Supporting Information

Intramolecular Energy and Solvent-Dependent Chirality Transfer within a BINOL-Perylene Hetero-Cyclophane

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Supplementary Information

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S1. General information

Unless otherwise noted, all the chemical compounds were purchased from commercial suppliers and were directly used without further purification. Column chromatography was performed on silica gel (particle size 0.040–0.063 mm). NMR spectra were recorded on Bruker Avance III HD 400 MHz and 600 MHz spectrometers. NMR data analysis are presented as following, s: singlet, d: doublet, t: triplet, m: multiplet, br: broad signal. Recycling gel permeation chromatography (GPC) was carried out on a Shimadzu semi-preparative recycling chromatography setup with two or three semipreparative columns (Japan Analytical Industries Co., Ltd.; JAIGEL-2H and JAIGEL-2.5 H) with CHCl₃ as eluent. Recycling semipreparative HPLC was carried out on a Bruker Daltonics microTOF-QIII focus instrument for high-resolution ESI or a Bruker Daltonics ultrafleXtreme mass spectrometer using DCTB as a matrix for high-resolution MALDI. UV/Vis absorption spectra were recorded on JASCO V-670 and V-770 spectrometers. Fluorescence spectra and lifetime measurements were measured with an Edinburgh Instruments FLS980 spectrometer. Lifetimes were measured using EPL picosecond pulsed diode laser (505.8 nm and 378.2 nm) as a light source. Fluorescence quantum yields were determined relative to common fluorescence standards for optically dilute solutions (A<0.05). Theoretical calculations were performed by Gaussian 16 program and 09 program at B3LYP/6-31G(d,p) level. Circular dichroism was measured on a JASCO J-810 spectrophotometer. Circularly polarized luminescence was measured on a JASCO CPL-300 spectrophotometer.

S2. Synthesis and characterization

Perylene bisanhydride 1 and BINOL bisanhydride 4 are known compounds and were synthesized according to literature methods.

Synthesis of tert-butyl 4-(aminomethyl)benzylcarbamate (2): p-xylalenediamine (500.0 mg, 3.67 mmol) and triethylamine (TEA, 0.5 mL) were added to a 250 mL round-bottom flask with 150 mL chloroform, then (Boc)₂O (800.0 mg, 3.67 mmol) was dropwise added to the above solution at RT. The reaction mixture was stirred overnight. Afterwards, the solvent was removed under reduced pressure, and the crude product was purified by dry load column chromatography (silica gel, eluent CH₂Cl₂, and then CH₂Cl₂/MeOH = 20:1, v/v), a colorless solid was obtained. Yield: 35 % (303.5 mg, 1.30 mmol). ¹H-NMR (400 MHz, 298 K, d6-DMSO/CDCl₃ = 1:1, v/v): δ = 7.24 (d, J = 8.04 Hz, 2 H), 7.17 (d, J = 8.00 Hz, 2 H), 6.91 (t, J = 5.80 Hz, 1 H), 4.12 (d, J = 6.20 Hz, 2 H), 3.77 (s, 2 H), 1.37 (s, 9 H).
Synthesis of perylene diamine 3: Perylene bisanhydride 1 (100.0 mg, 0.10 mmol), tert-butyl 4-(aminomethyl)benzylcarbamate 2 (55.0 mg, 0.22 mmol) and imidazole (300.0 mg, 4.40 mmol) were added to 100 mL toluene in a 250 mL round-bottom flask. The mixture was refluxed under a nitrogen atmosphere for 16 h. After completion of the reaction, the mixture was cooled to RT and solvent was removed under reduced pressure. The crude product was washed with chloroform (100 mL) and 1 M HCl (100 mL). The organic phase was collected and dried over anhydrous Na₂SO₄. After filtration and removing the solvent under vacuum, the crude product was purified by column chromatography (silica gel, eluent CH₂Cl₂/MeOH = 20:1, v/v), giving a red solid (135.0 mg, 0.095 mmol). This perylene bismide compound (50.0 mg, 0.035 mmol) was further dissolved in 20 mL CH₂Cl₂ in a 100 mL round-bottom flask, then 3 mL trifluoroacetic acid (TFA) was added. The color of the solution changed from red to dark blue immediately. After stirring at RT for 30 min, the solvent was removed under reduced pressure, giving a dark red solid in a quantitative yield (50.7 mg, 0.035 mmol).

