Photocontrol Over Self-Assembled Nanostructures of π–π Stacked Dyes Supported by the Parallel Conformer of Diarylethene

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Abstract: Diarylethenes (DAEs) have rarely been used in the design of photoresponsive supramolecular assemblies with a well-defined morphology transition owing to rather small structural changes upon photoisomerization. A supramolecular design based on the parallel conformation of DAEs enables the construction of photoresponsive dye assemblies that undergo remarkable nanomorphology transitions. The cooperative stacking of perylene bisimide (PBI) dyes was used to stabilize the parallel conformer of DAE through complementary hydrogen bonds. Atomic force microscopy, UV/Vis spectroscopy, and molecular modeling revealed that our DAE and PBI building blocks coassembled in nonpolar solvent to form well-defined helical nanofibers featuring J-type dimers of PBI dyes. Upon irradiating the coassembly solution with UV and visible light in turn, a reversible morphology change between nanofibers and nanoparticles was observed. This system involves the generation of a new self-assembly pathway by means of photocontrol.

Dynamic control over the morphologies of molecular assemblies through external stimuli is the key to developing dynamic soft-matter devices.[1] By virtue of various photochromic molecules, light is now regarded as the most useful external stimulus for dynamically controlling the morphology and functionality of supramolecular assemblies.[2] Among synthetic photoswitches, diarylethenes (DAEs) are particularly appealing because of their remarkably high photo-

reactivity and photofatigue resistance and because they show large changes in their optical and electronic properties upon photoisomerization.[3] Nevertheless, they have rarely been used in the design of photoresponsive supramolecular assemblies,[4] a situation in stark contrast to the many examples of azobenzene-based photoresponsive assemblies.[5] This is attributed to the fact that azobenzenes show large structural changes upon photoisomerization whilst those observed upon DAE photoswitching are rather small, thus enabling even photoinduced ring-closing/opening reactions of DAEs in the bulk state.[6] Most supramolecular assemblies based on DAEs therefore utilize the difference in stacking propensity between the flexible open-ring isomers and the rigid closed-ring isomers to control the assembly and disassembly of one-dimensionally stacked aggregates.[7,8]

A less investigated strategy for inducing drastic morphological changes in the assemblies is the use of the photochemically unreactive parallel conformers in equilibrium with the reactive antiparallel conformers in solution (Figure 1a). If well-defined supramolecular architectures can be designed based on the parallel conformers, the dynamic nature of solution assemblies could allow equilibration with the antiparallel conformers through aggregate–monomer exchange, thereby leading to a ring-closing photoreaction that would result in a completely different supramolecular structure. The involvement of the parallel conformers has been proposed for several supramolecular systems but the morphologies of those assemblies were not well-defined.[9] We herein demonstrate that the parallel conformation of diarylethenes can be stabilized through the cooperative π–π stacking of noncovalently bound π-conjugated molecules through specific intermolecular interactions, thereby producing supramolecular polymers with well-defined one-dimensional nanostructures. The nanostructures dispersed in solution can be reversibly converted into granular aggregates upon the ring-closing/opening photoreaction of the DAE moieties.

Following our earlier work on DAE-photocontrolled merocyanine aggregation[9d] and photochromic DAE–perylene bisimide dyads,[10] we herein report photoresponsive supramolecular polymers that make use of the tetratopic receptor 1_o[11] (Figure 1b) and the tetraphenoxy perylene bisimide ditopic guest PBI, which has a strong propensity to form π–π stacked slipped dimer aggregates.[12] The parallel conformer of 1_o can thus be stabilized by dimeric stacks of PBI (Figure 1b), and supramolecular polymerization of the resulting 1:2 (1_o/PBI) complex is anticipated to take place even at low concentrations. Because the closed-ring isomer 1_c cannot adopt the specific conformation required to bind the PBI-dimer aggregates, UV irradiation of the supramolecular

