Title: Photoswitching of intramolecular chiral stack in a helical tetrathiazole

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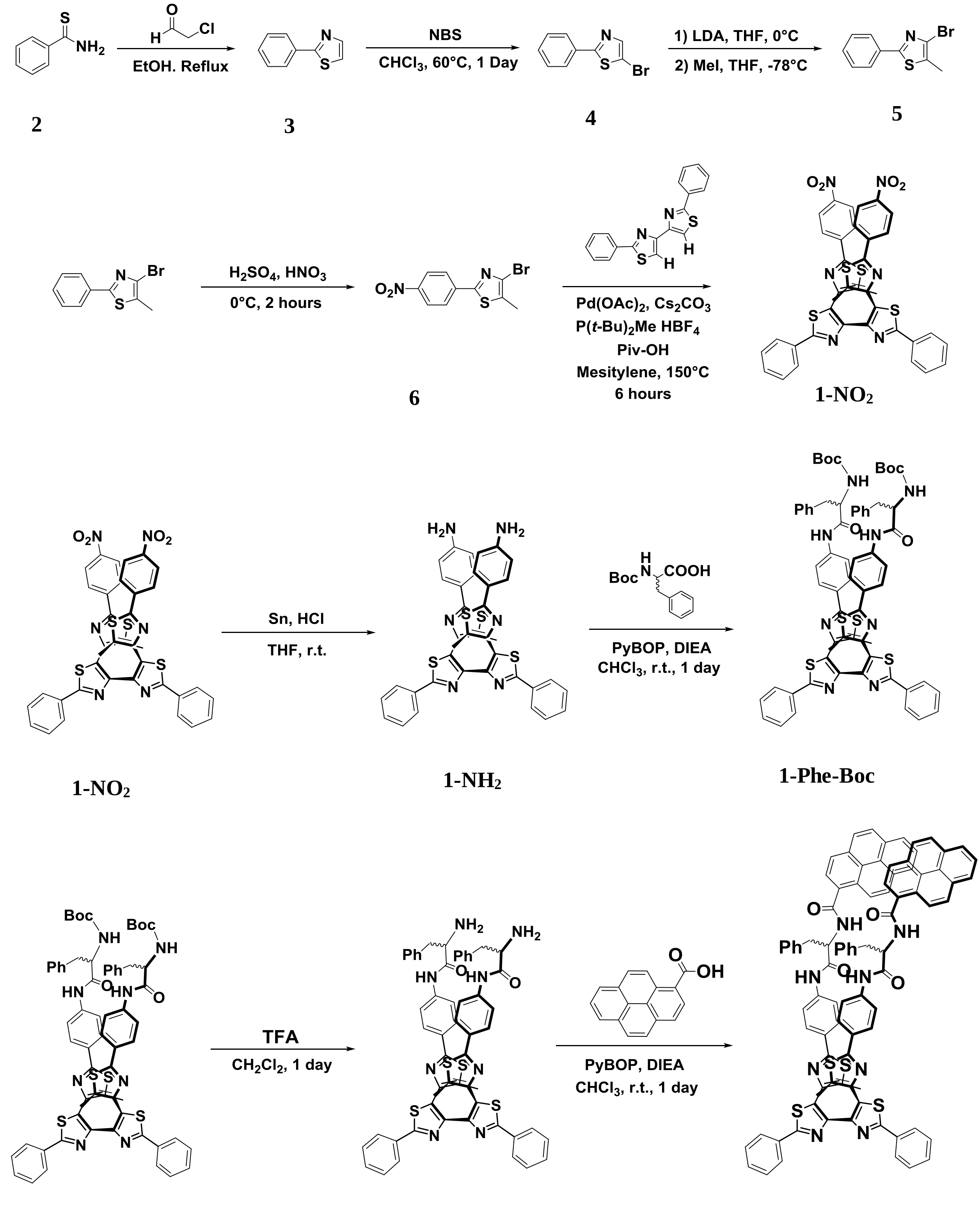
1. Experiments

1.1. General

Compounds were synthesized according to the reaction procedures as showed in Scheme S1. Their chemical structures were confirmed by high-resolution mass spectroscopy (Bruker Autoflex2), and ^{1}H-NMR and ^{13}C-NMR measurements (JEOL AL-300, JNM-ECX400 and JNM-ECA600). HPLC analysis was performed on L-2400 Series (HITACHI) or on LC-9110NEXT (GPC) (Japan Analytical Industry Co. Ltd). Absorption spectra in solution were studied with a JASCO V-670 spectrophotometer. Fluorescence spectra were measured with a spectrofluorometer (JASCO FP-6500). CD spectra were recorded by a JASCO J-725 spectropolarimeter. An absolute photocyclization quantum yield of **1o** was determined by a Shimazu QYM-01 setup.[1] Conformational search was performed on the CONFLEX program (CONFLEX Corp.).

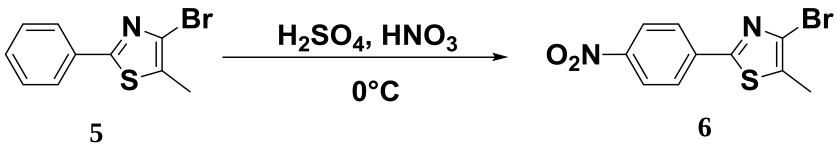
1.2. Synthesis



Scheme S1 Synthetic Scheme of Pyrene-**1o**

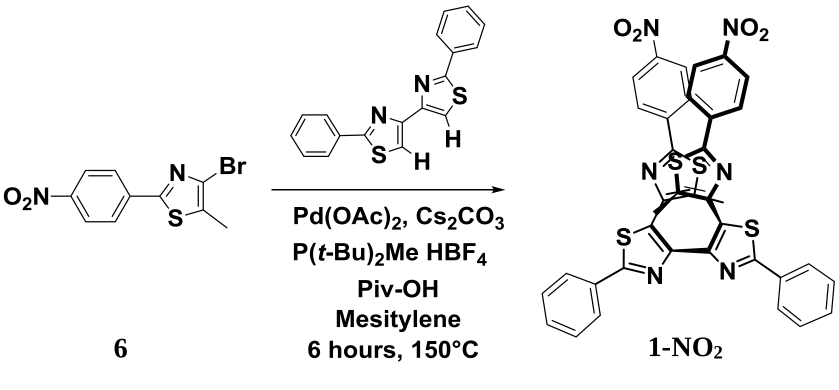
3, **4** and **5** were synthesized as described in the literature.[2]

