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Phenylene Ethynylene-Tethered Perylene Bisimide Folda-Dimer and Folda-Trimer: Investigations on Folding Features in Ground and Excited States

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Abstract: In this work, we have elucidated in detail the folding properties of two perylene bisimide (PBI) foldamers composed of two and three PBI units, respectively, attached to a phenylene ethynylene backbone. The folding behaviors of these new PBI folda-dimer and trimer have been studied by solvent-dependent UV/Vis absorption and 1D and 2D NMR spectroscopy, revealing facile folding of both systems in tetrahydrofuran (THF). In CHCl₃ the dimer exists in extended (unfolded) conformation, whereas partially folded conformations are observed in the trimer. Temperature-dependent ¹H NMR spectroscopic studies in [D₈]THF revealed intramolecular dynamic processes for both PBI foldamers due to, on the one hand, hindered rotation around C-N imide bonds and, on the other hand, backbone flapping; the latter process being energetically more demanding as it was observed only at elevated temperature. The structural features of folded conformations of the dimer and trimer have been

Introduction

Although the continuing progress in synthetic methodology and analytical methods enables the construction of defined molecules of greater size, chemists have to admit that the vast majority of their elaborate large-sized molecules are of irregular shape, even if the molecules are monodisperse due to the precise synthetic protocols applied. Among the few exceptions are the rather stiff conjugated oligomers^[1] and shape-persistent macrocycles,^[2] in which intramolecular contacts between non-neighboring building blocks are prohibited by the stiffness of the molecular backbone. When flexible units are introduced elucidated by different 2D-NMR spectroscopy (e.g., ROESY and DOSY) in [D₈]THF. The energetics of folding processes for the PBI dimer and trimer have been assessed by calculations applying various methods, particularly the semiempirical PM6-DH2 and the more sophisticated B97D approach, in which relevant dispersion corrections are included. These calculations corroborate the results of NMR spectroscopic studies. Folding features in the excited states of these PBI foldamers have been characterized by using time-resolved fluorescence and transient absorption spectroscopy in THF and CHCl₃, exhibiting similar solvent-dependent behavior as observed for the ground state. Interestingly, photoinduced electron transfer (PET) process from electron-donating backbone to electron-deficient PBI core for extended, but not for folded, conformations was observed, which can be explained by a fast relaxation of excited PBI stacks in the folded conformation into fluorescent excimer states.

into the backbone to allow for coiling into a structure with intramolecular contacts, a multitude of possible conformations usually show up and the supramolecular arrangement of the constituent building blocks becomes out of control. Thus, the co-existence of a large variety of conformers becomes apparent.^[3] In contrast, for selective backbones a transition from randomly coiled structures (unfolded state) into a small set of almost identical conformers (folded state) can be observed due to intramolecular ordering of the repeat units attached to the backbone.^[4] The issue of folding of polypeptides into precise three-dimensional structures has been intensively elucidated, but still the de novo design of synthetic proteins with

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functions that are prevalent in natural systems remains a big challenge.^[5] Nevertheless, such natural biomacromolecules have strongly inspired chemists and motivated the search for synthetic backbones that may fold into desirable three-dimensional architectures, being reminiscent of their natural counterparts. Among the first examples of such synthetic systems are the naphthalene diimide dihydroxynaphthalene aedamers of Lokey and Iverson,^[6] the phenylene ethynylene oligomers by Moore et al.,^[7] and oligopyridinecarboxamides by Huc and Lehn.^[8] Recently, Huc and co-workers have convincingly demonstrated by combined NMR spectroscopy and single-crystal X-ray analysis that large synthetic scaffolds may also organize into defined three-dimensional architectures, which are considered to be crucial if specific and highly sophisticated functions beyond simple molecular recognition or light harvesting were to be achieved.^[9]

Self-assembly of perylene bisimide (PBI) dyes has been a subject of extensive investigations over more than a decade.^[10] Whereas the intermolecular self-assembly approach enabled us to synthesize large PBI-based supramolecular architectures with fascinating functions such as photoinduced charge separation in supramolecular p-n-heterojunctions,^[11] charge transport in columnar stacks,^[12] and exciton migration in J-aggregates,^[13] we realized that it is rather elusive with currently available analytical tools to achieve unambiguous information on the exact supramolecular structure as desired to derive structure-property relationship guidelines for a rational design of advanced functional materials. Therefore, we paid attention to covalent scaffolds that preorganize PBI dyes in a suitable way with regard to intramolecular folding into specific three-dimensional architectures.^[14] Previously, we have investigated a phenylene ethynylene-tethered PBI oligomer **1** (Figure 1) and demonstrated solvent-dependent π - π -stacking of the backbone-embedded PBI units. This was attributed to a folding into a helical PBI π -stack surrounded by the alternating ortho-meta-(phenylene ethynylene) conjugated backbone (with structural resemblance to DNA double helices). However, the polydispersity restricted the structural elucidation, particularly by NMR spectroscopic methods.

Therefore, we altered our approach and decided to synthesize small but monodisperse PBI oligomers and study their folding properties as model systems to elucidate structureproperty relationships. Here, we present our comprehensive investigation on folding features of newly designed folda-dimer **2** and folda-trimer **3** (Figure 1). We have explored in detail the folding properties of PBI **2** and **3** in the ground and excited state in different solvents by steady state and time-resolved spectroscopy, and theoretical calculations as well. Our studies revealed that, through external control over the spatial arrangement of dye ensembles by the nature of solvent, foldadimer **2** and folda-trimer **3** can be triggered to adopt desired and predictable conformations in which the PBI moieties are arranged either randomly or in H-type stacked states.

Results and Discussion

Synthesis

The target phenylene ethynylene tethered folda-dimer **2** and folda-trimer **3** were synthesized according to the routes depicted in Scheme 1. Starting with the literature-known 4,5-diiodo-1,2-di-*n*-hexylbenzene **4**,^[15] the monosilyl-protected 1,2-diethynyl-benzene derivative **7** was synthesized by two sequential Pd/Cu-catalyzed Sonogashira–Hagihara reactions with 2-methylbut-3-yne-2-ol and triisopropylsilylacetylene in diisopropylamine under inert conditions, followed by quantitative cleavage of the tertiary alcohol protective group in precursor **6** with sodium hydroxide in a boiling toluene/ dioxane mixture in an overall yield of 63 %.

Compound **7** was previously synthesized by a different route;^[14b] however, the present pathway using a polar tagging strategy^[16] resulted in significantly higher yield. In the next step, 12-tricosanyl-substituted^[17] (first mentioned as "swallow-tailed"^[18] alkyl substituents for smaller branched alkyl chains



Figure 1. Chemical structures of PBI oligomer 1 $(n \approx 8)$,^[14a] and new folda-dimer 2 and folda-trimer 3 investigated here.