1H-NMR (400 MHz, 298 K, d6-DMSO): δ = 8.12 (s, 6 H), 7.92 (s, 4 H), 7.36 (d, J = 4.0 Hz, 8 H), 7.30 (d, J = 8.8 Hz, 8 H), 6.87 (d, J = 8.8 Hz, 8 H), 5.17 (s, 4 H), 4.00 (m, 4 H), 1.24 (s, 36H). 13C-NMR (101 MHz, 298 K, d6-DMSO): δ = 162.6, 158.2, 157.8, 155.2, 152.4, 147.0, 137.3, 132.8, 128.9, 127.4, 126.7, 122.4, 119.4, 119.1, 119.0, 118.6, 41.9, 34.1, 31.1. ESI-MS (positive mode, acetonitrile/chloroform = 1:1, v/v): calculated for C₃₀H₇₆N₄O₉Na, m/z 1243.5561, found: [M+Na]+, 1243.5531. Melting point: 266 °C.

Synthesis of BBI-PBI cyclophane: Perylene diamine 3 (84.0 mg, 0.058 mmol), racemic binaphthol bisanhydride 4 (26.0 mg, 0.058 mmol) and imidazole (1.1 g) were dispersed in 600 mL toluene in a 1000 mL round-bottom flask under a nitrogen atmosphere and the mixture was refluxed overnight. After cooling to RT, toluene was removed under vacuum, the residue was dissolved in chloroform (100 mL) and washed with 1 M HCl (100 mL). The organic phase was collected and dried over anhydrous Na₂SO₄. After filtration, the solvent was removed under vacuum and the product was purified by column chromatography (silica gel, eluent CH₂Cl₂/MeOH = 50:1) and recycling GPC to give a dark red solid, yield: 8 % (7.6 mg, 4.6 μmol). 1H-NMR (600 MHz, 347.8 K, C₂D₂Cl₄): δ = 8.35 (s, 2 H), 8.28 (m, 2 H), 8.14 (d, J = 7.8 Hz, 4 H), 7.41 (m, 10 H), 7.29 (m, 10 H), 6.82 (br, 4 H), 6.72 (br, 4H), 5.44 (br, 2H), 5.34 (br, 6H), 3.82 (s, 6H), 1.35 (s, 18H), 1.33 (s, 18H). 13C-NMR (150 MHz, 347.8 K, C₂D₂Cl₄): δ = 163.8, 163.7, 163.3, 163.2, 156.2, 153.2, 152.9, 147.7, 147.7, 137.4, 137.0, 132.7, 131.8, 131.5, 130.0, 129.8, 129.3, 129.3, 128.5, 127.7, 126.8, 126.8, 125.6, 124.8, 124.4, 123.9, 123.9, 123.2, 122.6, 122.5, 121.1, 120.7, 120.6, 120.5, 119.5, 119.2, 117.9, 116.9, 116.5, 99.9, 80.1, 80.0, 79.8, 57.1, 43.4, 43.1, 34.5, 34.5, 31.7, 31.7. HR-MALDI-TOF (pos. mode, chloroform): calculated for [M+H]+, C₁₀₆H₈₇N₄O₁₄: m/z 1639.614, found: 1639.610. Melting point: 331 °C.
Figure S1. 2D-COSY and 2D-NOESY spectra of BBI-PBI cyclophane, [BBI-PBI] = 3.0 mM in C$_2$D$_2$Cl$_4$, 347.8 K, 600 MHz.
Figure S2. Chemical structures with enantiomeric and diastereomeric relationships for the BBI-PBI cyclophane stereoisomers. Magenta double arrows represent enantiomers. Dark double arrows represent diastereomers. For better visualization, the side view CPK modes of P-BBI-P-PBI and P-BBI-M-PBI are shown at the top of each chemical structure. BBI is colored in cyan and PBI is colored in magenta. The 4-tert-butylphenoxy groups on bay position were omitted for clarity. Further, the cartoon figures on left and right sides represent the core twisting of BBI and PBI chromophores from a side view, in which solid and dashed blue lines indicate naphthalene imide planes of BBI, solid and dashed red lines indicate naphthalene imide planes of PBI.
Figure S3. HPLC chromatogram for BBI-PBI cyclophane on a recycling semi-preparative Trentec Reprosil 100 chiral-NR column. Dichloromethane/hexane as eluent, v/v = 4:1, flow rate: 1 mL/min.

