Supporting Information

Photoswitchable Intramolecular H-stacking of Perylenebisimide
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5. To a solution of compound 4 (700 mg, 4.0 mmol) in 40 mL acetonitrile was added aqueous H$_2$SO$_4$ (15%, 30 mL) at room temperature followed by NBS (750 mg, 4.16 mmol). The solution was stirred at 70 °C for 14h. After cooling to room temperature, the mixture was poured into 200 mL water and extracted with dichloromethane (DCM, 2 ×100 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/DCM (3/1) as the eluant affording 510 mg (50%) of 5 as a yellow solid. mp: 78.1-78.8 °C. $^1$H NMR (CDCl$_3$): δ = 7.54 (s, 1H), 3.18 (dd, $J$ = 17.2, 7.6 Hz, 1H), 2.67 (m, 4H), 2.48 (dd, $J$ = 16.0, 4.0 Hz, 1H), 2.28 (s, 3H), 1.30 (d, $J$ = 7.6 Hz, 3H). $^{13}$C NMR (CDCl$_3$): 210.2, 152.6, 138.1, 138.0, 136.0, 135.0, 134.5, 125.2, 42.5, 33.0, 17.4, 16.7. HRMS: m/z calcd for C$_{12}$H$_{14}$BrO [M+H]$^+$: 253.0233; found: 253.0216.

trans-6. To a suspension of zinc powder (2.0 g, 31.3 mmol) in 60 mL dry THF was added 1.63 mL TiCl$_4$ at 0 °C. The mixture was heated at reflux under N$_2$ for 2h. After cooling down to room temperature, compound 5 (2.0 g, 8.0 mmol) was added. The mixture was again heated at reflux under N$_2$ for 12h. After cooling to room temperature, the mixture was directly charged onto a silica gel column using DCM as eluant to remove the metal salts. The product was further purified by chromatography on silica gel using pentane/DCM (3/1) as eluant. The product was recrystallized from methanol/ dichloromethane, yielding trans-6 as a white solid. mp: 184.1-185.6 °C. $^1$H NMR (CDCl$_3$): δ = 7.28 (s, 2H), 2.84 (m, 2H), 2.59 (dd, $J$ = 14.7, 5.4 Hz, 2H), 2.47 (s, 6H), 2.24 (d, $J$ = 14.7 Hz, 2H), 2.18 (s, 6H), 1.11 (d, $J$ = 6.0 Hz, 6H) $^{13}$C NMR (CDCl$_3$): 142.8, 142.4, 141.8, 133.7, 131.8, 131.0, 123.8, 42.3, 39.0, 23.2, 19.0, 18.1. HRMS: m/z calcd for C$_{24}$H$_{26}$Br$_2$ [M-e$^-$]: 474.0381; found: 474.0357.

7. PPTS (100 mg, 0.4 mmol) and 3 (100 mg, 0.126 mmol) were dissolved in 15 mL MeOH. The mixture was heated at 75 °C in a sealed flask under N$_2$ for 2h. Then the mixture was cooled down and the solvent was evaporated under vacuum. The residue was purified by silica gel column chromatography using pentane/ethyl acetate (100/50) as the eluant affording 76 mg (96%) of 7 as a colorless oil. $^1$H NMR (CD$_2$Cl$_2$): δ = 6.86 (s, 2H), 3.64 (t, $J$ = 5.6 Hz, 4H), 2.90-2.78 (m, 2H), 2.73-2.53 (m, 6H), 2.38 (s, 6H), 2.24-2.14 (m, 8H), 1.73-1.26 (m, $J$ = 3, 2H), 1.10 (d, $J$ = 5.6 Hz, 6H). $^{13}$C NMR (CD$_2$Cl$_2$) δ 141.90, 139.9, 139.6, 131.2, 129.3, 128.8, 63.0, 42.5, 38.9, 33.6, 33.1, 31.0, 30.1, 29.8, 26.0, 19.0, 18.1. HRMS: m/z calcd for C$_{44}$H$_{67}$O$_2$ [M-H]: 627.5136; found: 627.4759.
8. Triphenylphosphine (192 mg, 0.73 mmol) and CBr₄ (121 mg, 0.36 mmol) were added to a solution of 7 (70 mg, 0.11 mmol) in 10 mL dry DCM. The mixture was stirred at room temperature for 20 min. Then the solvent was evaporated under vacuum. The residue was purified by silica gel column chromatography using pentane/DCM (3/1) as the eluant affording 82 mg (98%) of 8 as a colorless oil. ¹H NMR (CD₂Cl₂): δ = 6.87 (s, 2H), 3.45 (t, J = 5.6 Hz, 4H), 2.86-2.78 (m, 2H), 2.70-2.55 (m, 6H), 2.39 (s, 6H), 2.21 (d, J = 14.4 Hz, 2H), 2.18 (s, 6H), 1.94-1.82 (m, 4H), 1.70-1.25 (m, 28H), 1.07 (d, J = 5.6 Hz, 6H). ¹³C NMR (CDCl₃) δ 143.8, 143.7, 141.8, 141.5, 133.0, 131.3, 130.7, 44.4, 40.9, 36.4, 35.5, 35.0, 33.2, 33.0, 32.0, 31.7, 31.6, 31.0, 30.3, 21.0, 20.1. HRMS: m/z calcd for C₄₄H₆₇Br₂[M+H]+: 755.3593; found: 755.3595.

