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Photoswitchable Intramolecular H-Stacking of Perylenebisimide

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Abstract: Dynamic control over the formation of H- or J-type aggregates of chromophores is of fundamental importance for developing responsive organic optoelectronic materials. In this study, the first example of photoswitching between a nonstacked and an intramolecularly H-stacked arrangement of perylenebisimides (PBI) is demonstrated. The system is composed of a central switching unit (overcrowded alkene) tethered to two PBI chromophores. cis−trans isomerization of the switching unit, induced by alternate irradiation at 312 and 365 nm, can drive two PBI chromophores reversibly between an intramolecularly “aggregated” and “nonaggregated” state. Distinct changes in UV−vis absorption and fluorescence spectra are observed following photoisomerization. This approach allows for efficient control of intramolecular H-stack formation with no significant intermolecular interactions spanning over at least 4 orders of magnitude of concentration (from 10^{-8} to 10^{-4} M) and a range of solvents and temperatures.

Introduction

The precise spatial arrangement and orientation of functional units in molecular and biomolecular systems is central to their activity and performance. This is most apparent in the energy and electron flow seen in photosynthesis, in which exquisite spatial control of chromophores is achieved through noncovalent interactions.[1] Inspired by natural systems, numerous artificial photo- and electro-active counterparts have been prepared, capable of performing various functions, through the programmed arrangement of molecular or supramolecular entities.[2−4] In the case of optoelectronic materials and bioimaging, dynamic control of the interaction between chromophores and reversible tuning of fluorescence are often essential features.[5] For instance, the formation of H- and J-type aggregates of chromophores[6−9] including perylenebisimide (PBI), chlorin, cyanine, and organoplatinum acetylide compounds have been demonstrated to provide for exceptional control over their specific optical and electrochemical properties. This is a key phenomenon used for responsive organic optoelectronic materials.[5]

Organization of molecular architectures of aggregated chromophores via noncovalent interactions such as hydrogen bonding, dipolar interactions, and $\pi-\pi$ stacking is realized by a controlled balancing of these supramolecular interactions. Changes in conditions such as solvent composition, pH, and temperature allow for fine-tuning of the aggregation process, which in turn provides access to versatile optoelectronic functions. However, in these systems aggregation of multiple units is employed to achieve the required intermolecular spatial arrangements and hence concentration effects dominate the aggregation properties. A key challenge is to achieve control over spatial interactions in a reversible and, importantly, concentration independent manner. The important task therefore is to produce the desired uniform and pronounced changes in optoelectronic functions over a broad concentration range, especially in dilute conditions, or where diffusion is slow. Covalent connection of multiple chromophore units can provide a solution to this problem. Intramolecular dye aggregation can be achieved using specific molecular geometries to regulate the relative orientation of chromophores.[10−13] In this case, uniform optoelectronic properties can be achieved under a much wider range of concentrations and environmental conditions. However, achieving dynamic control, a central feature of responsive optoelectronic materials, over dye aggregation processes in an intramolecular system is not a trivial task compared with noncovalent intermolecular systems.

Incorporating photoswitchable units into a dye aggregating system is a promising strategy toward achieving convenient dynamic control over supramolecular interactions.[14−16] Changes in morphology, dipole moment, or electron density following photoisomerization reactions can result in remarkable effects on the aggregation behavior and can modulate the optoelectronic

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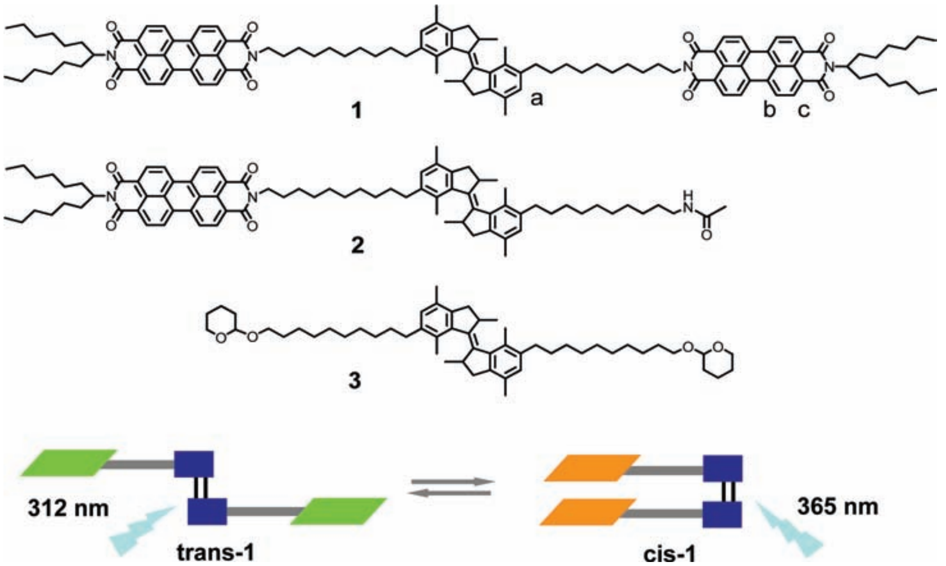