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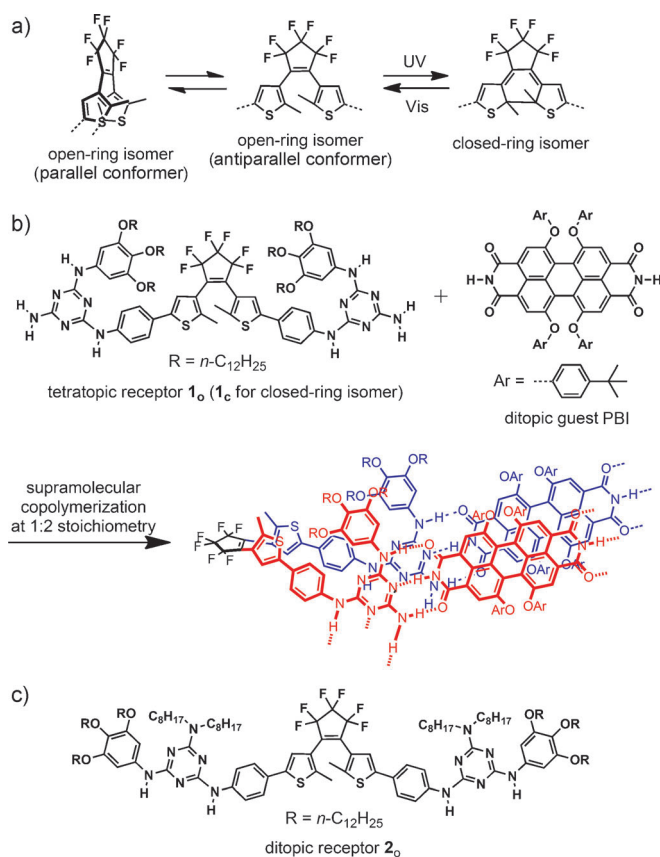
Figure 1. a) Conformational and photochemical isomerism of diaryl-ethene. b) Structures of the open-ring isomer of the tetratopic diaryl-ethene receptor **1$_o$** (**1$_c$** denotes the closed-ring isomer), the ditopic perylene bisimide guest PBI, and the expected binding motif between the parallel conformer of **1$_o$** and a PBI dimer. c) Structure of the ditopic diarylethene receptor **2$_o$**.
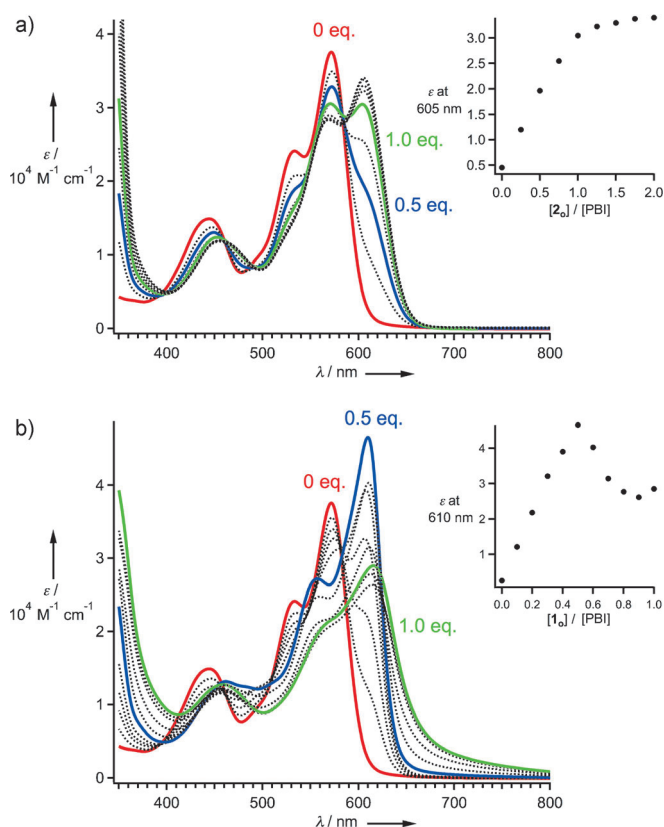