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Scheme 1. Synthetic routes to folda-dimer 2 and folda-trimer 3 as well as reference molecule 15.

attached to steroids by Louw et al.) perylene-3,4:9,10-tetracarboxylic acid-3,4-anhydride-9,10-imide $\boldsymbol{8}^{\scriptscriptstyle[19]}$ was treated with 3-iodoaniline to obtain PBI 9 in a yield of 97% in analogy to the literature-known reaction of symmetric 3,5-diiodoaniline with 8 affording PBI 12,^[14a] which was used to build up the inner PBI moiety in folda-trimer 3. The unsymmetrical PBI dye 9 was subjected to Sonogashira-Hagihara coupling reaction with 7 in degassed triethylamine (NEt₃) and dry tetrahydrofuran (THF) in the presence of triphenylphosphine to obtain the key intermediate 10 (65% yield) for the target compounds 2 and 3. The Sonogashira-Hagihara reaction of in situ-generated terminal alkyne 11, which could also be isolated for characterization purposes, from 10 by using tetra-n-butylammonium fluoride (TBAF) with either 9 or 12 under similar reaction conditions as applied for the synthesis of 10, afforded the desired folda-dimer 2 and folda-trimer 3 in 69 and 44% yields, respectively. The compounds 2 and 3 were separated from byproducts and purified by gel permeation chromatography (GPC). The syntheses of the reference compounds 9 and 15 (for structures, see Scheme 1) are described in the Supporting Information. All new compounds, including the target compounds 2 and 3, were characterized by NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis. The synthetic details and the characterization data of new compounds foldadimer 2 and folda-trimer 3 as well as those of 5, 6, 7, 9, 10, 11, 13, 14, and 15 are given in the Supporting Information.

Solvent-dependent folding properties in the ground state

We have investigated the folding properties of the newly synthesized folda-dimer **2** and folda-trimer **3** in the ground state by UV/Vis absorption and ¹H NMR spectroscopy. To ascertain the suitable solvents or solvent combinations for these studies, we have first measured UV/Vis absorption spectra of PBI **2** in a broad variety of solvents ranging from nonpolar methylcyclohexane to considerably polar chlorinated solvents and to highly polar benzonitrile (Figures S1 and S2 in the Supporting Information). Based on these solvent-dependent studies (for details, see the Supporting Information) we have chosen chloroform (CHCl₃) and tetrahydrofuran (THF), and mixtures of these two solvents for the elucidation of ground state folding properties of **2** and **3**.

The UV/Vis absorption spectra of folda-dimer **2** and foldatrimer **3** in pure $CHCI_3$ and THF and in different mixtures of these solvents are shown in Figure 2. The spectrum of foldadimer **2** in pure $CHCI_3$ exhibits two sharp absorption bands at

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Figure 2. Solvent-dependent UV/Vis absorption spectra of a) **2** $(c=5\times10^{-6} \text{ M})$ and b) **3** $(c=6\times10^{-6} \text{ M})$ in CHCl₃/THF mixtures at 25 °C starting in pure CHCl₃ (-··-) changed to pure THF (——) by increasing THF content in steps of 10 vol%. Inset: Plot of the absorption maxima A_{1-0} (**A**) and A_{0-0} (**a**) against the content of THF (0 to 100 vol%) in CHCl₃.

529 and 493 nm with extinction coefficients of 123600 and 96100 M^{-1} cm⁻¹, respectively, along with a shoulder at 462 nm and a broad slope in the region of 300 to 370 nm. Upon increasing the content of THF in CHCl₃/THF mixtures from 0 to 100% the lowest-energy band (at 529 nm) shows significant changes with large hypochromic shifts ($\Delta \varepsilon$ down to $49800 \,\mathrm{m}^{-1} \mathrm{cm}^{-1}$, which corresponds to a loss in intensity of about 40%) and a small hypsochromic shift of 3 nm, whereas the band at 493 nm remains nearly unchanged ($\Delta \varepsilon$ up to $4700 \text{ m}^{-1} \text{ cm}^{-1}$, loss in intensity < 5%). The plot of extinction coefficients ε of PBI 2 against the contents of THF in CHCl₃ (Figure 2a, inset) reveals a gradual decrease of the $\boldsymbol{\varepsilon}$ value for the band at 529 nm with increasing of the THF content from 0 to 60%. For solvent mixtures consisting of >60% THF, the intensities of both bands (at 529 and 493 nm) remain virtually unchanged. Accordingly, the ratio of absorption maxima of both prominent bands $A_{529 nm}/A_{493 nm}$ of folda-dimer **2** is 1.29 in CHCl₃ which gradually decreases down to 0.80 upon increasing the THF content from 0 to 100%. It is noteworthy that for the reference PBI dye 15, which contains one PBI unit and thus cannot fold, this ratio is close to 1.65 in both solvents (the Supporting Information, Figure S3). In this regard it should be mentioned that for a rigid cofacial stacked PBI dimer of Wasielewski, a A_{0-0}/A_{1-0} ratio of around 0.9 in CHCl₃ was reported,^[20] whereas for a rigid biphenyl-bridged PBI dimer of Langhals and co-workers,^[21] in which both chromophores are arranged away from each other, this value was reported to be 1.3 in CHCl₃. For the photoswitchable PBI dimer of Feringa and coworkers, this ratio was changed upon irradiation from 1.4 to 0.8 in THF.^[22] The fact that PBI folda-dimer **2** shows A_{0-0}/A_{1-0} values of 1.3 in CHCl₃ and 0.8 in THF implies that this dimeric PBI system exists in folded state in THF, whereas in the halogenated solvent it is unfolded and the data are in good accordance with the literature-reported values mentioned above.

Folda-trimer 3 exhibits similar solvent-dependent changes of absorption spectra (Figure 2b) as observed for 2. In CHCl₃, again two dominant absorption bands can be seen at 531 and 495 nm with ε values of 118300 and 124100 M^{-1} cm⁻¹, respectively, along with a shoulder at 468 nm (Figure 2b). However, the intensities of bands at 531 and 495 nm are already reversed compared with that of the corresponding bands of folda-dimer **2** and the ratio of the two bands, $A_{531 \text{ nm}}/A_{495 \text{ nm}}$, for 3 is 0.95. These observations can be taken as an indication for a stronger coupling between the PBI units in partially folded conformations of 3 in CHCl₃. Upon increasing the content of THF both bands are hypochromically shifted ($\Delta \varepsilon$ down to 51600 and $14800 \,\mathrm{m}^{-1} \mathrm{cm}^{-1}$, which correspond to an intensity loss of 44 and 12% for the bands at 531 and 495 nm, respectively). The ratio of $A_{535 nm}/A_{495 nm}$ in pure THF is reduced to 0.61, which is markedly smaller than that observed for folda-dimer 2. For a cofacial PBI trimer with a rigid xanthene spacer, a A_{0-0}/A_{1-0} ratio of 0.6 was reported by Wasielewski and co-workers. $^{\scriptscriptstyle [20]}$ Thus, a folded conformation of ${\bf 3}$ in THF can be implied, whereas in CHCl₃ this molecule is apparently in a more unfolded state.