Synthesis of 4-bromo-5-methyl-2-(4-nitrophenyl)thiazole(**6**)



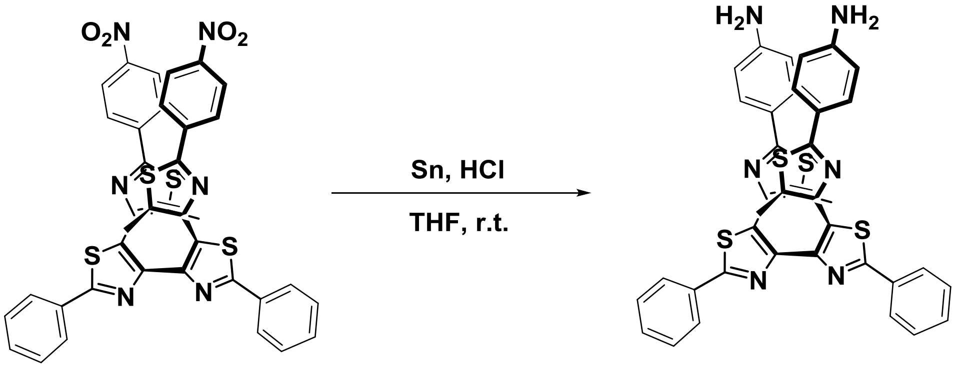
To a 200 ml flask, 4-bromo-5-methyl-2-phenyl thiazole; **5** (3.0 g, 12 mmol) and H_2SO_4 (3 ml) were added at 0°C and stirred for 15 min. Then, H_2SO_4 and HNO_3 solution (1:1, 6 ml) was added and stirred for 2 hours. After that, the reaction mixture was added and ice and water, and the participation was filtered and washed by water and 2 M NaOH aq. Next, the yellow solid was dissolve in chloroform and extracted with conc. $NaHCO_3$ aq and brine. Organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude product was purified with silica-gel column chromatography (ethyl acetate/ hexane 1:2) to yield product as an yellow solid (2.3 g, 64%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 8.30(2H, d, J = 9.0 Hz), 8.05 (2H, d, J = 9.0 Hz), 2.47 (3H, s)

Synthesis of 5,5'''-dimethyl-2,2'''-bis(4-nitrophenyl)-2',2''-diphenyl-4,5':4',4'':5'',4'''-quaterthiazole (**1-NO2**)



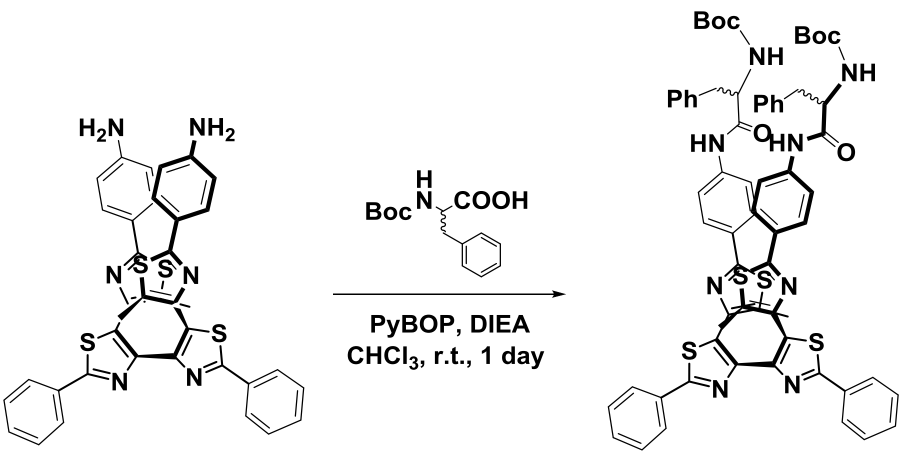
To a two-neck flask, 4-bromo-5-methyl-2-(4-nitrophenyl)thiazole ; **6** (892 mg, 3.0 mmol), 2,2'-diphenyl-4,4'-bithiazole (480 mg, 1.5 mmol), P(t-Bu)$_2$Me HBF_4 (74.4 mg, 0.3 mmol), $CsCO_3$ (1.9 g, 6.0 mmol), pivalic acid (46 mg, 0.4 mmol) and Pd(OAc)$_2$ (46 mg, 0.2 mmol) were added and degassed with N_2 . Then, Mesitylene (10 ml) was added to the reaction mixture and stirred for 6 hours at 150°C. After cooled to room temperature, the reaction mixture was extracted with chloroform, washed by conc. $NaHCO_3$ aq and brine. The combined organic layer was dried over Na_2SO_4, and filtered. After solvent was removed, crude product was purified with silica gel column chromatography using (Chloroform / Ethyl acetate, 4 : 1) as an eluent to yield product as a yellow solid(500 mg, 44 %). ^{1}H-NMR (400 MHz, CDCl3): δ (ppm) 8.08(4H, m), 8.01 (4H, d, J = 8.7 Hz), 7.63 (4H, d, J = 8.7 Hz), 7.49(6H, m), 2.08(6H, s).

Synthesis of 4,4'-(5,5'''-dimethyl-2',2''-diphenyl-[4,5':4',4'':5'',4'''-quaterthiazole]-2,2'''-diyl)dianiline (**1-NH₂**)