Figure 2. UV/Vis titration of PBI ($c = 3.0 \times 10^{-4}$ M) with increasing concentrations of receptors **2$_o$** (a; 0–2 equiv) and **1$_o$** (b; 0–1 equiv) in toluene. The red, blue, and green solid curves show the spectra at receptor/guest ratios of 0:1, 0.5:1, and 1:1, respectively. Insets: changes in ε at 605 nm versus equiv of **2$_o$** (a) and at 610 nm versus equiv of **1$_o$** (b).

copolymers should disrupt the unique supramolecular architecture. To emphasize the specific complexation between **1$_o$** and PBI, we also examined the complexation of PBI with the ditopic receptor **2$_o$** (Figure 1c), which would provide discrete 2+2 complexes by taking the parallel conformation. Both **1$_o$** and **2$_o$** were functionalized with tri(dodecyloxy)phenyl groups to make the supramolecular assemblies soluble in low-polarity solvents, thus ensuring nearly quantitative complexation through complementary triple hydrogen bonding.[13]

UV/Vis titration experiments of PBI ($c = 3.0 \times 10^{-4}$ M) with the ditopic DAE **2$_o$** were performed in toluene. Upon increasing the concentration of **2$_o$**, a transition from monomeric PBI ($\lambda_{max} = 572$ nm) to aggregates was indicated by a bathochromically shifted absorption band (J-band) at $\lambda_{max} = 605$ nm (Figure 2a).[14] A nearly stoichiometric 1:1 complexation was demonstrated by an almost linear increase of absorption at 605 nm upon increasing the concentration of **2$_o$** to 1 equiv (Figure 2a, inset).

Unlike the polymeric 1:2 assemblies of **1$_o$** and PBI described later, the 1:1 complexation of **2$_o$** or **2$_c$** with PBI is expected to provide small oligomeric species that are accessible by NMR characterization techniques. We thus recorded the ^{1}H NMR spectrum of the 1:1 mixture in [D$_8$]toluene at the same concentrations as in the UV/Vis

studies. The aromatic protons of the thiophene and phenylene moieties of **2$_o$** and the perylene core of PBI showed ill-defined resonances, thus indicating the presence of a dynamic equilibrium in which supramolecular species are slowly exchanging with monomeric species (Figure S1 in the Supporting Information). The particular broadening of the PBI aromatic resonances is consistent with the UV/Vis results shown in Figure 2a, which suggest the aggregation of these dyes. More importantly, the resonance of the central methyl groups of **2$_o$** appeared at δ = 2.43 ppm upon complexation with PBI (Figure S2b). This resonance appears at higher magnetic field in the absence of PBI.[15] This finding indicates that the population of the parallel conformer of **2$_o$** prevails over that of the antiparallel conformer , a situation consistent with an earlier observation by Irie et al.[16] Upon irradiation of the solution with UV light (303–323 nm) for 10 min, the signals of the aromatic protons sharpened and almost quantitative formation of **2$_c$** was observed. Because the chemical shifts are only slightly displaced compared to those of the individual molecules, we can conclude that the interaction between the rigid **2$_c$** and PBI is only weak at the given concentration and the degree of association is rather low, that is, monomeric species prevail. These NMR results led us to expect a large morphology change for assemblies of **1$_o$** and PBI upon photoirradiation.

The titration of PBI with the tetratopic receptor $\mathbf{1_o}$ showed more pronounced growth of the J-band (Figure 2b). Although the wavelength of the absorption maxima of the J-band did not differ significantly between the complexes of PBI with $\mathbf{1_o}$ (610 nm) and PBI with $\mathbf{2_o}$ (605 nm), the molar extinction coefficient (ε) at the maximum exceeded that of the monomer band when the concentration of $\mathbf{1_o}$ approached the stoichiometric amount (0.5 equiv).[17] The more pronounced J-band is indicative of the formation of supramolecular copolymers denoted $[\mathbf{1_o}\cdot(\text{PBI})_2]_n$, where conformational freedom of the repeating units could be suppressed by chain elongation. Upon the addition of excess $\mathbf{1_o}$, a broadening of the J-band was observed (Figure 2b, inset), thus indicating a decrease in the degree of polymerization.[18]