To assess whether any further self-assembly by intermolecular interactions between individual molecules occurs, temperature- and concentration-dependent UV/Vis studies were carried out for folda-dimer **2** (the Supporting Information, Figures S4– S6) and folda-trimer **3** (Figures S7 and S8) in CHCl₃ and THF. In both solvents, the temperature- and concentration-dependent spectral changes for **2** and **3** are almost negligible. These observations suggest that, on the one hand, the PBI molecules are appropriately solvated and do not build larger supramolecular ensembles and, on the other hand, the intramolecularly folded dimer **2** and trimer **3** are held together by rather strong π - π interactions in THF as no spectral changes were observed at higher temperatures (see the Supporting Information, Figures S4a, S6, S7 a, and S8).

To get more insight into the solvent-dependent conformations of folda-dimer **2** and folda-trimer **3**, and to explore whether additional dynamic processes are involved, we have conducted temperature-dependent ¹H NMR studies in [D₈]THF and CDCl₃. It has to be pointed out here that, in contrast to the research on biomolecules, application of NMR methods is much rarer for the elucidation of conformational preferences of synthetic oligomer backbones. However, in the field of naphthalene and perylene bisimide dyes a few studies have been reported, for example, by the groups of Li,^[23] Castellano,^[24] Sanders,^[25] and Wasielewski.^[26]

In CDCI₃, which is known as a good solvent for the solvation of π -extended aromatic systems, in particular PBI dyes,^[27] a sur-

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Figure 3. Aromatic regions of temperature-dependent ¹H NMR spectra (600 MHz) of folda-dimer 2 ($c=5 \times 10^{-4}$ M) in [D₈]THF at 274 to 333 K and in CDCl₃ at 293 K (top). The temperature is indicated above the respective spectrum. Solvent signals are marked with asterisks (*). In the proton spectrum of **2** in [D₈]THF at 333 K (bottom) signals of the low-populated conformer (see the discussion below) are marked with plus symbols (+). Inset: Chemical structure of folded **2** with the assignment of aromatic protons of PBI core (P1, P2, P3, and P4) and phenylene ethynylene scaffold (2, 4, 5, 6, and 3'). Long alkyl chains are represented by methyl substituents for simplicity. Strong interactions between adjacent protons observed in the 2D ROESY NMR spectrum (see the Supporting Information, Figure S10) are indicated by a grey arrow.

prisingly complex signal pattern was observed in the aromatic region ($\delta = 8.8$ to 7.2 ppm) for folda-dimer **2** at 293 K (Figure 3, top). Such signal pattern suggests a coexistence of different conformations of 2 in CDCl₃, whose interconversion is not fast enough on the NMR timescale for signal averaging. Whereas the signals for PBI core protons (between $\delta = 8.8$ and 8.2 ppm) are not reliably assignable due to signal overlapping, the major signals (between $\delta =$ 7.7 and 7.2 ppm) of phenylene ethynylene scaffold could be assigned (Figure 3, top spectrum). Variation of temperature in the range from 274 to 323 K did not simplify the spectra of 2 in CDCl₃ (the Supporting Information, Figure S9). On the other hand, variable temperature (from 274 to 333 K) ¹H NMR spectra of **2** in [D₈]THF showed comparatively simpler signal pattern with perylene core protons located in a narrow range ($\delta = 8.4$ to 8.2 ppm). At lower temperature (274 to 298 K) some dynamic broadening of the signals of perylene core protons at $\delta = 8.4$ to 8.2 ppm was observed. Upon increasing the temperature to 313 K and higher, the broadened perylene proton signals got increasingly sharper and nicely resolved in four doublets. Compared with the spectra in CDCl₃, the signals of the perylene protons of folda-dimer 2 in [D₈]THF are significantly higher-field shifted, which is in stark contrast to the monomeric PBI reference compound 15 since for the latter an opposite trend was observed in these

solvents (see the Supporting Information, Figure S11). The observed highfield shift for the perylene protons of PBI **2** in $[D_{\rm s}]$ THF can be taken as an indication for the formation of π - π -stacked PBI dimer, that is, folding of **2**. Since the temperature increase (from 274 to 333 K) resulted in a sharpening of the aromatic proton signals without any considerable shift or change of coupling pattern (Figure 3), an intramolecular dynamic process that preserves the π - π stacking should be responsible for the observed temperature-dependent changes of the NMR spectra of **2** in $[D_{\rm s}]$ THF.

To shed light on this dynamic process, the variable temperature NMR study of reference PBI **15** (Figure 4a), which is a simpler monomeric analogue of **2**, in [D₈]THF is very instructive. A selection of temperature-dependent ¹H NMR spectra of **15** in [D₈]THF is shown in Figure 4d (for the complete set of spectra measured at temperature range 274 to 333 K, see the Supporting Information, Figure S12). In the spectrum at lower temperature (274 K), four nicely separated doublets were observed at δ =8.94, 8.71, 8.68, and 8.64 ppm in a signal integral ratio of 4:2:1:1, respectively. These doublets could be assigned to the perylene protons as shown in Figure 4a.

Upon increasing the temperature, the two doublets at δ = 8.68 and 8.64 ppm (for protons P4/P4') become gradually broader and merge into a broad signal at around 303 K (see

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Figure 4. a) Chemical structure of **15** with the assignment of aromatic protons; b) representative CPK models of the two rotational conformations (**A** and **B**) arising from the hindered rotation of swallow tail around the C–N bond in PBI **15** schematically shown for *N*-(isopropyl)-1,8-naphthalene imide (view along the C–N bond, $R = n-C_{11}H_{23}$). The two different perylene core protons P4 and P4', distinguishable at low temperature, are labelled in both sketches; c) schematic representation of the energy profile for the dynamic interconversion of the two rotamers; d) aromatic regions of the selected temperature-dependent ¹H NMR spectra (600 MHz) of **15** ($c=5 \times 10^{-4}$ M) in [D₈]THF at 274 to 333 K (below). Temperatures are indicated above the respective spectrum. Signals are assigned as depicted in (a).

also the Supporting Information, Figure S12). Upon further increasing of temperature, this broad signal gets again narrower and above 323 K a doublet arises, which becomes very sharp at 333 K. With the concomitant separation of the signals for protons P2 and P3 the expected four doublets with intensity ratio of 2:2:2:2 are now realized. The observed temperaturedependent spectral changes for 15 in [D₈]THF can be attributed to a hindered rotation around the C-N bond with a swallowtail (12-tricosanyl) imide substituent. Indeed, perylene bisimides and similar imide compounds that exhibit restricted rotation around C-N imide bond with considerably high rotational barriers have been reported previously.[24, 28] Thus, such rotational isomers can be frozen at low temperature. For PBI 15 we have observed two doublets at $\delta = 8.68$ and 8.64 ppm for the two perylene ortho-protons P4/P4' at low temperature (274 K) in [D₈]THF, whereas for the other two ortho-protons (P1) only one doublet at $\delta = 8.71$ ppm was observed. This spectral feature can be attributed to a slower rotation of the swallowtail substituent around the respective C-N bond on the NMR timescale, and thus freezing of the two rotamers A and B shown in Figure 4b. Upon increasing the temperature, these doublets are gradually broadened, and at around 303 K show coalescence, revealing a dynamic equilibrium of these rotamers on the NMR timescale. At temperatures above 303 K, the rotation gets faster than the NMR timescale and thus the two perylene protons P4/P4' become chemically equivalent, giving rise to a sharp doublet. An energy barrier (ΔG^{\dagger}) of about 64 kJ mol⁻¹ (see Figure 4 c) could be estimated for this intramolecular rotation process by using the coalescence method.^[29] Similar values have been reported for the rotational barrier of PBIs bearing branched alkyl substituents at the imide positions.^[28a] By employing a smaller reference system, namely N-(isopropyl)-1,8-naphthalene imide, we have estimated an energy barrier of about 61 kJ mol⁻¹ by DFT calculations. For comparison, an energy barrier of only 25 kJ mol⁻¹ was calculated for a related 1,8-naphthalene imide bearing a meta-ethynyl phenylene (instead of isopropyl) imide substituent.^[30] Accordingly, also DFT calculations support our conclusion that the hindered rotation around the C-N bond with a swallowtail imide substituent, and not that of ethynyl phenylene substituent is responsible for the observed temperature-dependent ¹H NMR spectral changes in the 274-333 K temperature regime in [D₈]THF (also see the Section: Theoretical calculations).