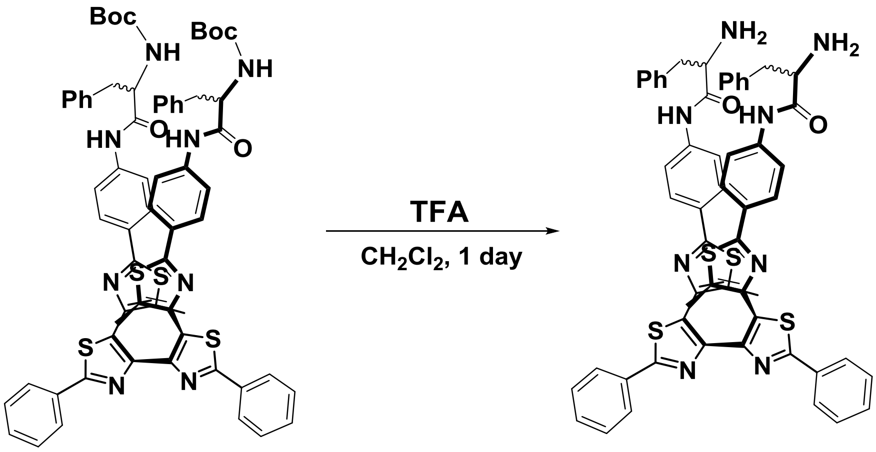
1-NO$_2$ (250 mg, 0.33 mmol) and powder Sn (500 mg, 4.2 mmol) in THF (5 mL) and conc. HCl (1 ml) were placed in a reaction vessel. The reaction mixture was stirred for 2 hours at room temperature. The excess of powder Sn was removed by celite. The reaction mixture was washed with 2M NaOH aq, brine, and dried over anhydrous Na_2SO_4. The volatiles had been removed in vacuo, the crude product was purified with silica-gel column chromatography(Ethyl acetate / MeOH=50:1) to yield product as a yellow solid(120 mg, 52%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ(ppm) 8.11-8.09(4H, m), 7.49-7.46(6H, m), 7.34-7.31(4H, d, J = 9.0 Hz), 7.6.54-6.51(4H, d, J = 9.0 Hz), 3.81(4H, s), 1.99 (6H, s)

Synthesis of di-tert-butyl ((((5,5'''-dimethyl-2',2''-diphenyl-[4,5':4',4'':5'',4'''-quaterthiazole]-2,2'''-diyl)bis(4,1-phenylene))bis(azanediyl))bis(1-oxo-3-phenylpropane-1,2-diyl))dicarbamate (**1-Phe-Boc**)



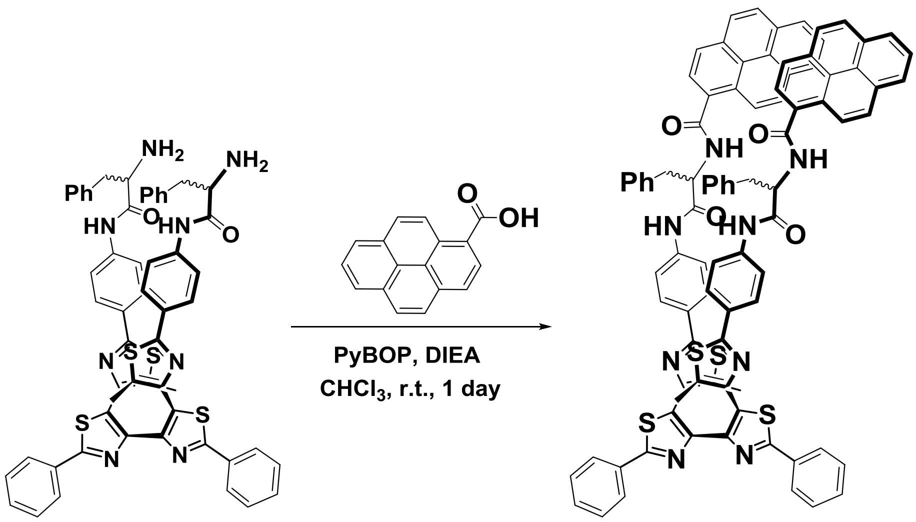
Boc-phenylalanine (190 mg, 0.72 mmol), PyBOP (374 mg, 0.72 mmol) and **1-NH$_2$** (170 mg, 0.24 mmol) in $CHCl_3$ (5 mL) were placed in a two-necked 20-mL roundbottomed flask with a septum under an atmosphere of argon. DIEA(125 μl, 0.72 mmol) was added and stirred for 1 day. The reaction mixture was extracted with ethyl acetate, washed with H_2O, conc. $NaHCO_3$ brine, and dried over anhydrous Na_2SO_4. After the volatiles had been removed in vacuo, the crude product was purified with silica gel column chromatography using ethylacetate /$CHCl_3$ (1 : 5) and GPC as an eluent to yield producr as a white solid (200 mg, 67%). ^{1}H-NMR (400MHz, $CDCl_3$): δ(ppm) 9.34(2H, s), 8.12(4H, m), 7.41(6H, m), 7.32-7.22 (14H, m), 5.22(2H, m), 4.81(2H, m), 3.23-3.20(2H, m), 2.96-2.95(2H, m), 1.95 (6H,s), 1.43(s, 18H), ^{13}C-NMR (150 MHz, $CDCl_3$): δ (ppm) 171.1, 168.6, 164.1, 156.9, 147.9, 142.0, 139.4, 136.29, 133.51, 132.06, 130.94, 130.35, 129.0, 128.9, 128.8, 128.5, 127.1, 126.9, 126.2, 119.1, 81.0, 56.5, 38.2, 28.52, 12.0. HRMS-MALDI-TOF(m/z): $[M+H]^+$ calc. for $C_{66}H_{63}N_8O_6S_4^+$,1191.3753; found 1191.3750

Synthesis of di-tert-butyl N,N'-((5,5'''-dimethyl-2',2''-diphenyl-[4,5':4',4'':5'',4'''-quaterthiazole]-2,2'''-diyl)bis(4,1-phenylene))bis(2-amino-3-phenylpropanamide) (**1-Phe-NH$_2$**)