9. NaN₃ (200 mg, 3.07 mmol) was added to a solution of 8 (50 mg, 0.066 mmol) in 15 mL DMSO. The mixture was stirred at 60 °C under N₂ for 15 h. After cooling to room temperature, the mixture was poured into 100 mL water and extracted with DCM (2 × 50 mL). The combined organic phase was dried and the solvent was evaporated under vacuum. The residue was purified by silica gel column chromatography using pentane/DCM (3/1) as the eluant affording 40 mg (88%) of 9 as a colorless oil. ¹H NMR (CDCl₃): δ = 6.88 (s, 2H), 3.28 (t, J = 6.8 Hz, 4H), 2.90-2.81 (m, 2H), 2.73-2.55 (m, 6H), 2.40 (s, 6H), 2.24-2.14 (m, 8H), 1.70-1.25 (m, 32H), 1.10 (d, J = 5.6 Hz, 6H). ¹³C NMR (CDCl₃) δ 142.0, 141.9, 139.9, 139.8, 131.1, 129.5, 128.8, 51.7, 42.5, 39.1, 33.7, 31.0, 30.2, 30.0, 29.8, 29.4, 29.1, 27.0, 19.3, 18.5. HRMS: m/z calcd for C₄₄H₆₇N₂[M-N₃+H]+: 623.5308; found: 623.5295.

10. Triphosphine (460 mg, 1.75 mmol) was added to a solution of 9 (300 mg, 0.44 mmol) in 50 mL dry THF. The mixture was stirred at room temperature for 3h. Then 3 mL water was added and the mixture was stirred at 55 °C under N₂ for 15 h. After cooling to room temperature, the solvent was evaporated under vacuum. The residue was dissolved in 100 mL DCM. After the addition of 2% aqueous hydrochloric acid (100 mL), a white precipitate (hydrochloric salt of 10, used in the next reaction, 264 mg, 86%) was obtained. The product was neutralized with saturated K₂CO₃(aq) and extracted with DCM followed by solvent evaporation, affording 10 as a colorless oil. ¹H NMR (CDCl₃): δ = 6.86 (s, 2H), 2.91-2.82 (m, 2H), 2.77-2.54 (m, 10H), 2.37 (s, 6H), 2.23-2.10 (m, 8H), 1.70-1.25 (m, 32H), 1.10 (d, J = 5.6 Hz, 6H). ¹³C NMR (CDCl₃) δ 142.0, 141.9, 139.9, 131.1, 129.5, 128.8, 51.7, 42.5, 39.1, 33.7, 31.0, 30.2, 29.8, 29.4, 29.1, 27.0, 19.3, 18.5. HRMS: m/z calcd for C₄₄H₇₁N₂[M+H]+: 627.5612; found: 627.5622.

1. 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 dry toluene. The mixture was heated at 120 °C under N₂ in a sealed flask for 4h. After cooling to room temperature, the mixture was directly purified by silica gel chromatography using CHCl₃ as eluant, yielding 1 as a red solid (62%, 46 mg, 0.026 mmol). mp 163.1-164.2 °C. ¹H NMR (CDCl₃): 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). ¹³C NMR (CDCl₃) δ 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, 140.7, 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 C₁₁₈H₁₁₇N₄O₈[M+H]+: 1739.0465; found: 1739.0471.
Figure S1. Changes to the UV-vis absorption spectrum of trans-3 upon irradiation at 312 nm (top), 50 s, $\Phi_{\text{iso}} = 0.159$, in THF at 20 °C and the reversal of the spectral changes (bottom) upon irradiation at 365 nm, 70 s, $\Phi_{\text{iso}} = 0.078$.