In light of the above discussion on variable-temperature ¹H NMR spectroscopic study of monomeric reference PBI **15**, the temperature-dependent spectral changes observed for the folda-dimer **2** in [D₈]THF (Figure 3) can be ascribed to a similar hindered rotation around the C–N bonds of two PBI units bearing swallowtail substituents. The broad signal observed at



 $\delta = 8.4$ to 8.2 ppm for the perylene protons of PBI **2** at low temperature (274 K) can be attributed to a slow rotation of the swallowtail substituents around C–N bonds on the NMR timescale. At higher temperatures (>313 K) the rotation around C–N bond gets much faster than the NMR timescale, and thus the perylene protons (P1, P2, P3, and P4) of the two PBI units are nicely resolved in four sharp doublets, which could be clearly assigned (as shown in Figure 3) based on the 2D NMR spectra. The observation of only four doublets at higher temperatures (323 K) for 16 perylene protons of folda-dimer **2**, implies that the respective proton pairs (P1, P2, P3, and P4) in both PBI units of **2** are chemically equivalent. This can be taken as an indication for a tightly packed and symmetric folding of PBI **2** in [D₆]THF.

A closer look at the high temperature ¹H NMR spectrum of 2 in [D₈]THF at 333 K reveals the appearance of an additional set of weaker signals (Figure 3, bottom). These signals presumably arise from a second folded conformation of 2 with quite different ¹H NMR chemical shifts, which are difficult to assign reliably as they are low in intensity and, moreover, overlap partially with the prominent signals. From signal integration of α -proton resonances of imide substituents at $\delta = 5.25$ to 5.10 ppm (for an enlarged spectrum see the Supporting Information, Figure S13) a 1:10 ratio of the conformers can be estimated. For this population distribution, an energy difference of approx. 6 kJ mol⁻¹ between the two conformers can be estimated by applying Boltzmann analysis. Backbone flapping in folded PBI 2 may indeed result in two different conformations as revealed below by theoretical calculations (local optimization of one gradually distorted phenylene unit in folded 2 with PM6-DH2), which provide an energy barrier of approximately $50 \ kJ \ mol^{-1}$ for the backbone flapping, which might be significantly underestimated by a factor of 2 (for details, see the Section: Theoretical calculations).

Temperature-dependent ¹H NMR spectroscopic studies of folda-trimer 3 in [D₈]THF and CDCl₃ were performed as well (Figure 5 a and the Supporting Information, Figure S15). In addition, the 2D-ROESY NMR spectra were measured (Figure 5 b and the Supporting Information, Figure S14). In CDCl₃ a broad signal pattern spreading over the complete aromatic range from $\delta = 8.9$ to 6.9 ppm is observed, which is, as expected, more complex than that observed for 2 in this solvent. Although the assignment of signals to the protons of 3 appears rather elusive, the large number of peaks provides an indication for the co-existence of different conformations with varying spatial arrangement of the PBI subunits. The variation of temperature from 274 to 333 K did not appreciably affect the spectral shape in CDCl₃ (the Supporting Information, Figure S15). However, the temperature-dependent ¹H NMR spectra of 3 in [D₈]THF exhibit, as in the case of 2, a simpler signal pattern (Figure 5a). Thus, the signals of all aromatic protons between $\delta = 8.4$ and 7.2 ppm become increasingly narrower with increasing temperatures from 274 to 333 K. Most significant temperature-dependent changes are observed for the two doublets at $\delta = 8.41$ and 8.37 ppm, and for the broad signals at $\delta = 8.2$ ppm that appear in the spectrum at 274 K. Upon increasing the temperature, the signals of the two doublets ($\delta =$

8.41 and 8.37 ppm) are gradually broadened and merge into a broad signal at around 313 K, and at higher temperatures (333 K) again become a doublet.

Likewise, with increasing temperature, the broad signals at $\delta =$ 8.2 ppm first change into a broad singlet and become finally resolved to a sharp doublet at higher temperature (333 K). Again the hindered rotation around the C-N bonds bearing branched alkyl substituents (swallowtail) may account for this dynamic spectral behavior of folda-trimer 3 as discussed before for the folda-dimer 2. As in the case of dimeric analogue 2, for folda-trimer 3 the existence of a second, lowpopulated conformer can be anticipated from the additional signal set (labelled with symbol +) observed at 333 K (Figure 5 a, bottom spectrum). A ratio of 1:4 between the two conformers was determined by signal integration in the higher field (C-H proton of the alkyl substituent, see the expanded spectrum in the Supporting Information, Figure S16). By applying Boltzmann analysis, an energy difference of approximately 4 kJ mol⁻¹ could be estimated for this distribution. This value is slightly smaller than that determined for 2. The reason for this might be that in 3 the two PBI bridging scaffold subunits are influencing and preorganizing each other.

Moreover, the 2D-NMR spectroscopic studies were performed to gain more insight into the structural features of folded conformations of folda-dimer 2 and trimer 3. Since the neighboring PBI units are arranged close to each other in the folded state, prominent cross-couplings would provide information on spatial arrangement of PBI dye units in conformers. However, due to the potentially high C_2 symmetry of the folded structures, the nuclear Overhauser effects (NOE) visualized by 2D-ROESY NMR spectroscopy can only partially be used to reveal the PBI interactions upon folding. The most expressive through-space proton-proton cross-couplings in the folded states are given between the two H2 protons in 2 (see the inserted structure in Figure 3) and the protons at the H2 and H2" positions in 3 of the phenylene imide substituents in [D₈]THF (see the inserted structure in Figure 5 a). These crosscouplings cannot be identified because of the overlapping with the diagonal signals in the ROESY spectra. In particular, couplings between perylene core protons P1 and P2 and H6 of the phenylene ethynylene scaffold can be observed for 2 in [D₈]THF (see the Supporting Information, Figure S10), which supports the proposed folded structure for dimer 2 (the evaluated distances between these protons, P1-H6 and P2-H6, respectively, by our calculations are 2.4 and 3.3 Å). On the other hand, the dominant signals of 2 in CDCl₃ do not show any cross-couplings (the Supporting Information, Figure S17). This corroborates our suggestion that unfolded states of 2 prevail in chlorinated solvent. As mentioned, PBI 2 adopts different conformations in $\mathsf{CDCl}_{\mathsf{3}}$, whereas few of them bring both chromophores in sufficient contact to each other to communicate. Although not completely folded, this PBI-PBI distance narrowing results in appreciable ROESY cross-couplings (see the Supporting Information, Figure S17). Likewise, the 2D ROESY spectrum of folda-trimer **3** in CDCl₃ (the Supporting Information, Figure S18) does not exhibit any significant cross coupling as the PBI dye units are apparently not arranged in