Both the binaphthol bisanhydride 4 and the tetraphenoxy-substituted PBI diamine 3 (Scheme 1 in main text) utilized in the synthesis are racemic, therefore, BBI-PBI cyclophane should consist of four isomers theoretically, including enantiomers and diastereomers, i.e. $P$-BBI-$P$-PBI, $P$-BBI-$M$-PBI, $M$-BBI-$P$-PBI and $M$-BBI-$M$-PBI (Fig. S2). However, the racemization barrier for tetraphenoxy-substituted PBI is only about 60 kJ/mol,\(^5\) which is not high enough for enantiomeric resolution on a chiral HPLC column. As a result, only two compounds, $P$-BBI-PBI and $M$-BBI-PBI cyclophanes were obtained after resolution on a semi-preparative chiral column (Fig. S3), for which the $P/M$-ratio of the perylene subunit depends on the degree of chirality transfer imparted by the BBI unit.\(^3\)
Table S1. Optical properties of reference compounds in CH$_2$Cl$_2$ at 293 K.

|                | $\lambda_{ab}$/nm | $\varepsilon_{max}$/M$^{-1}$cm$^{-1}$ | $\lambda_{em}$/ nm | $\Delta\tilde{\nu}_{Stokes}$/ cm$^{-1}$ | FLQY$^a$ | Lifetime |
|----------------|-------------------|---------------------------------------|-------------------|------------------------------------------|----------|----------|
| ref-BBI        | 397               | 2.7 x 10$^4$                          | 444               | 2666                                     | 0.68±0.05| 3.6 ns$^b$|
| ref-PBI        | 582               | 4.7 x 10$^4$                          | 614               | 895                                      | 0.91±0.05| 6.6 ns$^c$|

a. Perylene (FLQY 0.94 in cyclohexane) as a reference for ref-BBI, $N,N'$-bis(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-bis(dicarboximide) (FLQY 0.96 in chloroform) for ref-PBI. b. Diode laser excitation wavelength 378.2 nm, monitored emission wavelength for decay at 444 nm. c. Diode laser excitation wavelength 505.8 nm, monitored emission wavelength for decay at 614 nm.

**Figure S4.** a) Optical spectra of the mixture of ref-BBI and ref-PBI (1:1 in molar ratio) in CH$_2$Cl$_2$ at 293K. For UV-Vis measurements, [ref-BBI] = [ref-PBI] = 2.4 x 10$^{-5}$ M. The fluorescence spectra were obtained by photoexcitation at 380 nm (blue dotted line) and 550 nm (magenta dotted line), respectively. The excitation spectrum (black dashed line) was measured for the emission wavelength at 650 nm. b) HOMO and LUMO energy levels of reference compounds calculated by DFT, Gaussian 16, at B3LYP/6-311G(d,p) level.

In addition to the optical properties of the two individual dyes, also those for the ref-BBI/ref-PBI mixture (1:1 in molar ratio) were recorded. Here upon excitation of the PBI chromophore at 550 nm, only the PBI emission band was observed (Fig. S4a, magenta dotted line) whilst upon excitation at 380 nm mainly BBI emission was observed with relatively weak PBI emission (Fig. S4a, blue dotted line). The latter originates from direct photoexcitation of the weak absorption band of ref-PBI at 330-400 nm. These results indicate that the absence of energy transfer from ref-BBI to ref-PBI in dilute solution. This conclusion is further supported by the excitation spectra (Fig. S4a, black dashed line), which show that the absorption of ref-BBI at 330-400 nm is not responsible for PBI emission.
Figure S5. UV-Vis and FL spectra ($\lambda_{ex} = 550$ nm) of $P$-$BBI$-$PBI$ at a concentration of $1.8 \times 10^{-5}$ M in CH$_2$Cl$_2$ (for UV-Vis), 293 K.

When directly exciting the acceptor PBI at 550 nm, the emission curve of BBI-PBI cyclophane (Fig. S5, blue line) are almost identical to that of individual ref-PBI chromophore (Fig. 2a in main text, blue dashed line).