Figure 1. Structures of compounds **1**−**3** and a schematic presentation of the light induced trans−cis isomerization process.

properties efficiently. For instance, reversible photocontrol of intermolecular dye aggregation using a diarylethene−PBI system was reported to provide a clear fluorescence color change upon switching between different aggregation states.[14] Photoswitchable intramolecular dye "aggregation" is a different approach to supramolecular dye aggregation chemistry. In this approach, dynamic control of uniform optoelectronic properties over a wide range of concentrations and environmental conditions can be anticipated. This intramolecular approach has already been shown to allow for photocontrol over electron transfer between electron deficient and electron rich porphyrins.[17]

In this contribution we demonstrate that a simple light-driven cis−trans isomerization can switch two PBI units reversibly between an intramolecularly "aggregated" and "nonaggregated" state independent of concentration (Figure 1). This is achieved without compromising the operation of the functional components used in the system. Efficient control on intramolecular H-stack formation, spanning at least 4 orders of magnitude of concentration (1.0×10^{-8} to 10^{-4} M), is demonstrated. The behavior is observed over a range of solvent and temperature conditions.

In this design, the switching unit is based on the well-known overcrowded alkenes.[18,19] Two PBIs are connected through C_{10}-alkyl spacers to preclude through-bond electronic communication. In the trans state, the PBI groups of compound **1** show little interaction and spectral characteristics typical of PBI monomers are observed. When switched photochemically to the cis state by irradiation at 312 nm, the two PBIs are brought into a cofacial arrangement, and characteristic changes in the spectra, indicative of H-aggregation,[5] are observed, which is reversed by irradiation at 365 nm.

Experimental Section

Reagents were purchased from Acros, Aldrich, Fluka, or Merck and used as received. Tetrahydrofuran (THF), dichloromethane (DCM), and toluene were freshly distilled before use. Technical grade solvents were used for extraction and chromatography. Merck silica gel 60 (230−400 mesh ASTM) was used in flash chromatography. UVASOL grade solvent was employed for spectroscopic measurements. The syntheses of compounds **1**−**3** are shown in Scheme 1. For details of the synthesis and characterization of intermediates **4**−**11**, see the Supporting Information.

Compound 1. The hydrochloric salt of **10** (30 mg, 0.043 mmol), imidazole (200 mg, 2.94 mmol), and **11** (70.0 mg, 0.122 mmol) were added to 10 mL of dry toluene. The mixture was heated at 120 °C under N_2 in a sealed flask for 4 h. After cooling to room temperature, the mixture was directly purified by silica gel chromatography using $CHCl_3$ as eluant, yielding **1** as a red solid (62%, 46 mg, 0.026 mmol). mp 163.1−164.2 °C. ^{1}H NMR ($CDCl_3$): δ = 8.62−8.38 (m, 16H), 6.84 (s, 2H), 5.24−5.10 (m, 2H), 4.14 (t, J = 7.2 Hz, 4H), 2.86−2.73 (m, 2H), 2.70−2.51 (m, 6H), 2.37, (s, 6H), 2.33−2.12 (m, 12H), 1.96−1.82 (m, 4H), 1.80−1.68 (m, 4H), 1.66−1.20 (m, 60H), 1.07 (d, J = 6.3 Hz, 6H), 0.83 (t, J = 6.3 Hz, 12H). ^{13}C NMR ($CDCl_3$): 163.3, 141.8, 141.7, 139.9, 139.5, 134.6, 134.3, 131.1, 129.3, 128.8, 126.4, 126.3, 123.3, 123.1, 40.7, 38.9, 33.5, 32.5, 32.0, 31.0, 29.9, 29.7, 29.5, 29.4, 28.2, 27.3, 27.1, 22.8, 19.0, 18.1, 14.0. HRMS: m/z calcd for $C_{118}H_{137}N_4O_8$ $[M+H]^+$: 1739.0465; found: 1739.0471.