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Figure 5. a) Temperature-dependent ¹H NMR spectra of folda-trimer 3 in $[D_8]$ THF at 274 to 333 K and in CDCl₃ at 293 K (top) and b) ¹H, ¹H-2D-ROESY NMR spectrum of **3** in $[D_8]$ THF at 328 K (for (a) and (b): $c = 4 \times 10^{-4} \text{ M}$, 600 MHz). In (a) the solvent signals are marked with asterisks (*). In the proton spectrum in $[D_8]$ THF at 333 K (bottom) smaller signals are marked with plus symbols (+). Inset: The chemical structure of folded **3** with the assignment of aromatic phenylene protons. Alkyl chains are represented by methyl substituents for simplicity. Perylene protons of outer PBI units (PBI_o, bold black and orange in the sketch) are marked with P_o and those of the inner PBI (PBI_i, bold red in the sketch) with P_i. The blue arrow indicates a strong interaction between adjacent protons in the ROESY spectrum. The changes in chemical shifts of the signals in the region of $\delta = 7.5$ to 7.3 ppm upon increasing temperature are illustrated by dashed lines. In (b), signals which are marked with circles correspond to cross-couplings that are not present in the ¹H, ¹H-2D COSY NMR spectrum (see the Supporting Information, Figure S19).

spatial proximity. However, in the $[D_8]$ THF spectra of **3** prominent through-space interactions are present (Figure 5b, for an enlarged spectrum see the Supporting Information, Figure S14). These include signals that arise from couplings be-

tween protons of the two outer PBI moieties (P_o) with those of the inner PBI (P_i) as well as those between the outer PBI moieties (P_o) and the backbone H2" protons. These through-space couplings can take place only in the folded state (depicted by



the arrow in the structure shown in Figure 5a). A comparison of the 2D-COSY NMR spectrum of **3** in $[D_8]$ THF (the Supporting Information, Figure S19) with the 2D-ROESY spectrum (Figure 5b) reveals such through-space couplings. Additionally, the number of carbon atoms and C–H units comply with the signals present in the ¹³C NMR spectra (besides overlapping of signals with similar shifts) as well as in the 2D-HSQC NMR spectra both for PBI **2** and PBI **3** in $[D_8]$ THF (see the Supporting Information, Pages S51–S54).

DOSY NMR spectroscopic studies were performed to assess the molecular dimensions of the foldamers. For folda-dimer 2 in $[D_8]$ THF at 298 K, a diffusion coefficient (D) of $6.3 \times$ $10^{-10} \, \text{m}^2 \text{s}^{-1}$ was estimated, which corresponds to a diameter of 22.6 Å according to the Stokes-Einstein Equation^[31] by assuming a spherical molecule (see also the Supporting Information, Figure S20). For the folded state of dimer 2, the geometry optimized structure revealed a distance of 22.4 Å between the first carbon atom of the imide substituent and the alkyl chain on the middle phenylene spacer unit, which is in good accordance with the experimentally obtained value of 22.6 Å. Notably, the other set arising from the weaker NMR signals shows almost the same diffusion behavior, which is further in accordance with a second folded conformer of PBI 2. For folda-trimer 3, a diffusion coefficient of $3.3 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ was determined by DOSY NMR spectroscopy in [D₈]THF at 293 K (see the Supporting Information, Figure S21). Based on this data, a diameter of 27.8 Å was calculated for the folded trimer 3, which is, as expected, slightly higher than the value determined for 2 in [D₈]THF. As in the case of PBI 2, similar diffusion constants are obtained for the NMR signal set with low intensity for PBI 3. Therefore, both signal sets of 3 appear to correspond to the same state, that is, the folded state.

Theoretical studies on the conformational properties

Our NMR spectroscopic studies revealed that in $CHCI_3$ the PBI units of folda-dimer 2 and folda-trimer 3 adopt a larger conformational space due to good solvation of the aromatic scaffolds, whereas in THF the conformational diversity is appreciably reduced due to intramolecular folding into helically ar-

ranged π -stacks. To obtain more detailed information on the energetically most favorable structures for the PBI systems **2** and **3** and thus to corroborate the results of NMR studies, we performed calculations by applying various methods. We first used the force fields OPLS-AA, AMBER, and MM3* to determine the equilibrium structures of **2** and **3**. The resulting structures, which are summarized in Figure 6, indicate strong variations depending on the force fields. The force fields MM3* and AMBER predict folded structures, whereas the OPLS-AA force field computed open structures as the most favorable conformers.

In the next step, the structural moieties responsible for flexibility in dimer 2 and trimer 3 were identified and analyzed in terms of their impact on the overall energy. The most flexible linkages, which are capable of driving the molecules to folded or unfolded states, are the single and triple bonds between the inner imide moieties and the phenylene imide substituents as well as in the tolan subunits as schematically depicted for the reference PBI 15 (the Supporting Information, Figure S23 a). To test the accuracy of various approaches, we have compared the relative energies of gradual distortion (0 to $180^\circ)$ of dihedrals for the related, simple model compounds tolan and N-phenyl-1,8-naphthalimide determined by different force fields, semiempirical and DFT approaches (the Supporting Information, Figure S23b-d). On the basis of these theoretical studies, we decided to use the PM6-DH2 approach to perform molecular dynamic (MD) simulations for 2 and 3 to elucidate the flexibility of the systems.

PM6-DH2 includes dispersion forces and should be sufficiently flexible for the description of unusual conformations, which might be energetically overestimated by force field approaches. In addition, the PM6-DH2 approach is an ideal compromise between accuracy and efforts. As starting structures for the MD simulations we used the minimum structures predicted by the force fields (Figure 6).

The energy distributions given in Figure 7 a and b reflect the relative energies of the minima, which are obtained when the MD frames of the last 50 ps of the MD simulations are optimized. The abbreviation **i–iii** denotes that the MD run started from the structures **I–III** (see Figure 6), respectively. The



Figure 6. Geometry optimized structures (side view) of a) folda-dimer 2 and b) folda-trimer 3 obtained by different force field optimizations (I: MM3*; II: AMBER; III: OPLS-AA). The respective top views of these conformations are shown in the Supporting Information, Figure S22.

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Figure 7. Relative energies in kJ mol⁻¹ of a) folda-dimer 2 and b) folda-trimer 3 obtained from molecular dynamic simulations (PM6-DH2, 300 K, 50 ps) and subsequent local optimization. Lowest-energy structures (side view) of c) PBI dimer 2-i to 2-iii and d) PBI trimer 3-i to 3-iii obtained after MD simulations. The respective top views of these conformations are shown in Figure S24 (the Supporting Information).

energies summarized in Figure 7a and b are relative to the lowest-energy structures of folda-dimer **2** and folda-trimer **3**, respectively. All MD runs were performed for the gas phase.