Figure S2: Cyclic (a) and differential pulse (b) voltammetry of compound 1 (trans-1/cis-1 = 2/3) in CH$_2$Cl$_2$/0.1 M TBAPF$_6$ at 20 °C. Differential pulse voltammetry of the reference compound 7 (c, trans-7, d, trans-7/cis-7 = 1/1) was measured to assign the oxidation processes due to the overcrowded alkene.
Figure S3. Differential pulse voltammetry of trans-2 (1 mM) before (a) and after (b, c) UV irradiation at 312 nm in CH$_2$Cl$_2$/0.1 M TBAPF$_6$ at 20 °C. The oxidation potential of the overcrowded alkene decreases upon trans$\rightarrow$ cis isomerization.

Gibbs energy ($\Delta G_{ET}$) of photo-induced electron transfer (PET) is calculated using the Rehm Weller Equation

$$\Delta G_{ET} = e[E_{ox}(OA) - E_{red}(PBI)] - E_{00} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_sR_{CC}} - \frac{e^2}{8\pi\varepsilon_0}(\frac{1}{r^+} + \frac{1}{r^-})(\frac{1}{\varepsilon_{ref}} - \frac{1}{\varepsilon_s})$$

where $\frac{e^2}{4\pi\varepsilon_0} = 2.307 \times 10^{-28}$ J m, $E_{red}(OA)$ is the oxidation potential of the overcrowded alkene (OA), $E_{red}(PBI)$: the first reduction potential of the PBI unit (-0.58 V), $E_{red}$(trans-OA) = +1.01 V, $E_{red}$(cis-OA) = +0.80 V (Figure S2b), $E_{00}$: the energy of the $S_1$$\rightarrow$$S_n$ excited state (2.34 eV), $R_{CC}$: the distance (19.7 Å) between the centers of the electron donor (OA) and acceptor (PBI), $r^+$ and $r^-$: the effective ionic radii of the donor and acceptor radical cation and anion, respectively and $\varepsilon_{ref}$ and $\varepsilon_s$: the dielectric constant of the solvent used to determine redox potentials and the solvent used for spectroscopic measurements respectively (8.93 for CH$_2$Cl$_2$). All electrochemical data was obtained in the same solvent/electrolyte and hence the last term reduces to zero.

The quantum yield of trans-1 is lower, 30%, than that of trans-2. This might be ascribed to interaction with the PBI in the trans-state, resulting from the back-folding of the flexible C-10 alkyl chains. This is indicated by the higher $A^{11}$/$A^{00}$ ratio of trans-1 (0.71) than that of trans-2 (0.63, a value typical for non-aggregated PBI), see Figure 2a, c. But this interaction is very much less than that of H-stack in the PSS cis-state ($A^{11}$/$A^{00}$ = 1.18), where it is the dominant state.

Figure S4: Absorption spectra of compound 1 at several concentrations. No change on the spectral shape is observed during dilution from $1.0 \times 10^{-4}$ to $6.3 \times 10^{-6}$ M, indicating the absence of intermolecular interactions.
Figure S5. $^1$H NMR spectroscopy of trans-2 (Fig. a) before (top) and after (bottom) irradiation at 312 nm in CH$_2$Cl$_2$ at 20 °C.

Figure S6: Reversal absorption (a) and fluorescence (b, $\lambda_{ex} = 455$ nm) spectral changes of compound 1 upon irradiation at 365 nm in THF at 20 °C, and a schematic presentation of the cis$\rightarrow$trans switching process.

