Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information for

Reversible Fluorescence Modulation through Photo-Isomerization of an Azobenzene-Bridged Perylene Bisimide Cyclophane

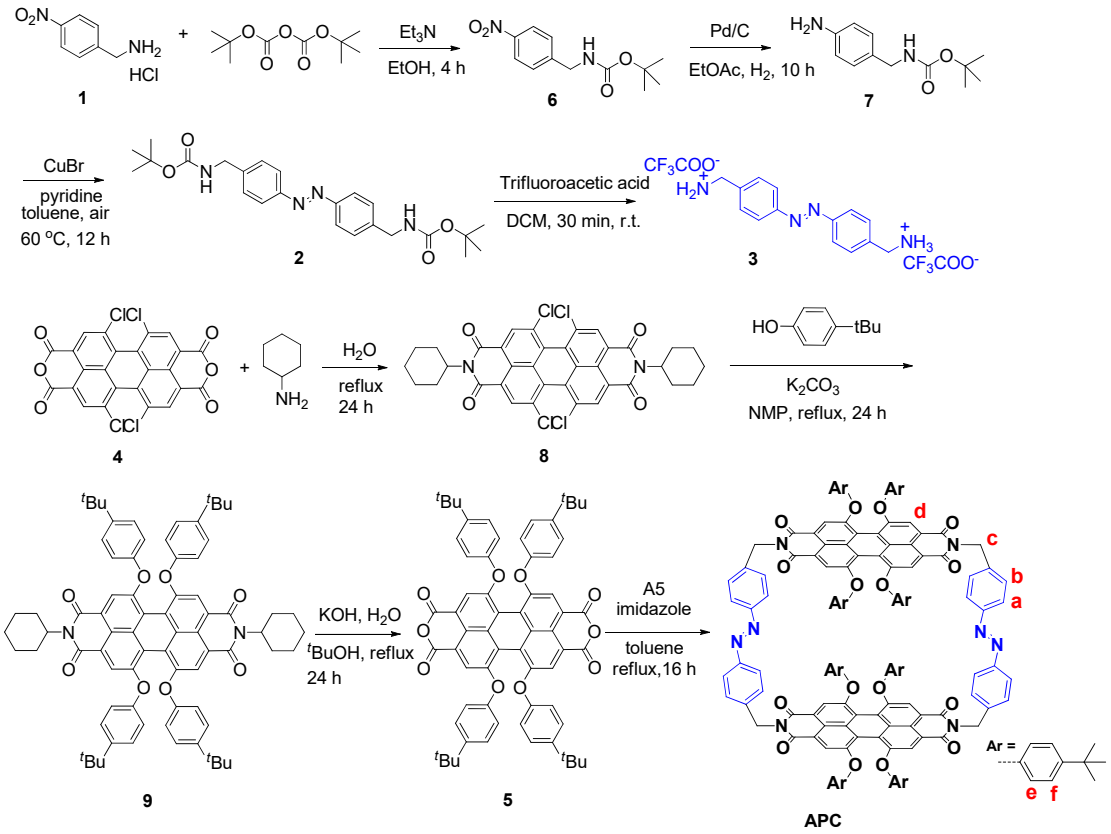
Guanghui Ouyang, David Bialas, and Frank Würthner

Table of contents

S1. General information

Unless otherwise noted, chemical compounds were purchased from Aldrich, TCI and other 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 spectrometers. NMR data analysis are presented as following, s : singlet, d : doublet, t : triplet, m : multiplet, br : broad. Recycling gel permeation chromatography (GPC) was carried out on a Shimadzu semi-preparative recycling setup (eluent: $CHCl_3$). Mass spectra were measured on a microTOF focus instrument for high-resolution ESI (Bruker Daltronik GmbH). 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) as a light source. Fluorescence quantum yields were obtained by using an integrating sphere. Theoretical calculations were performed by Gaussian 16 program[1] at B3LYP/6-31G(d,p) level. UV irradiation experiments were carried out in a Rayonet photochemical reactor with an RPR-3500A lamp (350 nm wavelength) and the samples were placed in cuvettes (light patch: 10 mm). Visible light experiments were performed with a white light lamp from NARVA type LT 80WT5/840 HQ.

S2. Synthesis and characterization



Scheme S1. Synthetic route of **APC**.