The morphology of the supramolecular copolymers $[\mathbf{1_o}\cdot(\text{PBI})_2]_n$ was studied by atomic force microscopy (AFM) of spin-coated samples on highly oriented pyrolytic graphite (HOPG). Well-defined fibrous nanostructures with lengths approaching the micrometer scale were visualized (Figure 3a). A closer inspection of the nanofibers revealed that they have a helical morphology with a height of approximately 2 nm and a helical pitch of approximately 20 nm (Figure 3b). The helical sense appears to be unbiased, which is reasonable in the absence of any chiral source. Such extended one-dimensional nanostructures were not found for the samples prepared from a 1:1 mixture of $\mathbf{2_o}$ and PBI

(Figure S4), PBI alone, or a 1:1 mixture of $\mathbf{1_o}$ and PBI (Figure S5), thus demonstrating that only the specific 1:2 complexation between $\mathbf{1_o}$ and PBI leads to structurally defined helical supramolecular copolymers.

Force-field molecular mechanics calculations for the supramolecular copolymer $[\mathbf{1_o}\cdot(\text{PBI})_2]_{12}$ support the spectroscopic and morphological features of the supramolecular polymers described above (Figure 3c).[19] In this modeled structure, quasi one-dimensionality of the supramolecular polymers was provided by a zigzag arrangement of dimeric stacks of PBI connected through $\mathbf{1_o}$ in the parallel conformation.[20] The modeled structure displays helicity provided by the twisting of the perylene cores (Figure 3d), thus corroborating the experimental results from AFM (Figure 3b). The helical morphology observed in the AFM images likely originates from the higher-order helical organization of one-dimensional supramolecular polymers with this intrinsic molecular-level helicity. The modeled structure also represents a slipped cofacial (J-type) stack of two PBI chromophores, which is supported by a staggered conformation of cofacial melamine moieties connected by the folded dithienylethene linker (Figure 3d).

With photoresponsive units comprised of well-defined multichromophoric supramolecular polymers in hand, photo-irradiation experiments were performed. Irradiation of a toluene solution of $[\mathbf{1_o}\cdot(\text{PBI})_2]_n$ ($[\mathbf{1_o}] = 1.5 \times 10^{-4}\,\text{M}$; $[\text{PBI}] = 3.0 \times 10^{-4}\,\text{M}$) with UV light resulted in the smooth progression of the ring-closing reaction of $\mathbf{1_o}$ to give $\mathbf{1_c}$ as shown by an increase of the absorption in the range of 550–700 nm and at 389 nm with bleaching of the band at 330 nm (Figure 4a). The quantum yield of the ring-closing reaction (Φ_{rc}) was determined to be 22%. This value is nearly half of that of free $\mathbf{1_o}$ in toluene ($\Phi_{rc} = 38\%$, Figure S7), thus suggesting an increase in the concentration of the parallel conformer of $\mathbf{1_o}$ through hydrogen-bond-directed complexation with PBI.[16] A photostationary state (PSS) was achieved after 120 s irradiation under the applied conditions,[19] where photoconversion of over 95% was confirmed by comparison with a UV-irradiation experiment of $\mathbf{1_o}$ alone. Notably, the difference spectrum obtained by subtracting the spectrum of $\mathbf{1_c}$ from that of UV-irradiated $[\mathbf{1_o}\cdot(\text{PBI})_2]_n$ revealed that the PBI J-band did not disappear after the ring-closing reaction (Figure S8), a result that further corroborates the tight stacking of PBI dimers in low-polarity media.

