Supplementary Information:

A Design Concept of Planar Conjugated Ladder Oligomers of Perylene Bisimides and the Efficient Synthetic Strategy via Regioselective Photocyclization

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1 Material and methods

Compound 8 was synthesized according to Scheme S1. Compound 13 and 15 were synthesized according to Scheme S2. Compound 1,17,18 and 19S3 were synthesized by literature methods. All other reactants were purchased from commercial sources.

NMR spectra were measured with a Bruker spectrometer using DSS as reference for potassium salt of 10 and 12, and for the other NMR spectra, TMS was reference.

Cyclic voltammetry (CV) was performed with a standard commercial electrochemical analyzer in a three electrode single-component cell under argon. The measurements were carried out at a concentration of 5×10^{-4} M with ferrocene as internal standard for the calibration of potential. Working electrode: glassy carbon; reference electrode: Ag/AgNO3; auxiliary electrode: Pt wire. Samples were measured in 0.05 M solution of Bu4NPF6 in THF with a scan rate of 100 mV/s.

Atomic structure of compound 6 was optimized with density functional theory (DFT) calculations using the B3LYP hybrid functional with the basis set 6-31G. The quantum-chemical calculations were performed with the Gaussian03 package.S4 Absorption spectra were determined on a HP-8453 UV-Vis spectrophotometer. Fluorescence spectra were measured on a JASCO FP-6500 fluorescence. The fluorescence quantum yields were determined with Rhodamine 6G as reference.S5

Scheme S1 Synthesis of Intermediate 8

Scheme S2 Synthesis of 13 and 15

Reference
S4: M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, T. Jr. Vreven, K.N. Kudin,
2 Synthesis of intermediates and target compounds

Synthesis of 18
A mixture of 3 g compound 17 (4.6 mmol), 3 g K₂CO₃ (21.7 mmol), 50 mL CH₂Cl₂ and 3 mL Br₂ (59 mmol) was stirred at 20 °C for 100 min. The excess bromine was removed by adding aqueous Na₂SO₃. Then, the crude product was purified through silica gel column chromatography with CH₂Cl₂ as eluent. The second band was collected, and removal of the solvent yielded compound 18 (20 mg, 33%). HRMS (API-ES): Calcd for C₆₆H₃₅BrO₇Na 1397.5814, found: 1397.5857 ([M+Na]⁺); 1H NMR (400 MHz, CDCl₃): δ = 0.98 (m, 24H), 1.48 (m, 16H), 1.88 (m, 16H), 4.37 (m, 16H), 8.50 (s, 4H), 7.65 (m, 4H), 9.02 (d, 4H, J = 8 Hz ), 10.00 (s, 4H), 10.84 ppm (s, 4H); 13C NMR (125 MHz, CDCl₃): δ = 13.8, 19.2, 30.6, 30.7, 65.4, 65.5, 119.4, 121.6, 122.3, 128.0, 129.5, 130.0, 130.1, 130.2, 130.4, 130.8, 130.9, 131.6, 132.2, 132.4, 132.5, 137.4, 167.1, 168.2, 168.3, 168.4 ppm.

Synthesis of 8
A mixture of 220 mg Compound 9 (0.3 mmol), 25 mg 1,4-phenylenebisboronic acid (0.15 mmol), 510 mg K₂CO₃, 10 mg Pd(dppf)Cl₂, 3 mL THF, and 1.5 mL H₂O were stirred at reflux for 6 h. Then, the crude product was purified through silica gel column chromatography with mixture of CH₂Cl₂ and THF as eluent. The second band was collected, and removal of the solvent yielded compound 8 as a brown solid (0.9 mg, 87%). HRMS (API-ES): Calcd for C₆₀H₄₉O₁₃Na 1379.5814, found: 1379.5857 ([M+Na]⁺); 1H NMR (400 MHz, CDCl₃): δ = 1.06 (m, 24H), 1.57 (m, 16H), 1.88 (m, 16H), 4.47 (t, 8H), 4.56 (t, 8H), 8.08 (d, 4H, J = 8 Hz ), 10.00 (s, 4H), 10.84 ppm (s, 4H); 13C NMR (125 MHz, CDCl₃): δ = 13.8, 19.2, 30.6, 30.7, 65.4, 65.5, 119.4, 121.6, 122.3, 128.0, 129.5, 130.0, 130.1, 130.2, 130.4, 130.8, 130.9, 131.6, 132.2, 132.4, 132.5, 137.4, 167.1, 168.2, 168.3, 168.4 ppm.