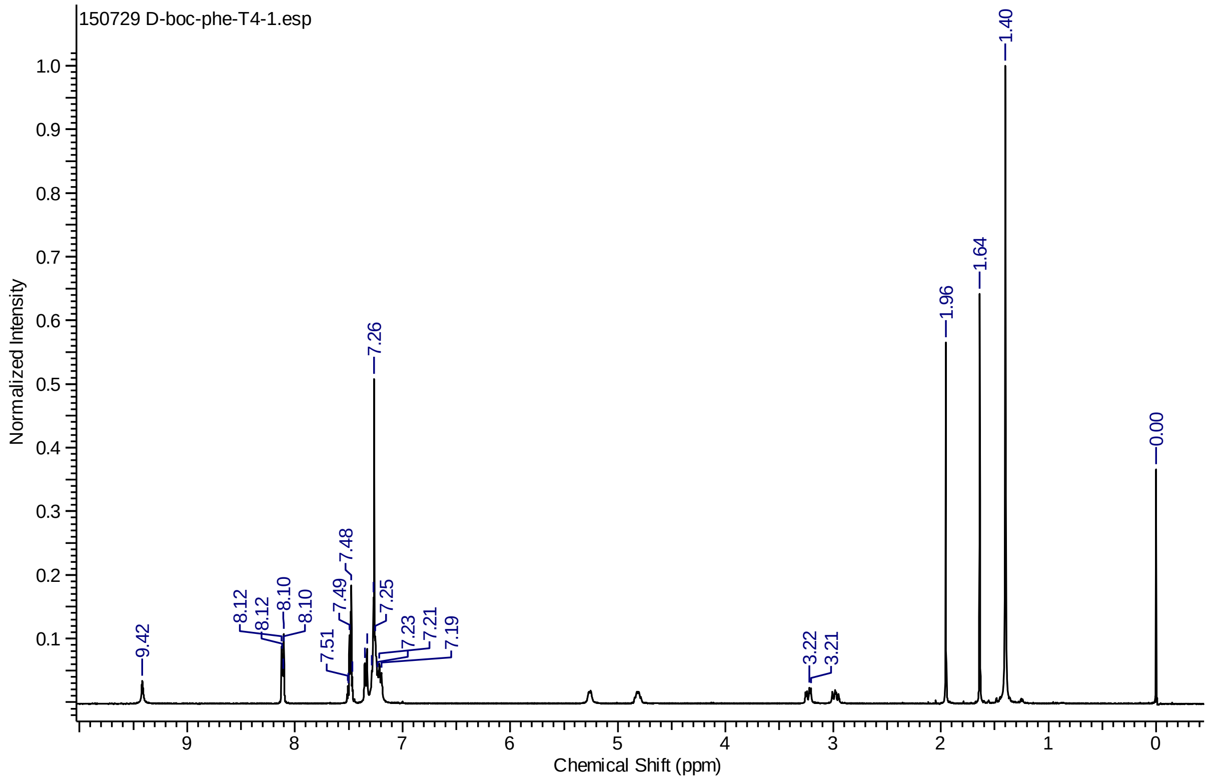
1-Phe-Boc (200 mg, 0.17 mmol) and TFA (2 ml) in dichloromethane (6 mL) were placed in a reaction vessel. The reaction mixture was stirred for 1 day at room temperature. The reaction mixture was extracted with ethyl acetate, washed with conc. $NaHCO_3$ aq, brine, and dried over anhydrous Na_2SO_4. The volatiles had been removed in vacuo. The yellow product were obtained. (143 mg, 85%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ(ppm) 9.58(2H, s), 8.10(4H, m), 7.47(6H, m), 7.32-7.22 (14H, m), 3.42(2H, m), 2.98(2H, m), 2.35 (2H, m), 1.95 (6H,s)

Synthesis of N,N'-((((5,5'''-dimethyl-2',2''-diphenyl-[4,5':4',4'':5'',4'''-quaterthiazole]-2,2'''-diyl)bis(4,1-phenylene))bis(azanediyl))bis(1-oxo-3-phenylpropane-1,2-diyl))bis(pyrene-1-carboxamide) **(1o)**



Pyrenecarboxylic acid (68 mg, 0.28 mmol), PyBOP (374 mg, 0.28mmol) and **1-Ph-NH$_2$** (70 mg, 0.07 mmol) in $CHCl_3$ (5 mL) were placed in a two-necked 20-mL roundbottomed flask with septum under an atmosphere of argon. DIEA(60 μl, 0.28 mmol) was added and stirred for 1 day. The reaction mixture was extracted with ethyl acetate, washed with H_2O, conc. $NaHCO_3$ brine, and dried over anhydrous Na_2SO_4. After the volatiles had been removed in vacuo, the crude product was purified with silica gel column chromatography using ethylacetate /CH_2Cl_2 (1 : 5) and GPC as an eluent to yield producr as a white solid (20 mg, 20%). ^{1}H-NMR (400 MHz, Tetrachloroethane-d$_2$ at 100°C): d (ppm) 9.40(s, 2H), 8.13(d, 2H, J = 9.2 Hz), 8.15-8.08(m, 8H), 8.00-7.96 (m, 4H), 7.86(d, 2H, J = 9.2Hz), 7.81(m, 6H), 7.53-7.51(m, 6H), 7.48-7.46(d, 4H, J = 8.0 Hz), 7.42-7.37(m, 8H), 7.32-7.30(m, 6H), 7.25(s, 2H), 5.60(m, 2H), 3.54-3.50(m, 2H), 3.55-3.30(m, 2H), 2.05(s, 6H) ^{13}C-NMR (150 MHz, $CDCl_3$ at 100°C): d (ppm) 170.9, 170.3, 167.8, 163.5, 148.1, 142.5, 139.1, 136.9, 134.0, 132.9, 132.2, 131.3, 131.2, 130.6, 130.3, 129.6, 129.4, 129.1, 129.0, 128.8, 128.7, 128.6, 127.3, 127.0, 126.6, 126.4, 126.0, 125.9, 124.8, 124.6, 124,3, 124.2, 124.0, 120.2, 56.6, 38.3, 12.0, HRMS-MALDI-TOF(m/z): [M+H]$^+$ calc. for $C_{90}H_{63}N_8O_6S_4^+$,1447.3855; found 1447.3849