The MD simulations revealed the following important results: First, both unfolded conformations III of PBI 2 and 3 already form completely folded structures after a time period of 8 ps (PBI dimer 2) and 25 ps (PBI trimer 3; see conformations iii in Figure 7 c,d), implying that the intramolecular folded arrangements are much more favored than the unfolded conformations. For dimer 2 and trimer 3, these folding processes from III to iii can nicely be visualized by the distance narrowing from 26 and 23 Å (in unfolded conformations III) to around 3.7 and 3.6 Å (in folded conformations iii) of adjacent PBI centers in 2 and averaged for 3 as shown in Figure S25 (the Supporting Information). Although gas phase calculations cannot take into account explicit solute-solvent interactions, that is, the difference between CHCl₃ and THF for the folding process, the outcome of our MD indicates a very flexible bridging unit of PBI 2 and 3. For the DFT-D geometry optimized structure of the unfolded conformation 2-III (the Supporting Information,

Figure S26), an energy difference to **2-I** of 165 kJ mol⁻¹ was computed on the B97D/STO-3G level of sophistication. Notably, this value is very similar to the binding energy of two PBI monomers forming the energetically most favorable π - π -stacked dimer (125 kJ mol⁻¹, BLYP-D/TZV(P)).^[32] The higher energy difference obtained in the present computations can be reduced to basis set superposition errors of the smaller STO-3G basis. The small variation in the calculated values strongly underlines that the phenylene ethynylene backbone is sufficiently flexible that both PBI units are not hindered in the formation of favorable π -stacked structures. In the case of PBI dimer **2-III**, the folding leads to the conformation 2-iii. The latter one is very similar to the conformation 2-i obtained from 2-I, that is, their energy difference is 0 kJ mol⁻¹, with **2-i** being almost identical with the MM3* geometry-optimized structure 2-I (ΔE (2-I-2i) = 4 kJ mol⁻¹). Notably, the relative energies of all structures adopted during MD simulations (after local optimizations with PM6-DH2 of the last 50 ps structures) of 2-i and 2-iii are in narrow distribution (0-8 kJmol⁻¹) as the structures are nearly congruent. In contrast, the MD simulation starting from 2-II



leads to structure **2-ii**. It differs from **2-i** and **2-iii** by the orientation of the bridge relative to the PBI planes. The average energies of the minima obtained by optimizing the corresponding MD frames are shifted to somewhat higher values (Figure 7a, 8 kJmol⁻¹). This indicates that the minima **2-II** and **2-ii** are separated from the other minima (**2-I**, **2-I**, and **2-iii**), by barriers that are not crossed during the MD simulations.

For the folda-trimer **3**, the MD simulations gave similar results as for the folda-dimer **2**. Also for the conformation **3-i** the relative energies are within 0 and 4 kJ mol⁻¹, which suggests that the ideal conformation has already been adopted. Although conformations **3-i** and **3-ii** possess virtually the same spatial arrangement after approximately 8 ps MD simulation and local optimization, the relative energies of structures from conformation **3-ii** show a wider distribution spreading from 0 to 24 kJ mol⁻¹. However, the main portion (\approx 80%) of the structures is again within 0 and 4 kJ mol⁻¹ (see Figure 7b). For the conformation **3-iii**, which is obtained from the MD simulation starting with the unfolded conformation **3-iII**, the primarily populated structures are higher in energy (energy difference about 4 kJ mol⁻¹) and the lowest energy conformation **3-iii** resembles more the non-optimal structure of **3-II**.

These results explain the appearance of a second low-populated signal set observed in ¹H NMR spectra of folda-dimer **2** and folda-trimer **3** in $[D_8]$ THF, which is most expressive at higher temperatures (see Figure 3 and 5, bottom spectra). Because **2-i** and **2-ii** are nearly identical to **2-I** and **2-II**, further considerations focus on these two structures. The schematic energy profile as well as the suggested dynamic process caused by backbone flapping between conformation **2-I** and **2-II** are shown in Figure 8. Notably, the conformations **2-I** and **2-II** with the backbone directed upwards and downwards, respectively, are chemically and energetically equivalent and thus are not distinguishable by NMR spectroscopy.

The energy difference between **2-I** and **2-II** is computed to approximately 4 kJ mol⁻¹ (by PM6-DH2), which enables a detectable population of **II** by NMR spectroscopy. By using geometry optimizations on the B97D/STO-3G level of sophistication



Figure 8. a) Schematic representation of the dynamic interconversion between conformations **I**, **II**, and I' of folded PBI **2** caused by flapping of phenylene ethynylene scaffold; b) schematic illustration of the energy profile for the dynamic interconversion of the flapping with relative energies calculated by local optimization (PM6-DH2) of gradually distorted phenylene spacer unit in the scaffold.

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an energy difference between **2-I** and **2-II** (see the Supporting Information, Figure S25) of about 8 kJmol^{-1} is obtained. Accordingly, the calculated values are in reasonable agreement with the NMR data (ca., 6 kJmol^{-1}).

For folda-dimer 2, a subsequent distortion of one phenylene spacer in conformation II was used to estimate the energy barrier of the flapping process. For this approach, gradually distorted structures were locally optimized using PM6-DH2. Small distortions did not significantly change the relative energies of the system since the conformation II, especially the mutual orientation of both PBI moieties, did not show a large impact. The barrier of the flapping process was calculated to be about 50 kJ mol⁻¹ (Figure 8b). This value might be significantly underestimated based on comparison of experimental and calculated energy barriers for the rotation of the swallowtail imide substituent. For the latter one, the energy barrier was computed to be about 33 kJ mol⁻¹ using local optimization on PM6-DH2 level, which is only about half of the experimental value of 64 kJ mol⁻¹ based on temperature-dependent NMR analysis (Figure 4). Accordingly, the barrier for the flapping process is expected to be about 100 kJ mol⁻¹, which explains why no coalescence of NMR signals of the major and the minor conformations of backbone-flapped folded species of PBI 2 could be observed in our accessible temperature range (Figure 3). The same situation holds true for PBI 3 in which the two conformations 3-i and 3-iii (Figure 7d) exhibit similar energies and the NMR experiment (Figure 5a) also revealed the coexistence of two conformations that show no coalescence in the accessible temperature range in [D₈]THF.

As expected, computations in which the solvent is approximated by a continuum cannot explain the differences in the folding behavior of our systems in THF and CHCl₃. Because accurate simulations describing the complete system in a large solvent box are very costly and this topic is not the central focus of this work, we only roughly estimated enthalpy effects for folda-dimer **2** (see discussion in the Supporting Information, Pages S34–S38, Figures S27–S30, and Tables S1 and S2). These estimates indicate that the differences in the folding behavior do not stem from the strengths of the interaction between individual solvent molecules with a PBI moiety. The number of solvent molecules that fit within the first solvent shell seems to be more important. Notably, entropy effects always support the folding processes because solvent molecules are set free during the folding processes.