Synthesis of 9
A mixture of 65 mg compound 8 (0.047 mmol), 5 mL toluene, and 1 mg I₂ was illuminated by sunlight under reflux for 3 h. Then, the reaction mixture was reflux for another 3 h after 35 mg (0.16 mmol) DDQ was added. The crude product was purified through silica gel column chromatography with CH₂Cl₂ as eluent and compound 9 was yielded as a black solid (30 mg, 100%). MALDI-TOF-MS: Calcd for C₅₈H₆₈O₁₃Na 1401.6127, found: 1401.6178 ([M+Na]⁺); 1H NMR (400 MHz, CDCl₃): δ = 0.98 (m, 24H), 1.48 (m, 16H), 1.79 (m, 16H), 4.37 (m, 16H), 8.50 (s, 4H), 7.65 (m, 4H), 8.12 (m, 6H), 8.31 ppm (m, 4H); 13C NMR (125 MHz, CDCl₃): δ = 13.8, 19.2, 30.6, 30.7, 65.4, 65.5, 119.4, 121.6, 122.3, 128.0, 129.5, 130.0, 130.1, 130.2, 130.4, 130.8, 130.9, 131.6, 132.2, 132.4, 132.5, 137.4, 167.1, 168.2, 168.3, 168.4 ppm.

Synthesis of 10
Compound 9 (42 mg, 0.030 mmol) was added to 4 mL Chlorosulfonic acid gradually and the mixture was stirred for 3 h at room temperature. Then the mixture was added to ice. After filtration compound 10 was yielded as dark solid (27 mg, 100%). MALDI-TOF-MS: Calcd for C₅₈H₆₇O₁₃Na 1401.6127, found: 1401.6178 ([M+Na]⁺); 1H NMR of potassium salt of compound 10 (400 MHz, D₂O): δ = 8.08 (d, 4H, J = 8 Hz ), 8.92 (d, 4H, J = 8 Hz), 9.78 (s, 4H), 10.88 ppm (s, 2H); 13C NMR of potassium salt of compound 12 (125 MHz, D₂O): δ = 120.0 122.3, 124.6, 124.7, 127.0, 127.4, 128.0, 128.4, 128.3, 131.9, 131.9, 139.0, 163.5, 163.8, 177.8, 177.9 ppm.

Synthesis of 6
Mixture of compound 10 (12 mg, 0.014 mmol), tricosan-12-amine (54 mg, 0.16 mmol) and 1.2 g imidazole was stirred for 6 h at 200 °C. The crude product was purified through silica gel column chromatography with CH₂Cl₂ as eluent and compound 6 was obtained as a black solid (30 mg, 100%). MALDI-TOF-MS: Calcd for C₁₆₀H₁₆₃NO₁₂ 2140.6, found: 2140.6; 1H NMR (400 MHz, CDCl₃): δ = 0.7-1.6 (m, 16H), 2.12 (m, 8H), 2.49 (m, 8H), 5.41 (m, 4H), 8.94 (m, 8H), 10.70 ppm (m, 6H); 13C NMR (125 MHz, CDCl₃): δ = 14.0, 14.1, 22.6, 22.7, 27.2, 27.7, 29.4, 29.5, 29.7, 29.8, 31.9, 32.7, 55.7, 56.0, 119.4, 122.7, 123.5, 124.1, 124.4, 125.2, 125.7, 128.2, 128.9, 133.0, 133.3, 163.8, 164.1, 164.7, 165.1 ppm.
Synthesis of 11
A mixture of 100 mg compound 8 (0.072 mmol), 50 mL CH₂Cl₂, and catalytic amount I₂ was illuminated by sunlight at room temperature for 6 h. The crude product was purified by recrystallization in a mixture of xylene and propanoic acid (1:1, v/v) and compound 11 was yielded as a red solid (91 mg, 91%). HRMS (API-ES): Calcd for C₉₅H₈₇O₃Na: 1397.5814, found: 1397.5842 ([M+Na]+); ¹H NMR (400 MHz, CDCl₃): δ = 1.03 (m, 24H), 1.57–1.88 (m, 32H), 3.93 (m, 4H), 4.47 (m, 12H), 8.57 (m, 4H), 8.95 (s, 2H), 9.20 (m, 4H), 9.47 (s, 2H), 9.78 ppm (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ = 13.2, 13.8, 13.9, 14.1, 18.6, 19.3, 19.4, 22.7, 29.8, 30.8, 31.6, 64.8, 65.4, 65.6, 65.8, 122.0, 122.1, 123.6, 123.9, 124.6, 125.1, 125.7, 127.0, 127.1, 127.2, 127.5, 127.8, 128.6, 129.1, 129.5, 129.6, 129.9, 130.6, 131.0, 132.5, 132.8, 133.1, 167.8, 168.5, 168.9 ppm.

Synthesis of 12
Compound 11 (103 mg, 0.075 mmol) was added to 7 mL chlorosulfonic acid gradually and the mixture was stirred for 3 h at room temperature. Then the mixture was added to ice. After filtration compound 12 was yielded as dark solid (65 mg, 100%). MALDI-TOF-MS: Calcd for C₉₅H₈₆O₁₂Na: 1463.5412, found: 1463.5369.