[1]H-NMR of 1-D-Phe-Boc



[13]C-NMR of 1-D-Phe-Boc

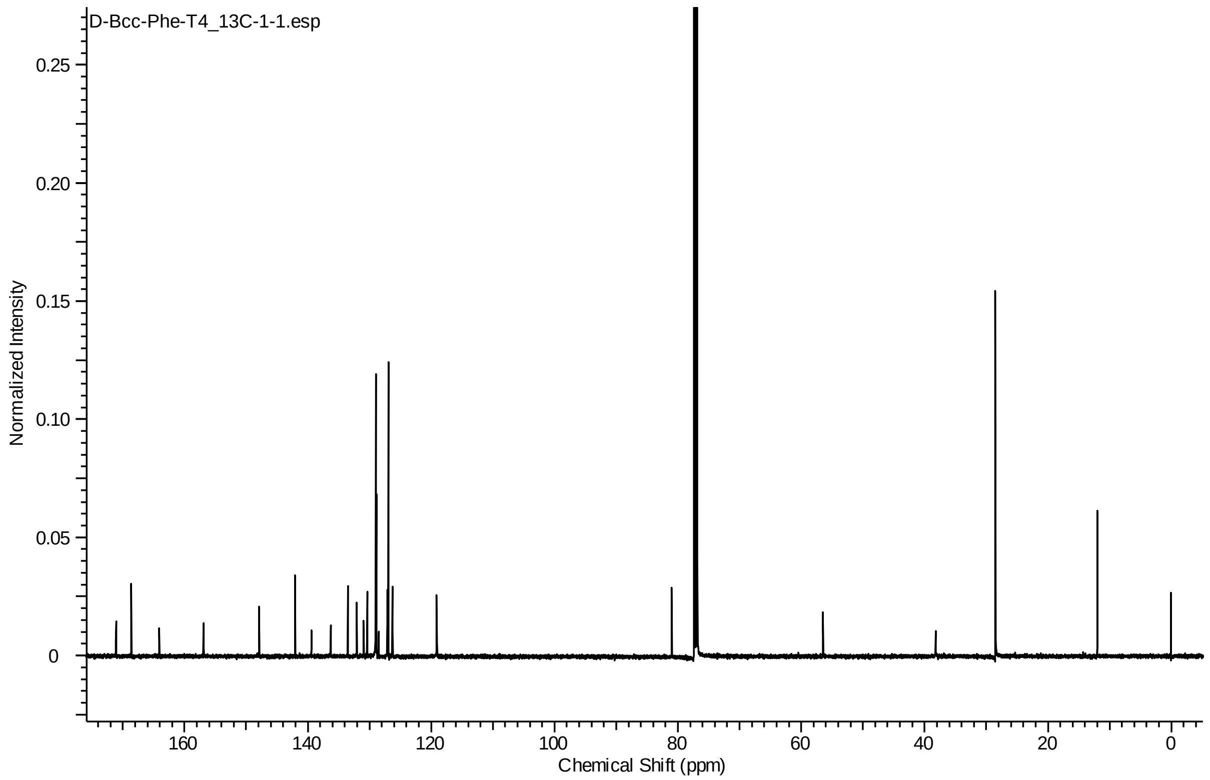
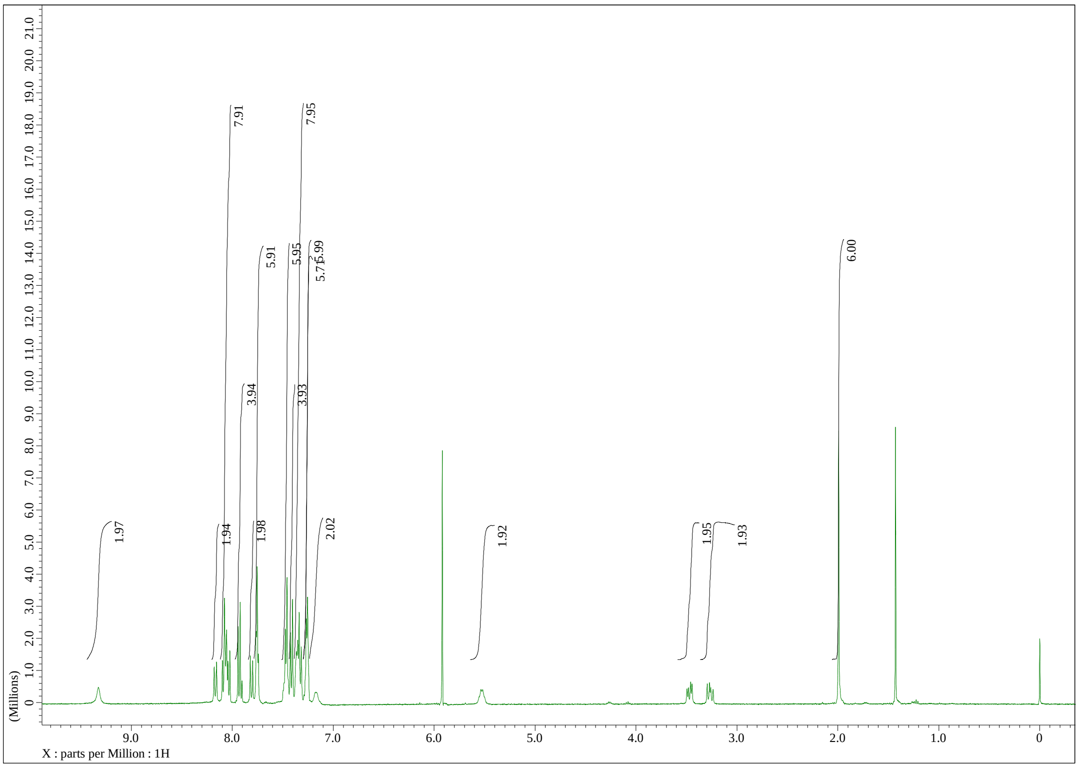


Fig. S1 ^{1}H- and ^{13}C-NMR of 1-D-Phe-Boc.