Synthesis of compound **6**[2]

Commercially available compound **1**, 4-nitrobenylamine hydrochloride (2.00 g, 10.60 mmol) and triethylamine (4.42 mL, 31.80 mmol) were added into ethanol (50 mL) and stirred for 10 min at room temperature. Di-*tert*-butyl dicarbonate (2.44 mL, 10.60 mmol) was then added and vigorously stirred at room temperature for 4 h. After the reaction was completed as monitored by TLC, the solvent was removed by rotary evaporation. The residue was dissolved in ethyl acetate and washed with distilled water for three times (3 x 100 mL). The organic phase was collected and dried with anhydrous Na_2SO_4. After filtration, the solution was removed under reduced pressure and the crude product was purified by flash column chromatography (silica gel, EtOAc/hexane = 1:2, v/v) to give the final product as a yellow solid. 2.49 g (9.86 mmol), yield 93 %. ^{1}H-NMR (400 MHz, 298 K, $CDCl_3$, ppm): δ = 8.20 (d, J = 8.8 Hz, 2 H), 7.45 (d, J = 8.8 Hz, 2 H), 5.02 (b, 1 H), 4.42 (d, J = 6.0 Hz, 2 H), 1.46 (s, 9 H).

Synthesis of compound **7**[2]

Compound **6** (6.05 g, 24.00 mmol) and 10 % Pd/C (0.13 g, 1.20 mmol) were dispersed in EtOAc (50 mL). The mixture was stirred under hydrogen gas (1 atm) for 10 h at room temperature. The reaction process was monitored by TLC until complete conversion. Pd/C was filtered through Celite and the solvent was evaporated under

vacuum. The crude mixture was purified by flash column chromatography (silica gel, EtOAc/hexane = 1:2, v/v) and recrystallization (DCM) to give a white solid, 5.23 g (23.5 mmol), yield 98 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 7.07 (d, J = 8.1 Hz, 2H), 6.64 (d, J = 8.3 Hz, 2H), 4.78 (br, 1H, NH), 4.18 (d, J = 5.1 Hz, 2H), 3.66 (s, 2H, NH), 1.45 (s, 9H).

Synthesis of compound **2**[2]

Compound **7** (444.5 mg, 2.00 mmol), CuBr (84.0 mg, 0.06 mmol) and pyridine (17.4 mg, 0.18 mmol) were dissolved in toluene (10 mL) and the mixture was stirred at 65 ^{o}C overnight by using ambient oxygen as oxidant. After the reaction finished, toluene was removed under vacuum and the crude product was purified by column chromatography (silica gel, DCM/MeOH = 50:1, v/v, R_f = 0.5 for *trans*-Azo, 0.3 for *cis*-Azo). Yellow solid, 793.0 mg (1.80 mmol), yield 90 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 7.89 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 4.92 (br, 1H), 4.41 (d, J = 5.8 Hz, 2H), 1.48 (s, 9H).

Synthesis of compound **3**[2]

Compound **2** (140.0 mg, 0.32 mmol) was dissolved in DCM (20 mL), then an excess amount of trifluoracetic acid (2 mL) was added and the mixture was stirred at room temperature for 30 min. The solvents were removed under vacuum to give the product as an orange solid, 144.2 mg (0.31 mmol), yield 97 %. ^{1}H NMR (400 MHz, DMSO, 298 K, ppm): δ = 8.44 (br, 6H), 7.89 (d, J = 8.4 Hz, 4H), 7.60 (d, J = 8.4 Hz, 4H), 4.07 (br, 4H).

Synthesis of compound **8**[3]

1,6,7,12-tetrachloro perylene-3,4:9,10-tetracarboxylic acid bisanhydride **4** (4.00 g, 8.00 mmol) was dispersed in water (150 mL), then adding cyclohexylamine (10 mL) and the mixture was refluxed overnight. After cooling to room temperature, 200 mL water was added and the mixture was filtered. The precipitate was washed with water and dried in vacuum to give a dark red solid, 4.99 g (7.20 mmol), yield 90 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 8.64 (s, 4H), 5.06 (m, 2H), 2.58 (m, 8H), 1.94-1.31 (m, 12H).

Synthesis of compound **9**[3]

Compound **8** (1.38 g, 2.00 mmol), 4-*tert*-butylphenol (3.00 g, 20.00 mmol) and K_2CO_3 (3.00 g, 22.00 mmol) were refluxed in 100 mL NMP under argon atmosphere for 24 h. After cooling to room temperature, 100 mL water was added and the mixture was filtrated to give a cyan red solid, 1.72 g (1.50 mmol), yield 75 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 8.19(s, 4H), 7.23 (d, J = 8.8 Hz, 8H), 6.83 (d, J = 8.8, 8H), 4.97 (m, 2H), 2.47 (m, 4H), 1.85 (m, 4H), 1.69 (m, 6H), 1.39 (m, 6H), 1.28 (s, 36H).

Synthesis of compound **5**[3]

Compound **9** (849.0 mg, 0.74 mmol) was added to alcoholic KOH (6.0 g KOH, 3 mL H_2O, 60 mL *tert*-butyl alcohol) and stirred under reflux overnight. After cooling down to room temperature, the organic layer was collected and maintained in 2 M HCl for 8 h. The red-brown precipitate was filtered, washed with water and dried in vacuum. The crude product was purified by column chromatography (silica gel, DCM to DCM/MeOH v/v 50:1) to give a red-brown solid, 496.0 mg (0.50 mmol), yield 68 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 8.21 (s, 4H), 7.27 (d, J = 8.8 Hz, 8H), 6.84 (d, J = 8.8, 8H), 1.30 (s, 36H).