Figure S6. Emission spectra of ref-BBI (dark line) was normalized with $P$-$BBI$-$PBI$ cyclophane (red line), $\lambda_{ex} = 380$ nm. [ref-BBI] = [$P$-$BBI$-$PBI$] = $1.0 \times 10^{-6}$ M in CH$_2$Cl$_2$, 293 K.

FRET efficiency ($\Phi_T$) is evaluated by the following equation:

$$\Phi_T = 1 - \frac{I_{DA}}{I_D},$$

where $I_{DA}$ and $I_D$ represent the fluorescence intensity of BBI in the presence and absence of PBI.

We obtain $\Phi_T = 1 - 0.003/0.820 = 99.6 \%$. 
Figure S7. UV-Vis, FL and excitation spectra of \( \text{P-BBI-PBI} \) cyclophane in different solvents, a) \( p \)-xylene, b) MeCN, c) CHCl\(_3\), and d) THF. \([\text{P-BBI-PBI}] = 1.8 \times 10^{-5} \text{ M}\) for UV-Vis, 293 K. Black solid lines, absorption spectra. Green dashed lines, excitation spectra (emission wavelength at 650 nm). Magenta dashed lines, emission spectra (\( \lambda_{\text{ex}} = 550 \text{ nm}\)). Blue dashed lines, emission spectra (\( \lambda_{\text{ex}} = 380 \text{ nm}\)). Emission spectra are normalized according to corresponding absorption maxima.

Table S2. Optical properties of \( \text{P-BBI-PBI} \) in different solvents.

| Solvent | \( \lambda_{\text{abs}} \) / nm | \( \varepsilon_{\text{max}}/ \times 10^4 \text{ M}^{-1}\text{cm}^{-1} \) | \( \lambda_{\text{em}} \) / nm | \( \Delta \tilde{\nu} \)Stokes / \text{cm}^{-1} | \( \text{Lifetime}^{a} \) PBI excitation | \( \text{Lifetime}^{b} \) BBI excitation | FLQY\(^{c}\) PBI excitation \( \pm 0.05 \) | FLQY\(^{d}\) BBI excitation \( \pm 0.05 \) |
|---------|------------------|-------------------------|-----------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| CHCl\(_3\) | 592 | 3.8 | 624 | 866 | 7.4 ns | 7.4 ns | 0.98 | 0.83 |
| \( p \)-xylene | 579 | 3.5 | 611 | 905 | 6.9 ns | 6.9 ns | 0.80 | 0.87 |
| CH\(_2\)Cl\(_2\) | 589 | 3.9 | 621 | 875 | 7.6 ns | 7.6 ns | 0.87 | 0.92 |
| THF | 582 | 4.0 | 614 | 748 | 7.7 ns | 7.7 ns | 0.92 | 0.98 |
| MeCN | 581 | 3.9 | 614 | 925 | 7.5 ns | 7.5 ns | 0.83 | 0.93 |

a. Diode excitation wavelength 505.8 nm, monitored PBI emission wavelength 650 nm; b. Diode excitation wavelength 378.2 nm, monitored PBI emission wavelength 650 nm; c. \( N,N' \)-bis(2,6-diisoproplyphenyl)-1,6,7,12-tetraphenoxy perylene \(-3,4,9,10\)-bis(dicarboximide) ("Perylene Red”, QY 0.96 in chloroform) used as reference d. Coumarin 153 (QY 0.90 in cyclohexane) used as a reference.
Figure S8. Energy levels and molecular orbitals of P-BBI-M-PBI cyclophane calculated by Gaussian 16 at B3LYP 6-311G (d,p) level.
**Table S3.** Molecular orbital (MO) transition contribution to excited states of *P-BBI-M-PBI* cyclophane, calculated by TD-DFT, Gaussian 09, B3LYP/6-311 G(d,p).

| States | MO contribution | Energy  | Wavelength | Oscillator strength |
|--------|----------------|---------|------------|--------------------|
| S1     | HOMO → LUMO (99.2%) | 2.07 eV | 599 nm     | 0.391              |
| S2     | HOMO → LUMO+1 (99.2%) | 2.45 eV | 506 nm     | < 0.001            |
| S3     | HOMO-1 → LUMO (99.6%) | 2.56 eV | 484 nm     | < 0.001            |
| S10    | HOMO-1 → LUMO+1 (93.9%) | 2.91 eV | 425 nm     | 0.185              |

**Figure S9.** Calculated transition dipole moment (red arrow)\(^6,7\) for the HOMO-LUMO transition of *P-BBI-M-PBI* cyclophane, TD-DFT, Gaussian 09 at B3LYP 6-311 G(d,p) level.