Compound 2. The hydrochloric salt of **10** (15 mg, 0.021 mmol), imidazole (50 mg, 0.73 mmol), and **11** (12 mg, 0.021 mmol) were added to 4 mL of dry toluene. The mixture was heated at 120 °C under N_2 in a sealed flask for 4 h. After cooling to room temperature, acetylchloride (200 mL) was added directly to the mixture. After 5 min, 2 mL of MeOH was added to quench the reaction. The solvent was evaporated under vacuum. The residue was purified by chromatography on a silica gel column using $CHCl_3$ as eluant, yielding **2** as a red solid (24%, 7 mg). mp 128.4−129.7 °C. ^{1}H NMR ($CDCl_3$): δ = 8.71−8.60 (m, 8H), 6.85 (s, 2H), 5.24−5.10 (m, 1H), 4.18 (t, J = 7.2 Hz, 2H), 3.19 (q, J = 6.4 Hz, 2H), 2.85−2.76 (m, 2H), 2.69−2.52 (m, 6H), 2.37 (s, 6H), 2.30−2.14 (m, 10H), 1.91 (s, 3H), 1.90−1.82 (m, 2H), 1.80−1.71 (m, 2H), 1.66−1.19 (m, 46H), 1.08 (d, J = 6.4 Hz, 6H), 0.84 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$): 163.5, 141.8, 141.7, 139.9, 139.5, 134.9, 134.5, 131.3, 131.1, 129.3, 128.8, 126.7, 126.6, 123.5,

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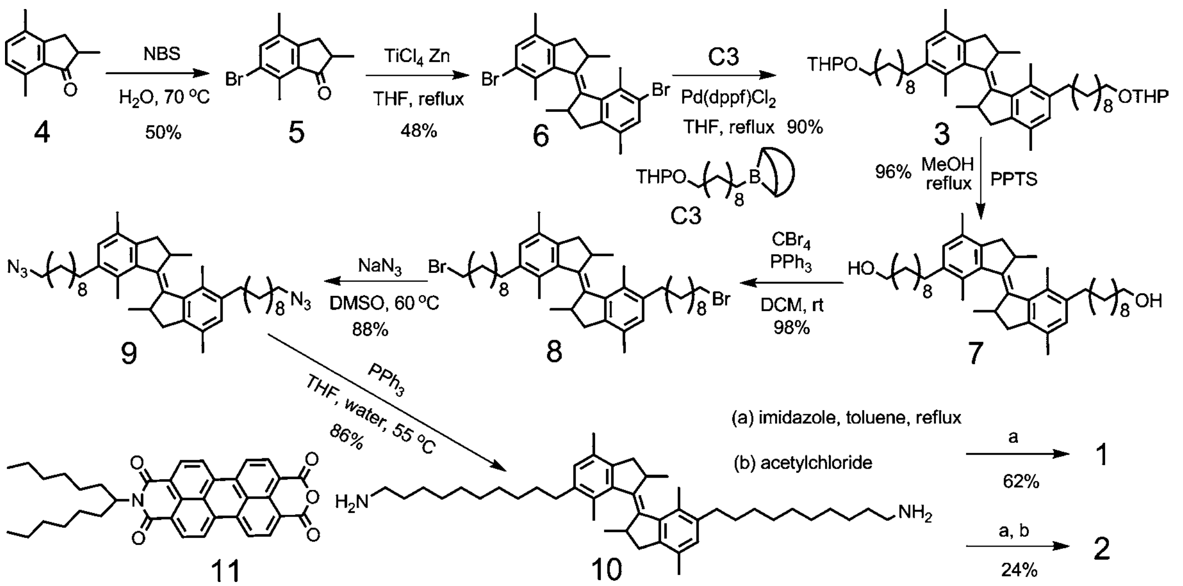
Scheme 1. Synthesis of Compounds **1**−**3**



123.3, 42.5, 40.7, 39.7, 38.9, 33.6, 32.6, 32.0, 31.0, 30.1, 29.8, 29.6, 29.5, 29.4, 28.3, 27.4, 27.1, 22.8, 19.0, 18.1, 14.0. HRMS: *m/z* calcd for $C_{83}H_{104}N_3O_5$ [M+H]$^+$: 1222.7971; found: 1222.7985.

Compound 3. To a solution of 9-decene-1-ol **C1** (3 g, 19 mmol) in 70 mL of dry DCM was added 1 g (4 mmol) of pyridinium *p*-toluenesulfonate (PPTS) and 3,4-dihydro-2H-pyran (10 mL). The mixture was stirred at room temperature for 12 h. The solvent and unreacted 3,4-dihydro-2H-pyran were evaporated under vacuum. The residue was purified by silica gel column chromatography using pentane:DCM (2:1) as the eluant affording 4.3 g (93%) of the known compound 2-(dec-9-enyloxy)tetrahydro-*2H*-pyran **C2** as a colorless oil. ^{1}H NMR ($CDCl_3$): $\delta = 5.86-5.75$ (m, 1H), 5.00−4.90 (m, 2H), 4.56 (s, 1H), 3.88−3.67 (m, 2H), 3.50−3.33 (m, 2H), 1.99−2.10 (m, 2H), 1.85−1.20 (m, 18H).