AFM observations revealed that the ring-closing reaction leads to a dramatic morphological change in the assemblies. When the ratio of $\mathbf{1_o}$ to $\mathbf{1_c}$ reached to 56:44, the elongated nanofibers observed before UV irradiation were fragmented into shorter nanofibers with lengths of several hundreds of nanometers (Figure 4b), as well as granular nanoaggregates (Figure S9). Further progression of the ring-closing reaction at $\mathbf{1_o}/\mathbf{1_c} = 19:81$ resulted in the complete conversion of the nanofibers into granular nanoaggregates with diameters and heights of approximately 10 and 1.2 nm, respectively (Figure 4c–e). Although the granular nanoaggregates precipitated within a few minutes by unspecific agglomeration, the irradiation of the precipitated solution with visible light (630 nm) with vigorous stirring enabled a smooth ring-opening reaction of $\mathbf{1_c}$ to give $\mathbf{1_o}$ (Figure S10), thereby restoring the
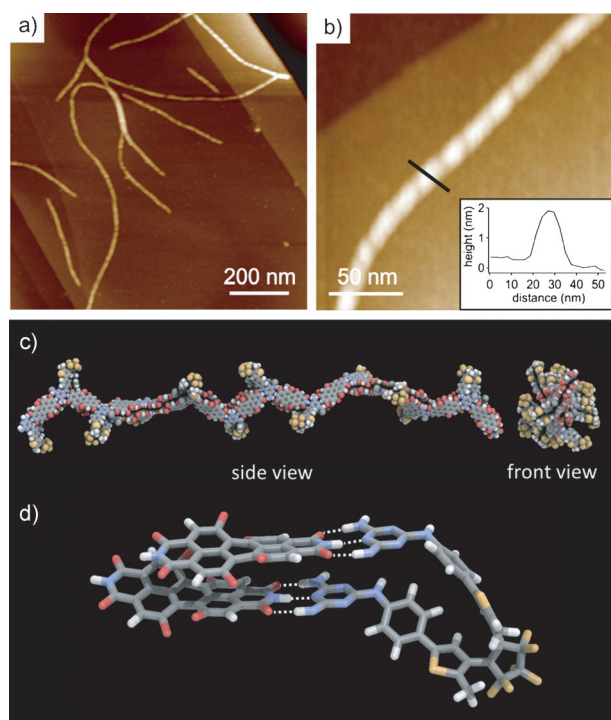

Figure 3. a) and b) AFM height images of coaggregates formed by the 1:2 complexation of $\mathbf{1_o}$ ($c = 1.5 \times 10^{-4}\,\text{M}$) and PBI ($c = 3.0 \times 10^{-4}\,\text{M}$) in toluene. The sample was prepared by spin-coating of the solution onto HOPG. The inset shows the cross-sectional analysis along the black line. c) Energy-optimized structures (AMBER force field) of $[\mathbf{1_o}\cdot(\text{PBI})_2]_{12}$. d) Extraction of the repeating unit $\mathbf{1_o}\cdot(\text{PBI})_2$. For these structures, the 3,4,5-tridodecyloxyphenyl groups of $\mathbf{1_o}$ and the *p-tert*-butylphenoxy groups of PBI were omitted after calculation for clarity.
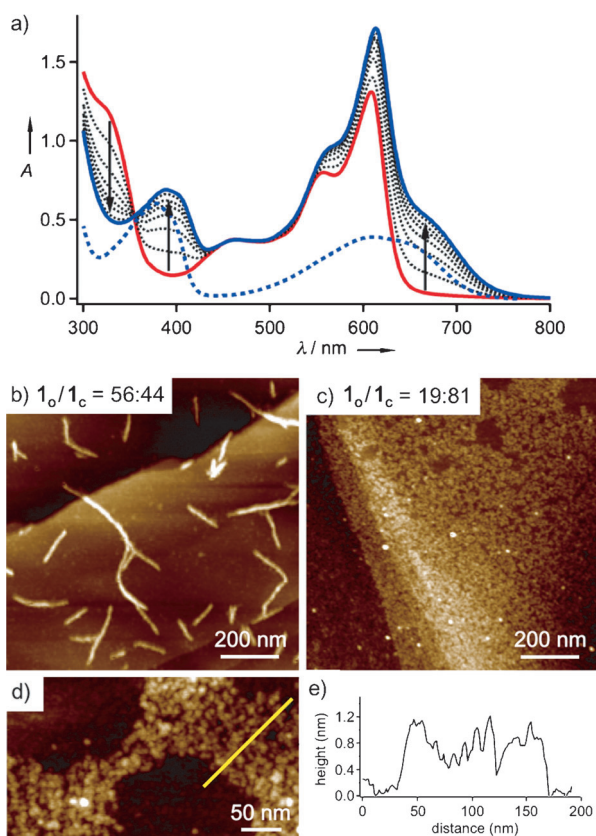
Figure 4. a) Red and blue spectra: Change in the UV/Vis spectra of the 1:2 mixture of $\mathbf{1_o}$ ($c = 1.5 \times 10^{-4}$ M) and PBI ($c = 3.0 \times 10^{-4}$ M) in toluene upon UV irradiation at 313 nm for 2 min at 20 °C. Arrows indicate the changes upon UV irradiation. Blue dotted spectrum: UV/Vis spectrum of pure $\mathbf{1_c}$. b–d) AFM of the UV-irradiated samples of $[\mathbf{1_o}\cdot(\text{PBI})_2]_n$ prepared in toluene solution at $\mathbf{1_o}/\mathbf{1_c}$ ratios of 56:44 (b) and 19:81 (c). (d) is a magnified image of (c), and (e) is the cross sectional analysis along the yellow line in (d).