[1]H-NMR spectra of 1o at 373 K



[13]C-NMR spectra of 1o at 373 k

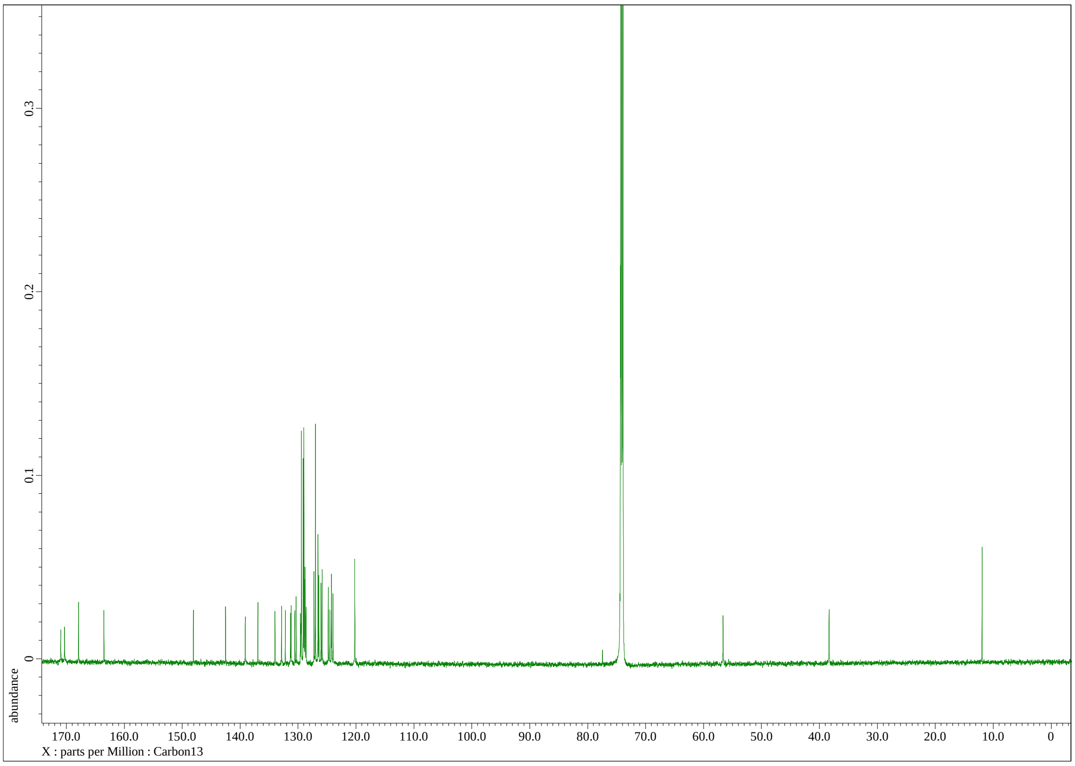


Fig. S2 ^{1}H- and ^{13}C-NMR of **1o** (D-delivative).

2. Supplemental study on the conformational behavior of 1o

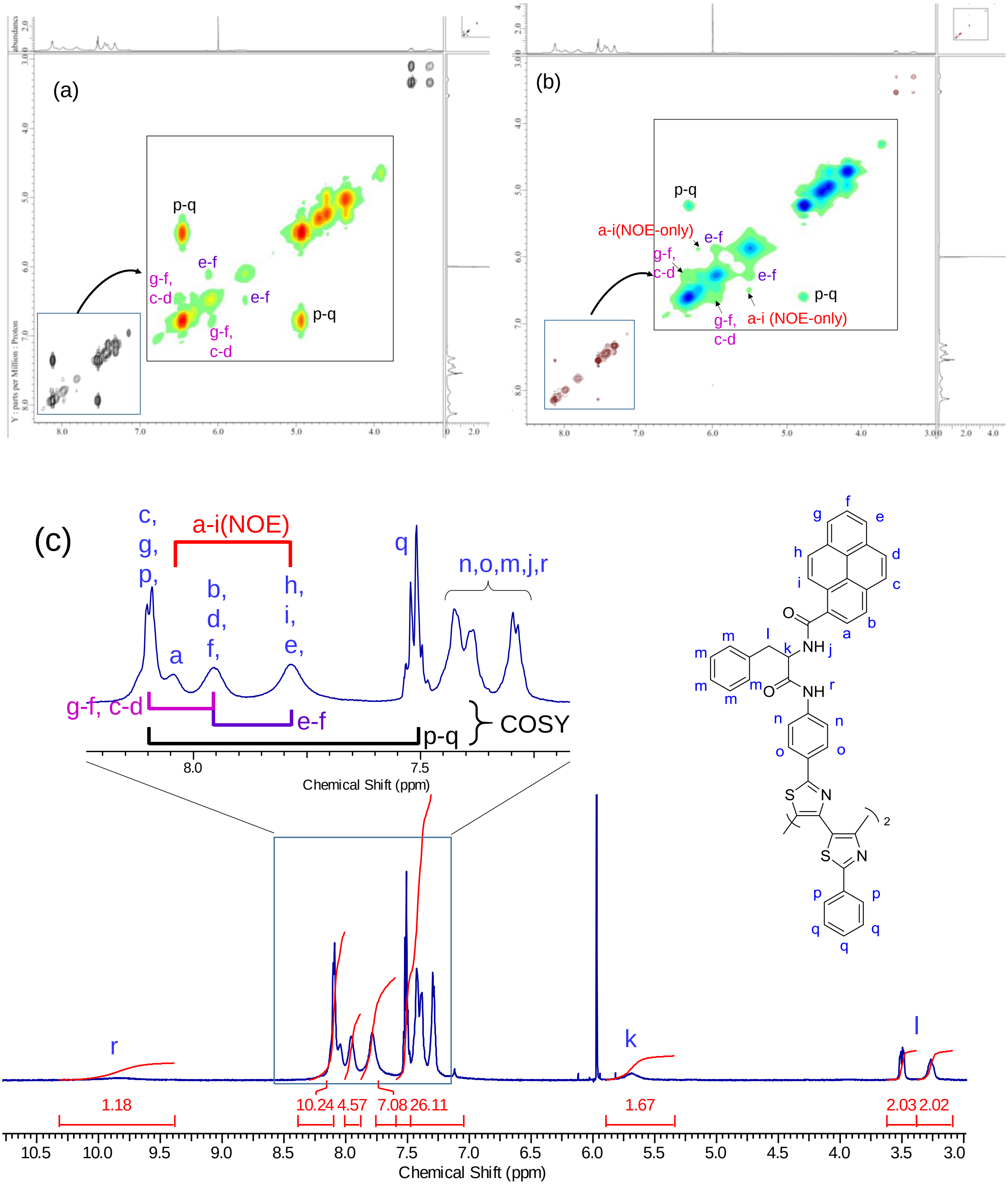
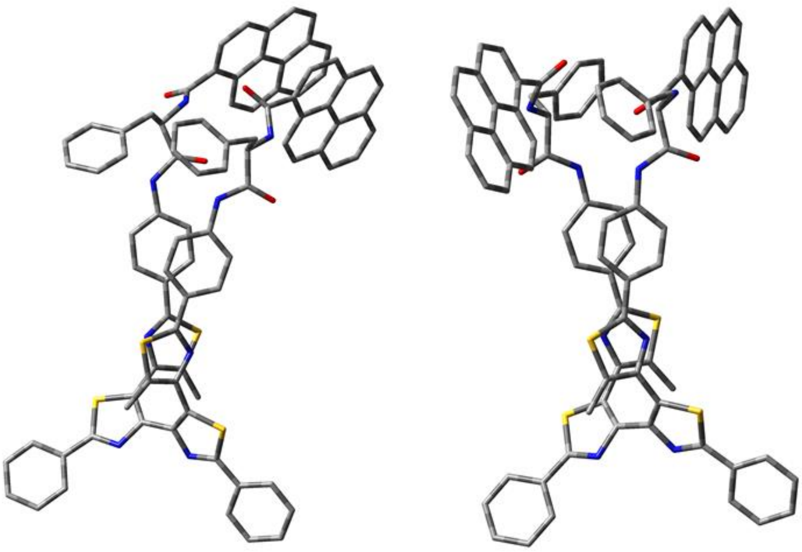