9-BBN (0.5 M in THF, 16.8 mL) was added to a solution of **C2** (1 g, 4.2 mmol) in 5 mL of dry THF at 0 °C. The solution was stirred at room temperature for 6 h to yield compound **C3**. To the above solution of **C3**, used directly without purification, was added to **6** (220 mg, 0.47 mmol), Pd(dppf)Cl_2 (34.3 mg, 0.047 mmol), and $K_3PO_4-3H_2O$ (1.1 g, 4.2 mmol). The mixture was heated at 75 °C under N_2 in a sealed flask for 15 h. After cooling to room temperature, the mixture was poured into 100 mL of water and extracted with DCM (2 × 50 mL). The combined organic phase was dried and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography using pentane: ethyl acetate (100:5) as the eluant affording 334 mg (90%) of **3** as a colorless oil.^{1}H NMR (CD_2Cl_2): $\delta = 6.86$ (s, 2H), 4.56 (s, 2H), 3.86−3.81 (m, 2H), 3.73−3.67 (m, 2H), 3.49−3.43 (m, 2H), 3.39−3.33 (m, 2H), 2.84−2.78 (m, 2H), 2.69−2.55 (m, 6H), 2.38 (s, 6H), 2.21 (d, $J = 14.4$ Hz, 2H), 2.17 (s, 6H), 1.70−1.20 (m, 44H), 1.09 (d, $J = 5.6$ Hz, 6H). ^{13}C NMR (CD_2Cl_2) δ 141.9, 141.8, 139.9, 139.6, 131.2, 129.3, 128.8, 98.9, 67.7, 62.3, 42.5, 38.9, 33.6, 31.0, 30.1, 30.0, 29.9, 29.8, 29.7, 26.5, 25.8, 19.9, 19.0, 19.0, 18.1. HRMS: *m/z* calcd for $C_{54}H_{84}O_4$ [M-e$^-$]$^+$: 796.6370; found: 796.6377.

UV−vis measurements were performed on a Jasco V-630 spectrophotometer. Fluorescence measurements were performed on a JASCO FP-6200 spectrophotometer. Electrochemical measurements were carried out on a model 630B Electrochemical Workstation (CH Instruments). A Teflon shrouded glassy carbon working electrode, a Pt wire auxiliary electrode, and an Ag/AgCl ion quasi reference were employed (decamethylferrocene was employed as internal reference). UV irradiation experiments were carried out under argon using a Spectroline model ENB-280C/FE lamp. NMR spectra were obtained using a Varian Mercury Plus (400 MHz) and a Varian VXR-300S (300 MHz). Quantum yields of fluorescence, Φ_f, were determined using core-unsubstituted PBI, $\Phi_f = 1$, as a reference. Quantum yields for photoisomerization reactions, Φ_{iso}, were determined using the monochromated (5 nm bandwidth) output of the Xe lamp of the JASCO FP-6200 spectrophotometer as a light source, using the method of total absorption at 312 and 365 nm. The iron(III) oxalate/phenanthroline actinometer system was used as a reference. Detailed information on quantum yield, Φ_f and Φ_{iso}, measurements is provided in the Supporting Information.

Results and Discussion

The synthesis and characterization of compound **1** and reference compounds **2** and **3** were carried out as shown in scheme 1 and described in the experimental section (see also the Supporting Information for details). The UV−vis spectrum of trans-**1** (Figure 2a) shows a broad absorption band at ca. 300 nm, which is assigned to the switching unit in the trans-state (by comparison with trans-**3**).[21] In the visible region, three pronounced absorptions at 455, 486, and 522 nm, corresponding to the 0−2, 0−1, and 0−0 electronic transitions of the PBI unit, respectively, are observed. Notably, the intensity of the 0−0 band is higher than that of the 0−1 band. The spectrum indicates that the Franck−Condon factors favor the lower (0−0) excited vibronic state, which implies the absence of significant interaction between the two appended PBI units.[22−24] The fluorescence spectrum of trans-**1** displays three bands at 529, 569, and 618 nm (Figure 2b). The green fluorescence (Figure 2b, inset, $\Phi_f = 0.35$) indicates that the PBI fluorophores are in a nonaggregated state,[6] consistent with the UV−vis absorption spectral data. The decrease in fluorescence quantum yield relative to core-unsubstituted-PBI ($\Phi_f = 1$) is assigned to photo induced electron transfer quenching (see ref 27).

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(21) See the absorption spectrum (Figure S1) of the reference compound **3**.