Synthesis of 7
A mixture of 73 mg Compound 8 (0.034 mmol), 25 mL THF, and catalytic amount I₂ was illuminated by sunlight at room temperature for 3 h. The crude product was purified through silica gel column chromatography with CH₂Cl₂ as eluent and compound 7 was obtained as red solid (16 mg, 90%). MALDI-TOF-MS: Calcd for C₉₅H₈₆O₁₂Na: 1459.5099, found: 1459.5164 ([M+Na]+); ¹H NMR (400 MHz, CDCl₃): δ = 0.93–1.02 (m, 24H), 1.50 (m, 16H), 1.79 (m, 16H), 4.37 (m, 16H), 7.40 (s, 2H), 7.60 (d, 2H, J = 9 Hz), 7.95 (d, 2H, J = 9 Hz), 8.01 (d, 2H, J = 7.5 Hz), 8.06 (d, 2H, J = 9 Hz), 8.20 ppm (m, 6H); ¹³C NMR (125 MHz, CDCl₃): δ = 13.4, 19.2, 19.3, 29.7, 30.6, 30.7, 65.4, 65.5, 65.6, 119.5, 121.4, 122.5, 128.1, 128.4, 128.9, 129.3, 129.5, 130.0, 130.1, 130.2, 130.3, 130.4, 130.5, 131.0, 131.1, 132.2, 132.8, 133.3, 135.2, 140.9, 147.1, 168.0, 168.4, 168.5, 168.6 ppm.

Synthesis of 13
A mixture of 12 (7 mg, 0.0082 mmol), tricosen-12-amine (50 mg, 0.15 mmol) and 1.2 g imidazole was stirred for 6 h at 200 °C. The crude product was purified through silica gel column chromatography with CH₂Cl₂ as eluent and compound 13 was yielded as dark solid (65 mg, 100%). MALDI-TOF-MS: Calcd for C₉₅H₈₆O₁₂Na: 1463.5412, found: 1463.5369.

Synthesis of 14
A mixture of 49 mg compound 13 (0.034 mmol), 25 mL THF, and catalytic amount I₂ was illuminated by sunlight at room temperature for 3 h. The crude product was purified through silica gel column chromatography with CH₂Cl₂ as eluent and compound 14 was yielded as a yellow solid (52 mg, 72%). HRMS (API-ES): Calcd for C₉₅H₈₆O₁₂Na: 1397.5814, found: 1397.5842 ([M+Na]+); ¹H NMR (400 MHz, CDCl₃): δ = 0.5–2.6 (m, 184H), 5.39 (m, 4H), 9.08 (s, 2H), 9.36 (m, 4H), 9.65 (s, 2H), 9.73 (s, 2H), 10.38 ppm (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ = 13.3, 19.0, 19.4, 29.7, 30.8, 30.9, 65.5, 65.6, 66.0, 122.1, 122.2, 122.8, 123.4, 123.6, 125.1, 126.2, 126.8, 127.0, 127.8, 128.4, 128.9, 129.0, 130.2, 130.4, 130.7, 131.3, 131.4, 131.7, 141.2, 168.3, 168.4, 168.6 ppm.

Synthesis of 15
A mixture of 88 mg compound 20 (0.137 mmol), 2.1 g K₂CO₃, 14 mL THF, and 6 ml H₂O were stirred at reflux for 5 h. Then, 200 mg Compound 18 (0.274 mmol) and 28 mg Pd(dppf)Cl₂ were added and reflux for another 4 h. The crude product was purified through silica gel column chromatography with mixture of CH₂Cl₂ and THF as eluent. The second band was collected, and removal of the solvent yielded compound 15 as a red solid (52 mg, 65%). HRMS (API-ES): Calcd for C₉₅H₈₆O₁₂Na: 1459.5099, found: 1459.5164 ([M+Na]+); ¹H NMR (400 MHz, CDCl₃): δ = 0.65–1.19 (m, 54H), 1.49 (m, 16H), 1.79 (m, 16H), 1.91 (m, 4H), 4.37 (m, 16H), 7.43 (m, 6H), 7.70–7.80 (m, 4H), 8.10 (m, 6H), 8.29 ppm (d, 4H, J = 9 Hz); ¹³C NMR (125 MHz, CDCl₃): δ = 13.9, 14.0, 19.4, 22.6, 24.0, 29.2, 29.3, 30.6, 30.7, 31.7, 40.1, 55.8, 65.3, 65.4, 65.5, 121.3, 121.4, 121.6, 122.3, 123.4, 127.7, 128.3, 128.5, 128.9, 129.4, 129.6, 130.1, 130.2, 130.3, 130.5, 131.2, 131.3, 133.3, 133.5, 135.1, 139.7, 140.4, 142.4, 152.9, 168.3, 168.4, 168.7 ppm.