Folding properties in the excited state

Optical excitation of folda-dimer **2** and folda-trimer **3** afford excited molecules whose initial conformational versatility equals the one given in the ground state (Franck–Condon principle). Subsequently, however, the molecules may relax into energetically more favorable excited-state conformations such as excimers^[12,33] (in which two PBI units exhibit a more coplanar arrangement) or interact with the electron-donating phenylene ethynylene backbone.^[34] To elucidate these processes we performed steady state and time-resolved fluorescence and transient absorption spectroscopy experiments.

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The fluorescence emission and excitation spectra as well as the absorption spectra of folda-dimer 2 and folda-trimer 3 in CHCl₃ and THF are shown in Figure 9. The emission spectrum of folda-dimer 2 in CHCl₃ consists of two sharp bands located at 537 and 580 nm, which are hypsochromically shifted to 533 and 575 nm in THF (Figure 9a and b). Moreover, a strong third band was observed at 615 nm in THF, whereas a small, barely recognizable shoulder appears in CHCl₃ at 630 nm. For each solution, fluorescence excitation spectra were recorded at the detection wavelengths ($\lambda_{det}\!)$ of 530 and 650 nm. In both solvents, the excitation spectra of folda-dimer ${\bf 2}$ for $\lambda_{ex}\!=\!530~\text{nm}$ perfectly resemble the absorption spectrum of 2 in CHCl₃, whereas the ones for λ_{det} = 650 nm match with the absorption spectrum of folda-dimer ${\bf 2}$ in THF. This result suggests that the observed fluorescence can be related to the ground state conformational populations of unfolded and folded molecules, that is, similar conformations prevail for excited molecules.

The fluorescence spectra of folda-trimer 3 in CHCl₃ and THF (Figure 9c and d) show stronger changes when compared with those of folda-dimer 2 or reference compounds 9 and 15 (the Supporting Information, Figure S3). The emission spectrum of PBI 3 in CHCl₃ is composed of a broad band with a maximum at 600 nm and a smaller signal at 540 nm, in which the former band could be ascribed to the emission of excited folded molecules. Upon solvent change from CHCl₃ to THF, both bands are hypsochromically shifted (532 and 617 nm, respectively) and the intensity of the smaller band significantly decreased, which indicates the prevalence of folded molecules. The fluorescence excitation spectra of **3** for $\lambda_{det} = 530$ nm in CHCl₃ and THF again resemble the absorption spectra of unfolded molecules in CHCl₃, whereas those at λ_{det} = 650 nm resemble the absorption spectrum of 3 in THF. Moreover, the fluorescence quantum yields $(arPsi_{\mathrm{fl}})^{\mathrm{[35]}}$ were determined and are collected together with other significant optical properties of folda-dimer 2, folda-trimer 3, and reference compounds 9 and 15 in Table 1.

As shown in Table 1, the fluorescence quantum yields of monomeric PBI dye 9 are close to unity (around 97%), which is in accordance with the generally observed outstanding fluorescence of monomeric PBI dyes. For the reference compound 15, which bears a phenylene ethynylene substituent, the quantum yields are significantly reduced to 21% in CHCl3 and 36% in THF, indicating an intramolecular electron-transfer process^[26, 34b, 36] between the electron-rich phenylene ethynylene backbone and the electron-deficient PBI chromophore, which becomes more efficient in CHCl₃ than in THF (see below). For folda-dimer 2 and folda-trimer 3, a contrasting behavior is observed, that is, the $arPhi_{
m fl}$ values are always lower in THF compared with those in CHCl₃, which suggests the presence of another non-radiative deactivation pathway in THF like folding into less emissive excimers.^[37] In THF this process is obviously more prominent because the individual dye molecules are already in a π -stacked folded conformation in the ground state. Likewise, the lower fluorescence quantum yields and more pronounced excimer emission of 3 compared to 2 suggest that only a very minor portion of unfolded molecules are present in the excited state.



Figure 9. Absorption (solid line, $c = 10^{-6} \text{ m}$), fluorescence emission $(\lambda_{exc} = 480 \text{ nm}; - \cdot - \cdot)$ and fluorescence excitation spectra $(\lambda_{det} = 530 \text{ nm}; - - -; \lambda_{det} = 650 \text{ nm}; \cdot \cdot \cdot \cdot \cdot)$ of **2** in a) CHCl₃ and b) THF, and **3** in c) CHCl₃ and d) THF at room temperature. The fluorescence excitation spectra are normalized to the absorption spectra at approximately 490 nm.

The time-resolved fluorescence decay profiles of folda-dimer 2 and folda-trimer 3 along with those of 9 and 15 as reference compounds were measured by using the time-correlated

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 Table 1. Optical properties of folda-dimer 2 and folda-trimer 3 as well as those of the reference compounds

 PBI 9 and PBI 15 in different solvents.

PBI	Solvent	λ_{abs} [nm] ($arepsilon_{max}$ [$m^{-1}cm^{-1}$]) ^[a]	$\lambda_{_{ m em}}$	$arPsi_{fl} = [\%]^{[b,d]}$
2	CHCl ₃	529 (123600), 493 (96100), 462 (37300)	537, 580	28±2 (31)
2	THF	526 (73 800), 493 (91 400)	533, 575, 615	16±2 (16)
-	CHCl₃	531 (118300), 495 (124100)	540, 600	22 ± 2 (24)
3	THE	534 (66700), 495 (109300)	532, 617	12±1 (13)
9	CHCl₃	528 (83 100), 491 (50 000), 460 (18 100)	532, 574, 622	97±3 (89)
	THE	522 (81 900), 486 (49 700), 456 (18 100)	531, 571, 618	97±6 (94)
	CHCl₃	528 (84200), 491 (50800), 460 (18800)	537, 579, 627	21±1 (17)
15	THF	523 (80400), 487 (49200), 457 (18200)	531, 571, 617	36 ± 5 (38)
[a] Measurements at 25 °C, $c = 10^{-6}$ m; [b] using high dilution method (OD _{max} < 0.05) at RT; [c] $\lambda_{axx} = 480$ nm;				
[d] under magic angle conditions ($\theta = 54.7^{\circ}$), $\lambda_{or} = 470-490$ nm; values in brackets are the results obtained				
from measurements without magic angle conditions.				

713, 800, and 960 nm, we focused our attention on the detection of this spectral feature in the transient excited-state absorption (ESA) signals. The TA spectra of all compounds probed at visible region showed negative ground-state bleaching (GSB) signals at 450-530 nm and stimulated emission (SE) up to pprox 600 nm (for THF, see Figure 10; for CHCl₃, see the Supporting Information, Figure S32). Strong positive signals which come from the excitedstate absorption from S₁ state to

single photon counting (TCSPC) technique and their fitted fluorescence lifetimes are collected in the Supporting Information, Figure S31 and Table S3. In the case of monomeric PBI dye 15, the observed fluorescence lifetimes (2.7 ns in CHCl₃) and 2.3 ns in THF) were relatively short in both solvents as compared with those of 9 (3.9 ns in CHCl₃ and 4.0 ns in THF) and other PBI monomers.^[38] In addition to the long decay components, shorter components with the time constants of 80 ps (81%) in CHCl₃ and 160 ps (36%) in THF were observed for PBI 15, which was absent in the backbone-free monomer 9. This can be attributed to the existence of a non-radiative pathway originating from the photoinduced electron-transfer (PET) process from the electron-donating backbone to the electrondeficient PBI core. Here, the much higher amplitude value (81%) of the short time constant corroborates our previous interpretation of the trends in fluorescence quantum yields that this process is more efficient in CHCl₃, that is, in the extended form.