Figure 5. Schematic representation of the photocontrol of the aggregation pathway of a mixture of the diarylethene receptor $\mathbf{1_o}/\mathbf{1_c}$ and the perylene bisimide guest PBI.

quite different from those obtained by photoirradiation. These findings imply the possibility of the photogeneration of specific supramolecular nanomaterials that are not obtainable through the self-assembly of ground state molecules under either kinetic or thermodynamic control, thus indicating a new self-assembly pathway[21] that is under photocontrol (Figure 5).

In conclusion, we have demonstrated that the proper design of supramolecular building blocks based on the parallel conformers of diarylethene derivatives can produce soluble supramolecular polymers that exhibit remarkable morphology changes upon photoirradiation. A key feature of our approach is the stabilization of the parallel conformer of diarylethene by strongly π-stacked perylene bisimide chromophores through directional hydrogen-bonding interactions. The application of a similar strategy to various functional π systems would expand the potential of photoresponsive supramolecular nanomaterials.

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fibrous nanostructures (Figure S11). This cycle could be repeated at least three times (Figure S12), thereby demonstrating the photoreversibility of the supramolecular system.

Taken together, the experimental results show that the tetratopic diarylethene receptor $\mathbf{1_o}$ can connect J-dimers of PBI through the formation of multiple hydrogen bonds from the parallel conformation, thereby providing photoresponsive one-dimensional supramolecular copolymers. Because such assemblies are in dynamic exchange with monomeric or small oligomeric species, $\mathbf{1_o}$ can undergo ring closing through the antiparallel conformation. Because the photogenerated $\mathbf{1_c}$ is a rigid and divergent hydrogen-bond receptor, it may act as a "dispersant" for the J-dimer of PBI without the formation of specific and uniform supramolecular architectures (Figure 5). It should be noted that such a dispersing solution of the J-dimer could be obtained only through the UV-irradiation of the supramolecular copolymer solution, whilst the direct self-assembly of preformed $\mathbf{1_c}$ and PBI by cooling the molecularly dissolved mixture at 90 °C (Figure S13) did not show the characteristic sharp J-band of PBI dimers (Figure S14). Moreover, the resulting aggregates were film-like aggregates with a thickness of around 0.8 nm (Figure S15), structures
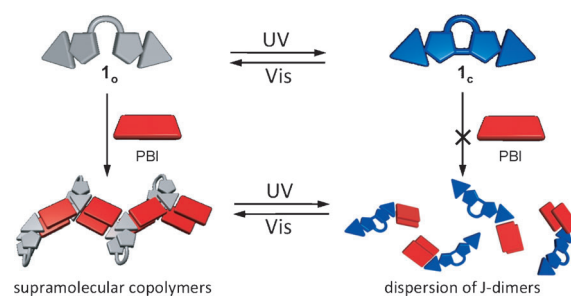
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