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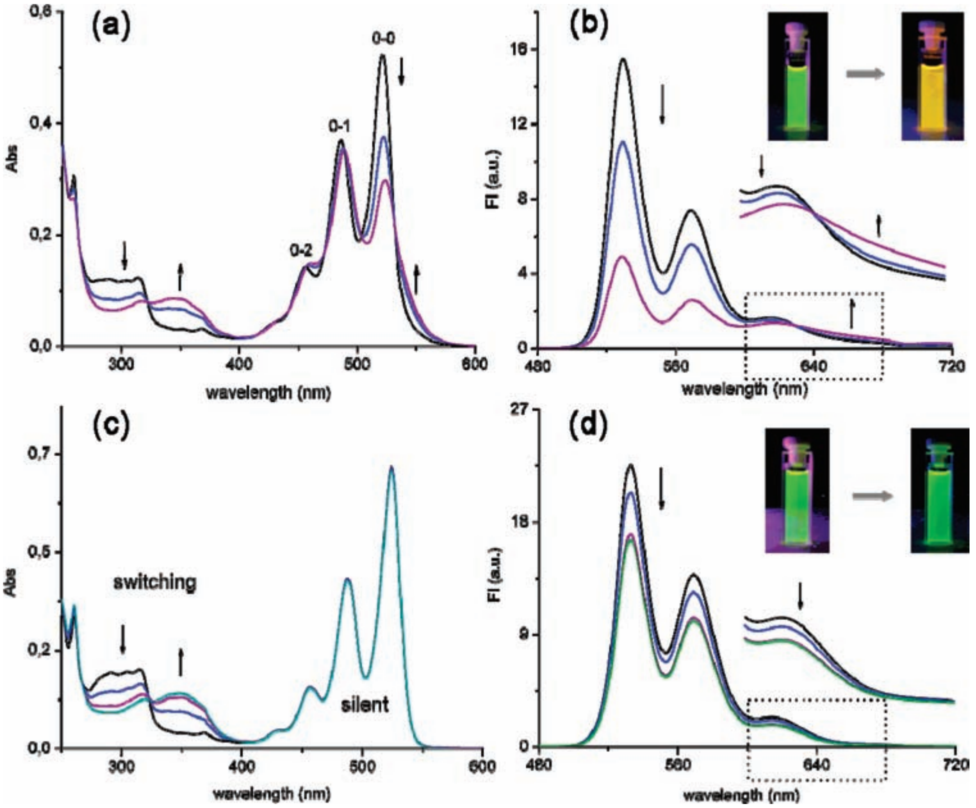

Figure 2. UV−vis absorption and fluorescence spectra (λ_{ex} = 455 nm) of trans-**1** (4 × 10^{-6} M, a and b) and trans-**2** (8 × 10^{-6} M, c and d) upon irradiation at 312 nm in THF at 20 °C for 50 s. Inset: Pictures of solutions of **1** and **2** under a hand-held UV lamp in trans (λ_{ex} = 365 nm) or cis state (λ_{ex} = 312 nm) and the expansion of the spectra between 600 and 680 nm.

Upon irradiation at 312 nm, both the absorption of the central switching and pendent PBI units of trans-**1** undergo concomitant spectral changes (Figure 2a). The expected absorption at 350 nm, of the switching unit in the cis state appears.[19,21] The isosbestic point at 322 nm indicates a smooth trans → cis transformation. In the visible region, the 0−0 transition of PBI at 522 nm decreases in intensity and a new absorption ~550 nm appears with an isosbestic point maintained at 532 nm. The intensity reversal observed for the 0−0 and 0−1 bands, upon trans → cis isomerization, indicates that the Franck−Condon factors now favor the higher (0−1) excited vibronic state, which suggests the formation of H-type[25] cofacial $\pi-\pi$ stacking between the PBI units.[6,22−24] Similarly the fluorescence spectrum of trans-**1** is changed upon trans → cis isomerization (Figure 2b) manifested in a decrease in intensity (${}^{cis}\Phi_f = 0.13$) and a change from green to orange fluorescence. This spectral change implies the formation of PBI $\pi-\pi$ stacks, in which emission to the lower vibronic ground states ($0 \rightarrow v$; $v = 0$ and 1; λ_{em} = 529 and 569 nm) is disfavored.[6,22,26] In contrast, the absorption spectrum of the single PBI unit in reference compound trans-**2** is unaffected by photoisomerization of the switching unit (Figure 2c) and the green emission ($\Phi_f = 0.50$) is preserved in addition to a modest quenching by 25% (Figure 2d).[27] The absence of a change in spectral shape on going from trans- to cis-**2** indicates that there is no intermolecular interactions between PBI units.