Synthesis of 16
A mixture of 99 mg compound 15 (0.058 mmol), 50 mL THF, and catalytic amount I₂ was illuminated by sunlight at room temperature for 3 h. The crude product was purified through silica gel column chromatography with toluene as eluent and compound 16 was yielded as a yellow solid (64 mg, 65%). HRMS (API-ES): Calcd for C₉₅H₈₆O₁₂Na: 1459.5099, found: 1459.5164 ([M+Na]+); ¹H NMR (400 MHz, CDCl₃): δ = 0.65–1.19 (m, 54H), 1.58 (m, 16H), 1.90 (m, 16H), 2.62 (m, 4H), 4.50 (m, 16H), 8.51 (m, 4H), 9.05 (m, 4H), 9.20 (s, 2H), 9.73 (s, 2H), 9.93 ppm (s, 4H); ¹³C NMR (125 MHz, CDCl₃): δ = 13.9, 19.4, 19.5,
22.4, 24.3, 29.1, 29.2, 30.1, 30.7, 30.8, 31.6, 42.1, 56.2, 65.6, 65.7, 115.7, 117.8, 121.9, 122.0, 124.1, 124.4, 127.0, 127.4, 127.6, 127.7, 127.8, 129.1, 129.4, 129.7, 129.9, 130.1, 130.4, 132.7, 132.8, 141.2, 151.9, 168.8, 168.9, 169.1 ppm.

3 HPLC spectrum of M9

![HPLC spectrum of M9]

C-18 Column, CHCl3: THF (49: 1 v/v) as mobile phase

**Figure S1** HPLC spectrum of M9

4 Mass spectrum of 8 and M9

![Mass spectrum of 8 and M9]

Molecular ion peak: 1401.6178

**Figure S2** Mass spectrum of 8
Figure S3 Mass spectrum of M9

5 Computed structure of conjugated core of 6 and 7

Figure S4 The B3LYP/6-31G computed structure of conjugated core of 6
Figure S5 The B3LYP/6-31G computed structure of conjugated core of 7

6 Cyclic voltammograms of compound 1, 6 and 7

Figure S6 Reductive cyclic voltammograms of 1

Figure S7 Reductive cyclic voltammograms of 6

Figure S8 Reductive cyclic voltammograms of 7
7 Copy of NMR spectrum

7.1 $^1$H $^{13}$C NMR spectrum of 9

$^1$H NMR (400 MHz) spectrum of 9 in CDCl$_3$ and its enlarged low-field section (inserted figure)

![NMR spectrum diagram]
$^{13}$C NMR (125 MHz) spectrum of 9 in CDCl$_3$
7.2 $^1$H $^{13}$C NMR spectrum of potassium salt of 10

$^1$H NMR (400 MHz) spectrum of potassium salt of 10 in D$_2$O and its enlarged low-field section (inserted figure)

Potassium salt of 10
$^{13}$C NMR (125 MHz) spectrum of potassium salt of 10 in D$_2$O
7.3 $^1$H $^13$C NMR spectrum of 6

$^1$H NMR (400 MHz) spectrum of 6 in CDCl$_3$ and its enlarged low-field section (inserted figure)
$^{13}$C NMR (125 MHz) spectrum of 6 in CDCl$_3$
7.4 $^1$H $^13$C NMR spectrum of 11

$^1$H NMR (400 MHz) spectrum of 11 in CDCl$_3$ and its enlarged low-field section (inserted figure)
$^{13}$C NMR (125 MHz) spectrum of \textbf{11} in CDCl$_3$
7.5 $^1$H $^{13}$C NMR spectrum of potassium salt of 12

$^1$H NMR (400 MHz) spectrum of potassium salt of 12 in D$_2$O and its enlarged low-field section (inserted figure)

Potassium salt of 12
$^{13}$C NMR (125 MHz) spectrum of potassium salt of 12 in D$_2$O

Potassium salt of 12

R = COOK
7.6 $^1$H $^{13}$C NMR spectrum of 7

$^1$H NMR (400 MHz) spectrum of 7 in CDCl$_3$ and its enlarged low-field section (inserted figure)
$^{13}$C NMR (125 MHz) spectrum of 7 in CDCl$_3$
7.7 $^1$$^H$ $^{13}$C NMR spectrum of 14

$^1$$^H$ NMR (400 MHz) spectrum of 14 in CDCl$_3$ and its enlarged low-field section (inserted figure)
$^{13}$C NMR (125 MHz) spectrum of 14 in CDCl₃
7.8 $^1$H $^{13}$C NMR spectrum of 16

$^1$H NMR (400 MHz) spectrum of 16 in CDCl$_3$ and its enlarged low-field section (inserted figure)
$^{13}$C NMR (125 MHz) spectrum of 16 in CDCl$_3$