with Ar for 15 min and subsequently stirred and heated at 70 °C for 16 h. The solution was filtered over diatomaceous earth to remove the precipitate and concentrated in vacuo. The crude product was purified by pressure column chromatography (CH₂Cl₂/pentane 1:1, R_f = 0.1 and CHCl₃/pentane 3:2 to 4:1, R_f = 0.1) to yield 23 mg (48%) of a yellow waxy solid. ¹H NMR (CDCl₃, 400 MHz): δ 8.22–8.14 (m, 21 H), 8.38–8.18 (m, 2H), 8.08 (t, 1H), 7.89–7.87 (m, 12 H), 7.86–7.84 (m, 2H), 7.81(t, 1H), 7.42–7.59 (m, 4H), 7.19 (s, 2H), 7.17 (s, 1H), 7.10 (s, 1H), 7.02 (s, 1H), 6.73 (s, 1H), 4.48–4.32 (m, 24H), 4.00–3.74 (m, 12H), 2.25 (s, 3H), 2.05–1.78 (m, 18H), 1.70–1.47 (m, 42H), 1.40–0.9 (m, 150H), 0.90–0.81 (m, 72H), 0.26 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz): δ 165.30, 165.09, 154.58, 151.67, 151.24, 150.93, 150.47, 150.36, 138.68, 138.23, 138.01, 132.67, 131.44, 131.26, 131.18, 129.46, 128.08, 127.64, 126.65, 125.13, 124.85, 124.22, 124.10, 123.59, 123.27, 122.04, 121.62, 117.07, 116.27, 111.49, 110.18, 109.87, 109.65, 108.36, 92.09, 89.38, 89.03, 88.77, 88.62, 74.64, 74.28, 73.37, 64.28, 39.18, 37.10, 35.51, 35.11, 34.99, 29.93, 27.93, 26.34, 26.28, 24.59, 22.68, 22.59, 19.65, 16.80, 16.69, 11.47, 11.37, –0.22. MALDI-TOF MS (*M*_w = 4321.78) *m/z* = 4320.17 [M]⁺ (See Supporting Information).

OPV–FOLD–PERY (10). Similar to the procedure for the synthesis of PERY–FOLD a mixture of **2** (6 mg, 0.009 mmol), **9** (31 mg, 0.0072 mmol), Pd(PPh₃)₄ (1 mg, 0.0008 mmol) and potassium acetate (1 mg, 0.01 mmol) in toluene (1 mL) and *N,N*-dimethylformamide (1 mL) was heated to 100 °C for 5 h, the solvent was evaporated in vacuo. The residue was triturated with water and extracted with methylene chloride. The methylene chloride extract was worked up to give crude products, which were purified by pressure column chromatography (CH₂Cl₂/pentane to 9:1, R_f = 0.4) to yield 3 mg (9%) of **10** as a light red solid. ¹H NMR (CDCl₃, 400 MHz): δ 8.76–8.65 (m, 8H), 8.20–8.15 (m, 23H), 8.12 (t, 1H), 7.91 (t, 1H), 7.90–7.87 (m, 10H), 7.84 (t, 1H), 7.74 (d, 2H), 7.56–7.41 (m, 4H), 7.38 (d, 2H), 7.18 (s, 2H), 7.16 (s, 1H), 7.09 (s, 1H), 7.01 (s, 1H), 6.72 (s, 1H), 5.11–5.02 (m, 1H), 4.45–4.35 (m, 24H), 3.97–3.74 (m, 12H), 2.31–2.24 (m, 5H), 2.05–1.78 (m, 20H), 1.70–1.47 (m, 42H), 1.40–0.95 (m, 156H), 0.88–0.84 (m, 72H).MALDI-TOF MS (*M*_w = 4784.90) *m/z* = 4783.38 [M]⁺ (See Supporting Information).

Absorption and Photoluminescence. UV–vis/near-IR absorption spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer. Fluorescence spectra were recorded on an Edinburgh Instruments FS920 double-monochromator spectrometer and a Peltier-cooled red-sensitive photomultiplier. Spectroscopic studies were performed on solutions with concentrations in the order of 10^{–6} M, at room temperature. Samples were allowed to equilibrate for at least 12 h before the measurement. For determining the conformation of the foldamer bridge, the absorbance of the shoulder at ~304 nm (*A*_s) and the peak at 288 nm (*A*_p) were determined from the UV–vis spectra.^{11–16} The accuracy of the *A*_s/*A*_p absorption ratios determined from the UV–vis spectra is better than 3%, based on experiments where independently prepared solutions were prepared.

Time-correlated Single Photon Counting. Time-correlated single photon counting fluorescence studies were performed using an Edinburgh Instruments LifeSpec-PS spectrometer. The LifeSpec-PS comprises a 400 nm picosecond laser (PicoQuant PDL 800B) operated at 2.5 MHz and a Peltier-cooled Hamamatsu microchannel plate photomultiplier (R3809U-50). Lifetimes were determined from the data using the Edinburgh Instruments software package.

Electrochemistry. Cyclic voltammograms were measured in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte in dichloromethane using a Potentiostat Wenking POS73 potentiostat. The working electrode was a Pt disk (0.2 cm²), the counter electrode was a Pt plate (0.5 cm²), and a saturated calomel electrode (SCE) was used as reference electrode, calibrated against Fc/Fc⁺ (+0.43 V).

Transient Subpicosecond Photoinduced Absorption. The femtosecond laser system used for pump–probe experiments consisted of an amplified Ti/sapphire laser (Spectra Physics Hurricane). The single pulses from a cw mode-locked Ti/sapphire laser were amplified by a Nd:YLF laser using chirped pulse amplification, providing 150 fs pulses at 800 nm with an energy of 750 μ J and a repetition rate of 1 kHz. The pump pulses at 450 nm were created via optical parametric amplification (OPA) of the 800 nm pulse by a BBO crystal into infrared pulses which were then two times frequency doubled via BBO crystals. The probe beam was generated in a separate optical parametric amplification setup in which 1450 nm pulses were created. The pump beam was focused to a spot size of about 1 mm² with an excitation flux of 1 mJ cm⁻² per pulse. A RG 850 nm cutoff filter was used to avoid contributions of residual probe light (800 nm) from the OPA. The probe beam was reduced in

intensity compared to the pump beam by using neutral density filters of OD = 2. The pump beam was linearly polarized at the magic angle of 54.7° with respect to the probe, to cancel out orientation effects in the measured dynamics. The temporal evolution of the differential transmission was recorded using an InGaAs detector by a standard lock-in technique at 500 Hz. Solutions in the order of 10⁻⁵ M were excited at 450 nm, i.e., providing primarily excitation of the OPV part within the molecules.

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Supporting Information Available: Additional graphs and spectra of the optical properties (UV–vis, CD, PL, cyclic voltammetry, MALDI-TOF) of the compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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