Further support that the light-induced spectral changes observed for **1** indeed result from intramolecular interactions of the PBI units is provided by the concentration dependence of the UV−vis spectrum.[6] A linear relation between absorption and concentration is observed (Figure 3a). Furthermore, the ratio of absorbance at 0−1 and 0−0 band, A^{0-1}/A^{0-0}, remains constant over the concentration range from 1.0 × 10^{-8} to 1.0 × 10^{-4} M, in both the trans- and at the $\text{PSS}_{312\text{nm}}$ state (Figure 3b). These results confirm the absence of intermolecular interactions and support the assignment of the light-driven spectral changes of the PBI unit in trans-**1** (Figure 2a) as arising from intramolecular, and hence concentration independent, $\pi-\pi$ stacking.

Results obtained from UV−vis and fluorescence spectroscopy are supported by ^{1}H NMR spectroscopic experiments (Figure

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[25] *J*-type PBI stacking would be expected to result in a strong absorption band centered at 600 nm, see for example: Würthner, F.; Bauer, C.; Stepanenko, V.; Yagai, S. *Adv. Mater.* **2008**, *20*, 1695–1698.

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[27] Previously, it has been shown by Würthner, Scandola and co-workers in a PBI/diarylethene system that luminescence intensity can be on-off modulated photochemically through photoinduced electron transfer (PET). See: Berberich, M.; Krause, A.-M.; Orlandi, M.; Scandola, F.; Würthner, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 6616–6619. In the present systems, the relative propensity for the involvement of PET quenching was estimated using the Gibbs energy (ΔG_{ET}, see the SI) of PET from the overcrowded alkene to the excited PBI unit. For trans-**1**/**2** and cis-**1**/**2**, it is calculated to be ca. −0.82 eV and −1.05 eV, respectively, indicating an energetically favored PET process. The oxidation potential of the overcrowded alkene becomes more positive upon trans → cis isomerization, which suggests a stronger PET quenching process in the cis state than that in the trans state. This accounts for the change in fluorescence intensity observed for compound **2** following photoisomerization (Figure 2d). However the changes in the nature of the emissive excited state of compound **1** in the cis state (i.e. as a H-stack) serve to mask this effect. Nevertheless the potential involvement of PET quenching in the trans state of both **1** (Φ_f = 0.35) and **2** (Φ_f = 0.50) may account for the decreased quantum yield of fluorescence compared with the core-unsubstituted PBI fluorophore (Φ_f = 1), see also SI page S5.

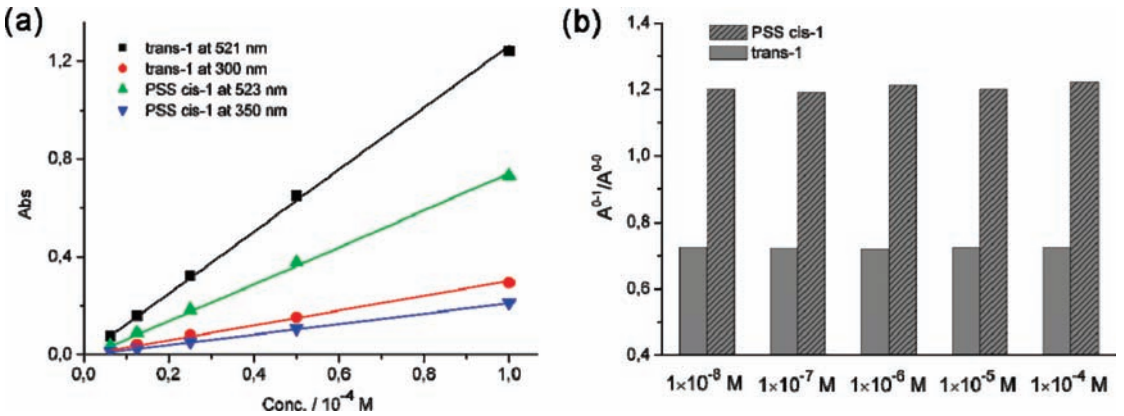

Figure 3. Concentration dependence of (a) the UV−vis absorption and (b) the ratio of the 0−1 and 0−0 transitions for compound **1** in trans- or PSS cis state (81% cis-**1** as determined from ^{1}H NMR spectra).

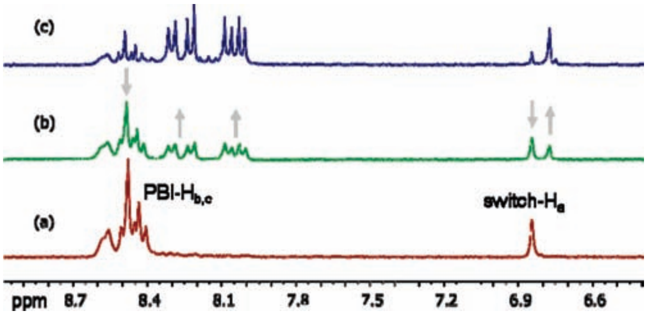

Figure 4. (Low field) ^{1}H NMR spectroscopy of trans-**1** before (a) and after irradiation at 312 nm for 3 and 10 min and (b and c) in CD_2Cl_2 at 20 °C. The arrow indicates the changes in absorption intensity.