For folda-dimer **2** and folda-trimer **3**, fluorescent species with about 10-fold longer lifetimes (20–26 ns) grew dominant, which can be assigned as the enhanced lifetimes of molecules in relaxed excited states, that is, excimer states.^[37] In particular, for the folded structure of **3** in THF, the relative amplitude of the long-lived species was found to be as high as 77% when the excimer emission band was directly probed. Meanwhile, when the 0–0 fluorescence peaks (530–540 nm) were monitored in **2** and **3**, short components with the time constants of approximately 100 ps were observed in all cases in addition to the singlet excited-state lifetimes of the PBI units (2.0–3.1 ns). The shorter components here can be related to the fast fluorescence quenching by the PET process as discussed above.

To acquire an in-depth understanding of the fast dynamics responsible for the reduced fluorescence of the PBI foldamers, that is, photoinduced charge separation (CS) and charge recombination (CR), we performed femtosecond transient absorption (TA) spectroscopy for **2**, **3**, and **15** in CHCl₃ and THF. As it is already known that formation of PBI radical anions (PBI⁻) through chemical reduction is easily recognized by the decrease of PBI absorption in the range of 400–550 nm and the concomitant increase of new absorption bands^[34a, 39] at

higher (S_n) states were revealed in the 600–850 nm spectral range.^[34a, 39] Interestingly, the characteristic sharp structures with peaks at \approx 705 nm, attributed to one of the absorption bands of a PBI radical anion,^[34a, 39] turn progressively broader and lose their structures as the molecules go from the extended forms to the compact folded forms in THF, suggesting a decreased efficiency of the CS process from the monomer to the trimer (Figure 10a–c). In CHCl₃ this trend is also visible but is not as pronounced (see the Supporting Information, Figure S32).

Further analysis of the PET dynamics was performed by assessing the TA spectra at near-infrared (NIR) wavelengths of 860-1100 nm, which are partly shown in Figure 10 d-f (THF; for comparison with the spectra in CHCl₃, see Figure S33 in the Supporting Information). The spectra of 15 and 2 show characteristic features in which the broad (\approx 850–1100 nm) ESA of the neutral PBI decays in time and a sharper band that peaks at \approx 960 nm emerges at the same time, which is another evidence of the photoinduced formation of PBI⁻⁻ by the PET process. Interestingly, whereas this prominent signature for the PBI radical anion of the monomer 15 is already decreased for folda-dimer 2, it is almost entirely vanished for folda-trimer 3. A similar tendency is given in CHCl₃, in which the radical anion signatures are even more prominent than in THF. From these results, we can conclude that the efficiency of the PET process is closely related to the spatial configuration of the chromophores within the systems. In other words, the more the molecules are folded, the less efficient the PET process is.

To further substantiate our findings, we have analyzed the time constants (see Table 2) extracted from the kinetic traces, which gave rise to double exponential decay profiles for PBI **2** and PBI **3** in both solvents. Here, the two time components are ascribable to CS and CR times, respectively. Since it was impossible to directly probe the rising PBI⁻ band, which is largely immersed in the strong ESA signal, we instead monitored the decay rate of the ESA of neutral PBI (\approx 920 nm), which was gradually converted into the PBI radical anion absorption band (\approx 960 nm) with time (see the Supporting Information, Figure S34). In dimer **2**, the CS time was about three times faster in the extended form in CHCl₃ (1.5 ps) than that of its folded counterpart in THF (4.3 ps). A similar trend was observed in

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Figure 10. Femtosecond transient absorption spectra of reference compound **15** (a, d), folda-dimer **2** (b, e), and folda-trimer **3** (c, f) in THF probed at the visible region (left column) and at the near-infrared region (right column; $\lambda_{ex} = 520$ nm; $c = 1 \times 10^{-5}$ M).

Table 2. Charge separation (CS) and recombination (CR) time constants of folda-dimer 2 and folda-trimer 3 from TA measurements in $CHCl_3$ and THF.					
PBI	m CH $ au_{ m CS}~[m ps]^{[a]}$	HCI_{3} $ au_{CR} [ps]^{(a)}$	$ au_{\sf CS} [{\sf ps}]^{[{\sf a}]}$	HF $ au_{CR} [ps]^{[a]}$	
2 3	1.5 3.9	50 57	4.3 4.5	60 96	
[a] Probe wavelength of $\lambda =$ 920 nm was applied.					

folda-trimer **3** despite much less clear difference in the CS rates (3.9 and 4.5 ps in $CHCl_3$ and THF, respectively). This complies with our previous findings that **3** already resides in a more folded structure even in $CHCl_3$.

Conclusion

By attaching PBI chromophores to a defined phenylene ethynylene scaffold, we were able to build up new oligomeric PBI foldamer systems folda-dimer **2** and folda-trimer **3**. As an outstanding characteristic, these ensembles are capable of adopting different conformations triggered by the solvents. With these solvent-dependent conformational preferences, the PBI chromophore units are either brought in close π - π -contact to each other or appear in unfolded conformations, in which the dye moieties are arranged randomly. The folding/unfolding equilibria governed by solvation could be monitored by UV/Vis absorption and 1D and 2D NMR spectroscopy (ROESY, DOSY) and rationalized by theoretical calculations. Because the same conformations, that is, folded and unfolded also prevail in the excited state, we were able to elucidate the different excited-

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state dynamics of folded and unfolded PBI oligomers. For the extended structures, the intrinsic PET process from the electron-donating phenylene ethynylene backbone to the electron-deficient PBI units is very prominent. As long as the molecules are in the folded state, this pathway becomes replaced by the preferential relaxation of the PBI stack into a fluorescent excimer state. Accordingly, in this latter state, in which the distance between dyes is short enough, the charge separation is highly suppressed. This interesting switching of excited state processes by conformational control through external stimuli^[40] will be investigated in more depth in the near future.

Experimental Section

See the Supporting Information for the experimental details.

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FULL PAPER



Where are the electrons? A detailed investigation on the behavior of two foldable perylene bisimide (PBI, see figure) systems was carried out with regard to the structural and optical peculiarities of the phenylene ethynylene-tethered PBI chromophores. By solvent regulation the dye–dye arrangement can be influenced externally thus enabling switching between solvated monomers or small π -stacks. Consequently, either excimer formation or photoinduced electron transfer dominates the properties of the photoexcited systems.

Foldamers

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Phenylene Ethynylene-Tethered Perylene Bisimide Folda-Dimer and Folda-Trimer: Investigations on Folding Features in Ground and Excited States