TD-DFT calculations indicate that the major MO contribution to the S1 state is the HOMO-LUMO transition (Table S3). These two frontier orbitals are mainly located on the PBI chromophore (Fig. S9). Accordingly, the transition dipole moment of the S\(_0\)-S\(_1\) transition of *P-BBI-M-PBI* cyclophane is polarized along the long axis of PBI, which is only slightly interfered by the presence of the BBI chromophore.
Figure S10. CD spectra of P-BBI-PBI cyclophane in a) CHCl₃ (stabilized with amylene, filtered over Alox), and b) CHBr₃ (stabilized with 4 wt% EtOH), $[P\text{-BBI-PBI}] = 2.6 \times 10^{-4}$ M, cuvette path length 1 mm, 293K. The results are similar to those in CHCl₃ stabilized with 4 wt% ethanol (shown in Fig. 3a in main text).
Figure S11. CD and UV/Vis spectra of BBI-PBI cyclophane in various solvents. [BBI-
PBI] = 2.6 × 10⁻⁴ M, cuvette path length 1 mm, 293 K.
**Figure S12.** a) Variable-temperature CD spectra of $P$-BBI-PBI cyclophane in CH$_2$Cl$_2$. Concentration at 293 K is 3.16×10$^{-4}$ M, cuvette path length is 1 mm. b) Plot of absorption dissymmetry factor ($|g_{\text{abs}}|$) of the cyclophane at 596 nm against temperature. $|g_{\text{abs}}|$ is calculated by the following equation: $|g_{\text{abs}}| = \text{CD}/(32980 \times \text{Abs.})$, where CD and Abs. values are obtained from Fig. S12a.

The ee value of PBI subcomponent at 263 K is estimated to be $3.24 \times 10^{-4}/0.0018 = 0.18$, where 0.0018 is the absorption dissymmetry factor of an enantiopure $P$-helical tetraphenoxy-substituted PBI based on our previous report.\textsuperscript{5}

**Figure S13.** Calculated CD spectrum of $P$-BBI-$M$-PBI cyclophane without consideration of the solvent, TD-DFT, Gaussian 09, B3LYP/6-311+G(d,p) level.
Figure S14. CD spectra of \textit{P-BBI-PBI} in CHCl$_3$/CH$_2$Cl$_2$ co-solvents with different CHCl$_3$ volume ratios. [\textit{P-BBI-PBI}] = 1.7 \times 10^{-5}$ M, cuvette path length 10 mm, 293 K.

Figure S15. CD spectra of a) \textit{P-BBI-PBI} and b) \textit{M-BBI-PBI} cyclophanes in \textit{R}-limonene and \textit{S}-limonene. [\textit{BBI-PBI}] = 2.5 \times 10^{-5}$ M, cuvette path length 10 mm, 293 K.
**Figure S16.** CPL spectra of \( P\text{-BBI-PBI} \) and \( M\text{-BBI-PBI} \) isomers in a) THF, and b) \( \text{CHCl}_3 \). \([\text{BBI-PBI}] = 2.3 \times 10^{-4} \text{ M}, \) cuvette path length 1 mm, 293 K. Black and red lines are obtained by photoexcitation at 350 nm, blue and magenta lines are obtained by photoexcitation at 520 nm.
S4. Supplementary spectra

Figure S17. $^1$H-NMR (400 MHz, 298 K, d$_6$-DMSO) spectrum of perylene diamine 3.

Figure S18. $^{13}$C-NMR (101 MHz, 298 K, d$_6$-DMSO) spectrum of perylene diamine 3.
Figure S19. $^1$H-NMR (600 MHz, 347.8 K, C$_2$D$_2$Cl$_4$) spectrum of BBI-PBI cyclophane.

Figure S20. $^{13}$C-NMR (150 MHz, 347.8 K, C$_2$D$_2$Cl$_4$) spectrum of BBI-PBI cyclophane.
Figure S21. HR-MALDI-TOF (pos. mode, chloroform) spectrum of BBI-PBI cyclophane.

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