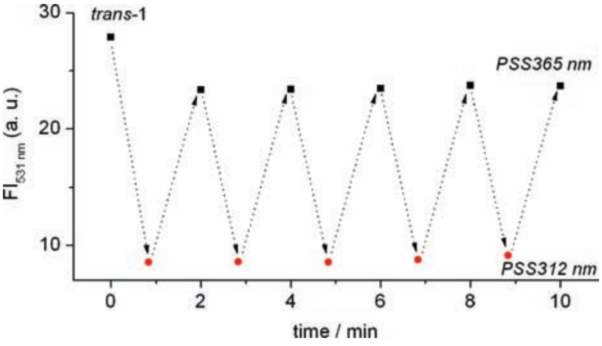

Figure 5. Fluorescence response of compound **1** to alternate irradiation at 312 (PPS, 81%, cis-**1**) and 365 nm (PSS, 83%, trans-**1**).

4). Trans → cis isomerization of compound **1** is manifested by a decrease of the absorption at 6.85 ppm, assigned to the proton ($^{trans}H_a$) on the switching unit (Figure 1) and the appearance of a new absorption at 6.77 ppm ($^{cis}H_a$). Notably, trans → cis isomerization induces a significant change in the chemical shift of the aromatic protons of the PBI units. The original multiplet around 8.50 ppm ($^{trans}H_{b,c}$) decreases. New doublets at 8.25 ($^{cis}H_c$) and 8.00 ($^{cis}H_b$) ppm, respectively, are observed. This upfield shift suggests a cofacial $\pi-\pi$ stacking of the PBI units in the cis state, which is expected to shield protons by interaction between aromatic units.[22] The inner PBI protons ($^{cis}H_b$) experience a stronger ring current, thus displaying a larger upfield shift (0.50 ppm) than the outer protons ($^{cis}H_c$, 0.25 ppm).[28] At the photostationary state (PSS), 81% of trans-**1** is isomerized to cis-**1** as determined by integration of the absorptions of the switching unit (H_a). Moreover, after photoirradiation, integration of PBI absorptions that are shifted upfield due to $\pi-\pi$ stacking ($^{cis}H_{b,c}$/$^{trans}H_{b,c}$) yields a value consistent with the ratio of shifted absorptions of the switching unit ($^{cis}H_a$/$^{trans}H_a$). This result suggests that photoisomerization of the overcrowded alkene induces quantitative formation of H-dimer in the cis state. The sharp and well-resolved NMR signal of the PBI protons indicates the absence of noticeable intermolecular aggregation. This is also supported by the persistent chemical shift of the PBI protons in the trans and cis state. Intermolecular aggregation would result in a gradual chemical shift during the course of the photoisomerization. For compound **2**, ^{1}H NMR absorptions of the PBI protons are unaffected by photoswitching of the overcrowded alkene, indicating the absence of PBI stacking (Figure S5).

The intramolecular cofacial arrangement of the PBI units in the cis state of compound **1** can be switched back to the "nonaggregated" trans state (PSS, 83%) by irradiation at 365 nm (Figures 5, S6, and S7). Within 10 min, 5 cycles of photoswitching with high fidelity are achieved by alternate irradiation at 312 nm ($\Phi_{iso} = 0.091$) and 365 nm ($\Phi_{iso} = 0.045$). The efficiency of cis → trans photoisomerization is lower than that of the reverse direction (i.e., the photochemical quantum yield is lower). However, this is an inherent characteristic of the switching unit employed in this system: a similar difference is also observed in control molecule **2** ($^{312nm}\Phi_{iso} = 0.141 > {}^{365nm}\Phi_{iso} = 0.085$) and **3** ($^{312nm}\Phi_{iso} = 0.159 > {}^{365nm}\Phi_{iso} = 0.078$). It is difficult to judge from the Φ_{iso} values whether the H-stack interaction has an effect on photoisomerization. The preservation of the reversible photoswitching activity of the overcrowded alkene benefits from the absence of significant energy transfer from the switching unit to PBI, as confirmed by excitation spectra (Figure S8); that is, the absorption of the overcrowded