Fig. S3 (a) ^{1}H-^{1}H COSY, (b) NOESY and (c) ^{1}H NMR spectra above 3.0 ppm in 1,1,2,2-tetrachloroethane-d_2 with peak assignment of D-**1o** (measured at 50 °C). Below 3.0 ppm, only the singlet methyl peak at 2 pm was observed (Fig. S2).



Most stable
(D-1o)

Non-stacked
ΔE = +5.96 kcal/mol

Fig. S4 The most stable geometry and a non-stacked conformation of D-**1o** calculated on the CONFLEX program.

3. Characterization of photoproducts

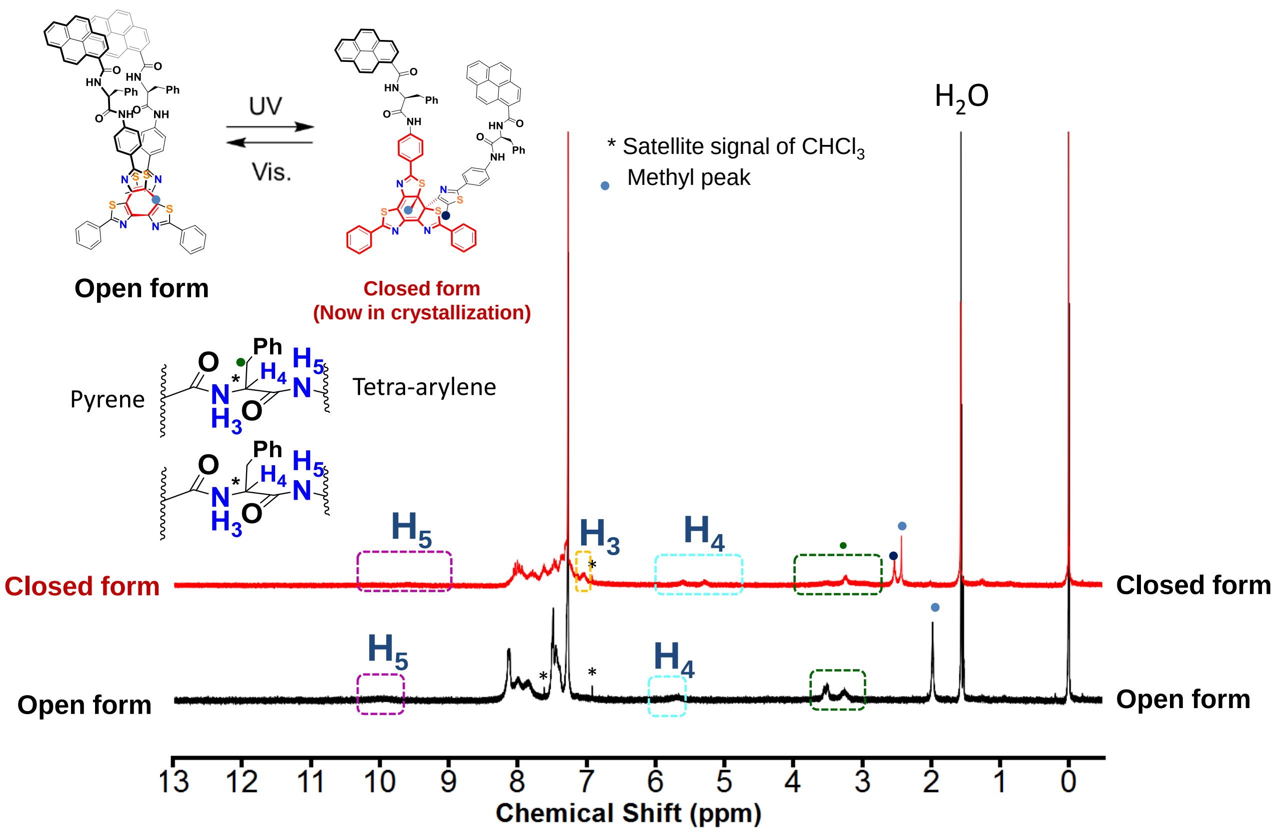


Fig. S5 [1]H NMR spectral change of L-**1** after the photoreaction measured in $CDCl_3$. The closed form was isolated from the solution at PSS by a reversed phase HPLC.

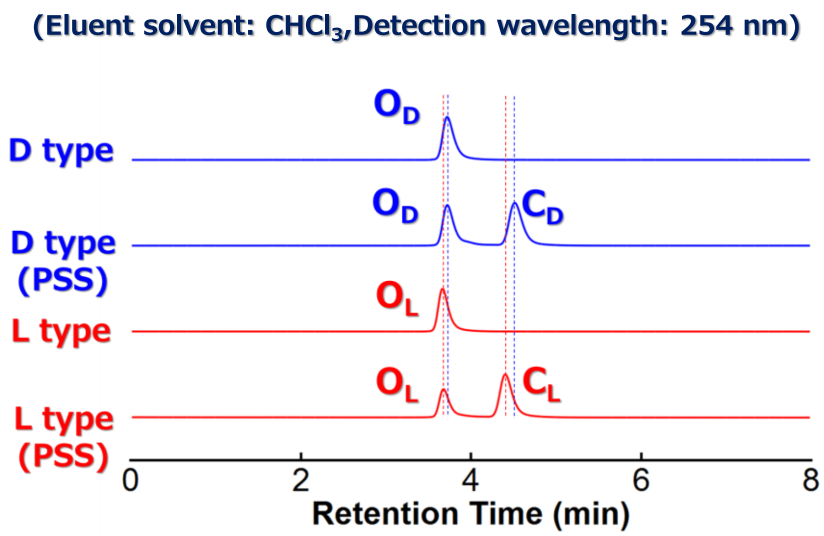


Fig. S6 Chiral HPLC charts of **1o** and photoproducts.