Figure S7. Absorption spectral changes of compound 1 upon alternate irradiation at 312 and 365 nm in THF.
At the photo stationary state, based on Figure S7, mole ratio \((\alpha_1, \alpha_2)\) of the isomer was calculated using the following two equations:

1) \(A_{\text{cis}} \times \alpha_1 + A_{\text{trans}} \times (1 - \alpha_1) = pss A_{\text{trans} \rightarrow \text{cis}}\)

2) \(A_{\text{trans}} \times \alpha_2 + A_{\text{cis}} \times (1 - \alpha_2) = pss A_{\text{cis} \rightarrow \text{trans}}\)

\(A_{\text{cis}}\): absorbance of the cis isomer, which can be calculated using equation 1; \(\alpha_1\): mole ratio of the cis isomer, 81\%, determined from the \(^1H\)-NMR spectroscopy; \(A_{\text{trans}}\): absorbance of the trans isomer (starting line, Figure S7); \(pss A_{\text{trans} \rightarrow \text{cis}}\): absorbance of the photo stationary state (trans→cis). \(pss A_{\text{cis} \rightarrow \text{trans}}\): absorbance of the photo stationary state (cis→trans); \(\alpha_2\): mole ratio of the trans isomer.

**Figure S8**: Excitation (a, \(\lambda_{\text{em}} = 618\) nm) and absorption (b) spectra of compound 1. For comparison, the excitation spectrum of a control compound PBI (c) is also presented.

**Figure S9**: Absorption spectral changes of compound 1 upon alternate irradiation at 312 nm in different solvents.
Figure S10. Absorption spectra of compound 1 at different temperatures. In the trans-state (a), the 0-1 band is lower than 0-0 band at different temperatures, indicating a monomer-type PBI chromophore. In the cis-state (b, c), the 0-1 band is higher than 0-0 band at different temperatures indicating a H-type PBI stacking.

Figure S11. Thermal isomerization of the overcrowded alkene from unstable cis- to stable cis-state followed by absorption changes at 350 nm at four different temperatures (40, 50, 55 and 60 °C, Fig. 11a). A half life of 58.5 h at 20 °C was determined (Fig 11b, $E_a = 97.3$ kJ/mol). UV-vis spectral changes of cis-1 at 60 °C for 20 min. (Fig 11c). Decreasing of the absorption at 350 nm indicates the isomerization the overcrowded alkene from unstable cis- to stable cis-state, see ref. 2. Thermal isomerization of the overcrowded alkene does not have noticeable effect on the PBI interactions.

**Determination of Quantum yield of fluorescence:**

The fluorescence quantum yield was determined by comparison of the integrated area (480 nm-720 nm) of the emission ($\lambda_{ex} = 455$ nm) spectrum of the sample with that of the

![PBI](image)

**Determination of Quantum yield of photoisomerization:**

3 mL of aqueous ferrioxalate (0.006 M) solution (0.05 M H$_2$SO$_4$) was transferred to a cuvette and irradiated with the monochromated (5 nm bandwidth) output of the Xe lamp of the JASCO FP-6200 spectrophotometer. The concentration was such that the absorbance at the excitation wavelength was above 3. 2 mL of the irradiated solution were mixed with 2 mL of aqueous phenanthroline solution (5 mM) and 1 mL of CH$_3$COONa/H$_2$SO$_4$ buffer (pH = 3.5, 0.6 M) in a 20 mL graduated flask and diluted to 20 mL with water. The solution was kept in the dark for 1 h, and the absorption spectrum was measured. The absorbance at 510 nm (absorption of the Fe$^{2+}$-phenanthroline complex, $\varepsilon_{510\text{ nm}} (1.11 \times 10^4$ l/mol·cm)) was recorded. As a control, 2 mL of the non-irradiated ferrioxalate (0.006 M) solution was treated in exactly the same way. The spectrum was used for baseline correction. The procedure was repeated using several irradiation times (10-60 min) and a plot of the absorbance at 510 nm as a function of time was used to determine the photon flux together with the reported quantum yields ($312\text{nm} \Phi_{\text{pr}} = 1.24, 365\text{nm} \Phi_{\text{pr}} = 1.21$).

For compounds 1-3, quantum yields were measured in THF (at 0.2 mM, the monochromated light was totally absorbed). 2.2 mL of solution was subjected to irradiation for different times (10-60 min). The irradiated samples were diluted and the UV-vis absorption spectra recorded. Plotting the absorbance at 350 nm (absorption of the overcrowded alkene in the cis-state) as a function of time provided the change in absorbance $\Delta A_{\text{t2}}$ at 350 nm at irradiation time $t_2$. Non-irradiated samples were used for baseline correction.

**References**
Compound 5

Compound 6
Compound 8

Compound 9
Compound 10

Compound 1
Compound 2