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[28] Changes in the chemicals shifts of PBI protons are less pronounced compared with that observed in the tightly π-stacked PBI systems,[22] which suggests that the two PBI chromophores in cis-**1** hold an equilibrium state between more close and more distant conformations. This is a reasonable conclusion as the noncovalent interaction energy between PBI units in solvents such as dichloromethane does not easily overcome the entropic penalty associated with conformational restriction of the C_{10}-alkyl chains. (a) Chen, Z.; Lohr, A.; Saha-Möller, C. R.; Würthner, F. *Chem. Soc. Rev.* **2009**, *38*, 564–584. (b) Hippius, C.; van Stokkum, I. H. M.; Zangrando, E.; Williams, R. M.; Wykes, M.; Beljonne, D.; Würthner, F. *J. Phys. Chem. C* **2008**, *112*, 14626–14638. (c) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312–1319.

alkene, in both trans- and cis-state, does not contribute to the fluorescence of the PBI unit.[29]

The system shows considerable robustness over a wide range of temperatures[30] and solvent conditions. Efficient intramolecular H-stack formation controlled by photoisomerization can be performed in a wide range of solvent conditions (Figure S9) including toluene, dichloromethane, THF, or the mixture of ethanol and THF (1/2, v/v), as demonstrated by the reversible changes in the absorbance ratio (A^{0-1}/A^{0-0}) following photoirradiation.[31] Temperature dependent UV−vis spectroscopy of cis-**1** shows that the relative intensity of the 1−0 band compared with the 0−0 absorption band is largely maintained ($A^{0-1}/A^{0-0} > 1$) over a temperature range from −60 to +60 °C (Figure S10). At lower temperature, −60 °C, increased $\pi-\pi$ stacking is observed manifested in a 15% enhancement of the A^{0-1}/A^{0-0} value, compared with that at 20 °C. The preference of H-stack formation in the cis state of compound **1** takes advantage of (1) the enhanced effective PBI concentration due to the intramolecular nature of the process and (2) a predetermined conformation exerted by the overcrowded alkene: geminal substituents of the central alkene unit are incorporated through two 5-membered rings, which ensures a favorable parallel orientation of the two PBI arms.

Conclusions

In summary, light-driven dynamic control of intramolecular H-stacking of PBI units using a molecular switch is demonstrated. Photoswitchable intramolecular H-stacking of chromophores opens up new possibilities in using spectral changes in absorption and fluorescence in areas such as security marking, cell labeling, and memory devices.[32−34] The approach presented here takes advantage of the large and defined structural changes of the overcrowded alkenes between trans and cis states, which allows for uniform and significant spectral changes spanning at least 4 orders of magnitude of concentration (from 10^{-8} to 10^{-4} M). This approach could be extended to control other processes including molecular recognition, electron, and energy transfer, which are critically dependent on the active units' distance and orientation,[35,36] and hence holds considerable promise in future applications.

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Supporting Information Available: Synthetic procedures and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) It should be noted also that two distinct mechanisms for excited state quenching can be invoked to rationalise the behaviour of the present systems: (a) Energy transfer quenching of the excited state of the switching unit to the PBI and (b) photoinduced electron transfer quenching of the PBI excited state by the switching unit. (a) The excited state lifetime of the switching unit is of the order of 1−5 ps during which isomerisation takes place prior to relaxation to the ground state. For energy transfer from the excited switching unit to the ground state PBI unit to take place the energy transfer would have to proceed at a similar rate which is unlikely as previously we and others have shown that such energy transfer typically proceeds at rates of the order of 10−20 ps. (b) The excited state lifetime of the PBI excited state is of the order of 5−10 ns. Hence for the switching unit in the ground state to be able to engage in photoinduced electron transfer quenching then the rate would only have to be of the order of several nanoseconds to be competitive. Hence PET can be several orders of magnitude slower than energy transfer and still be competitive.

(30) Thermal stability of the overcrowded alkene was also examined. A half life of 58.5 h at 20 °C, from unstable cis to stable cis state, was determined (E_a = 97.3 kJ/mol), this value is essentially the same as for the isolated switching unit itself, suggesting that PBI functionalization does not affect the thermal relaxation of the switching unit, Figure S11, see ref 19 and also Würthner, F.; Rebek, J., Jr. *J. Chem. Soc. Perkins Trans. 2* **1995**, 1727–1734. In the present study, the cis state refers to the overcrowded alkene in the unstable cis state because spectroscopic measurements are carried out within 10 min of photoirradiation, which precludes significant thermal isomerization. Note: in both the unstable and stable cis state, the PBI absorption displays identical behavior in terms of the A^{0-1}/A^{0-0} ratio.

(31) In solvents such as heptane and acetone, intermolecular aggregation occurs manifested in the formation of precipitation and a more intense 0−1 band in both trans and cis state. Photoisomerization does not result in significant change in the absorption of PBI chromophore.

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