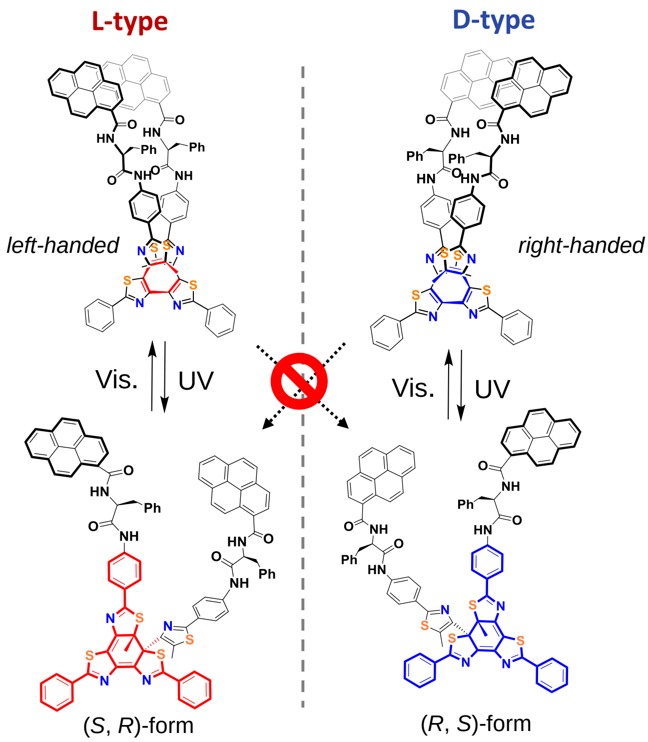


Fig. S7 Diastereoselective photoreaction of **1o**.

4. Emission lifetime

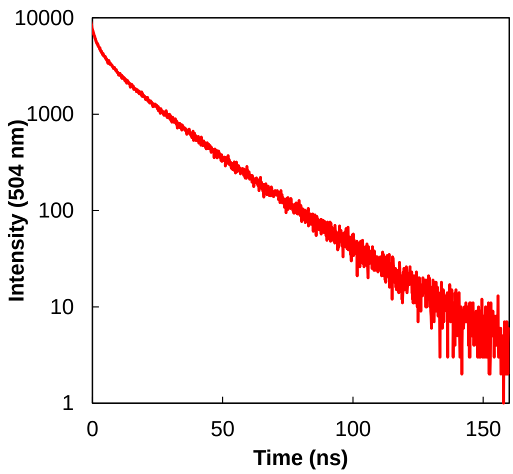


Fig. S8 Biexponential decay of emission in **1o** with lifetime of 21 ns (88%), 3.6 ns (12%).

5. Emission quenching of pyrene-1-carboxylic acid with the photoisomerization of 1-D-Phe-Boc

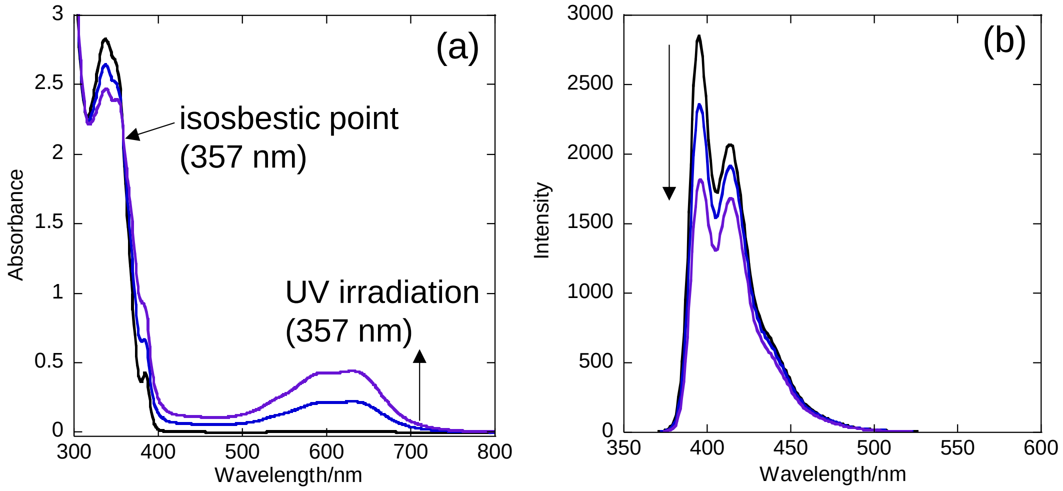


Fig. S9 (a) Absorption and (b) emission spectral change of the mixture of **1-D-Phe-Boc** and pyrene-1-carboxylic acid in chloroform (5×10^{-5} M).

Emission of pyrene-1-carboxylic acid was quenched by UV irradiation in the presence of **1-D-Phe-Boc**. Irradiation for the emission spectra was conducted at the isosbestic point (357 nm) so that the absorbance at the excitation wavelength should be constant during the experiment. The degree of quenching was dependent on the conversion of ring-closed isomer. The emission quenching of pyrene-1-carboxylic acid thus could be attributed to the energy transfer to the ring-closed colored isomer of **1-D-Phe-Boc**. Since the energy transfer was diffusion-controlled, the quenching efficiency was not as high as the emission quenching in **1c** (Fig. 4a in the main text).

References

1. T. Sumi, Y. Takagi, A. Yagi, M. Morimoto and M. Irie, *Chem. Commun.*, 2014, **50**, 3928.
2. R. Li, T. Nakashima, O. Galangau, S. Iijima, R. Kanazawa and T. Kawai, *Chem. Asian J.*, 2015, **10**, 1725.