Synthesis of **APC**

Equal equivalents of **3** (105.4 mg, 50.8 μmol) and **5** (50.0 mg, 50.8 μmol) were refluxed in anhydrous toluene (300 mL) under nitrogen atmosphere for 16 h in the presence of excess imidazole (1.35 g, 19.8 mmol). After purification by flash column chromatography and recycling gel permeation chromatography (GPC), 30.1 mg **APC** was obtained as a reddish brown solid: 15.1 mg (6.35 μmol; 24.9 % yield). Melting point > 300 °C. ^{1}H-NMR (400 MHz, 360 K, $C_2D_2Cl_4$): δ = 8.22 (s, 8 H), 7.72 (d, J = 8.4 Hz, 8 H), 7.59 (d, J = 8.4 Hz, 8 H), 7.28 (dd, J = 8.8 Hz, 2.0 Hz, 16 H), 6.86 (d, J = 8.8 Hz, 16 H), 5.41 (s, 8 H), 1.36 (s, 72 H) ppm; ^{13}C-NMR (100 MHz, 360 K, $C_2D_2Cl_4$): δ = 163.3, 156.2, 153.1, 152.5, 147.8, 140.6, 133.0, 130.4, 126.8, 123.1, 122.7, 121.0, 120.4, 119.8, 119.5, 77.5, 43.2, 34.5, 31.7 ppm; HR-MS (ESI, pos. mode, acetonitrile/chloroform 1:1) : m/z calculated for $C_{156}H_{137}N_8O_{16}$: 2378.01471 $[M+H]^+$, found: 2378.01840; UV-vis ($CHCl_3$, $c_0 = 5 * 10^{-6}$ M): λ_{max} (ε_{max}) = 587 nm (74400 M^{-1} cm^{-1}), 559 nm (49740 M^{-1} cm^{-1}); Fluorescence ($CHCl_3$, $c_0 = 6.3 * 10^{-7}$ M): λ_{max} = 626 nm (λ_{ex} = 545 nm), FLQY (0.16 in DCM).

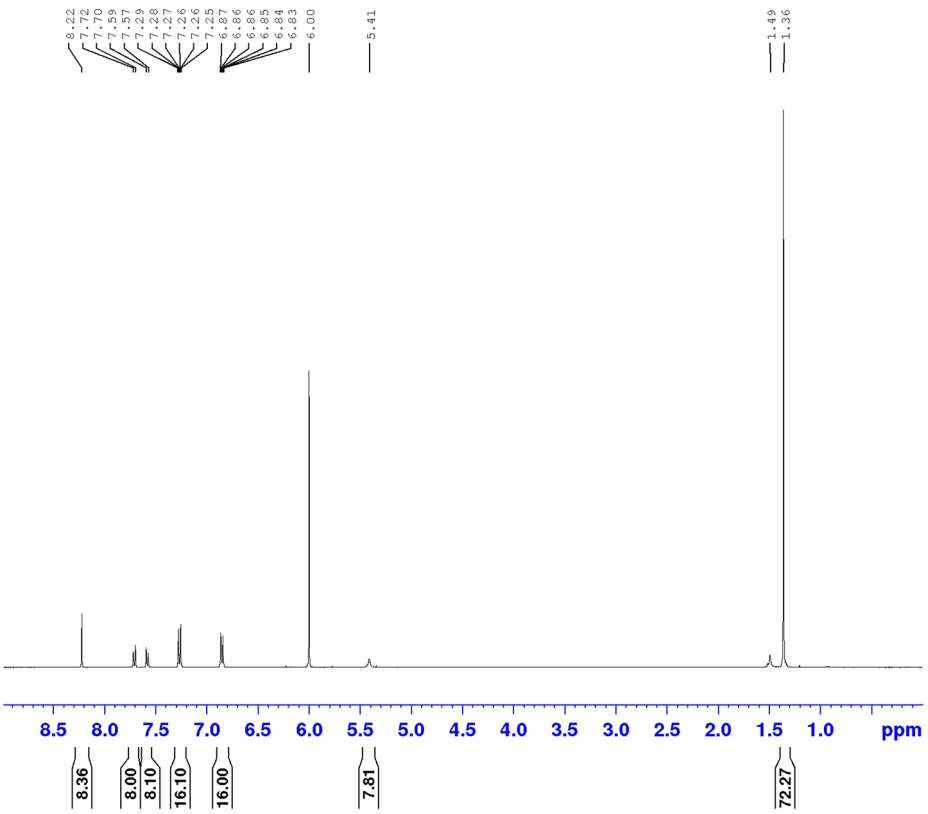


Fig. S1. ^{1}H-NMR spectrum of **APC** (400 MHz, $C_2D_2Cl_4$, 360K).

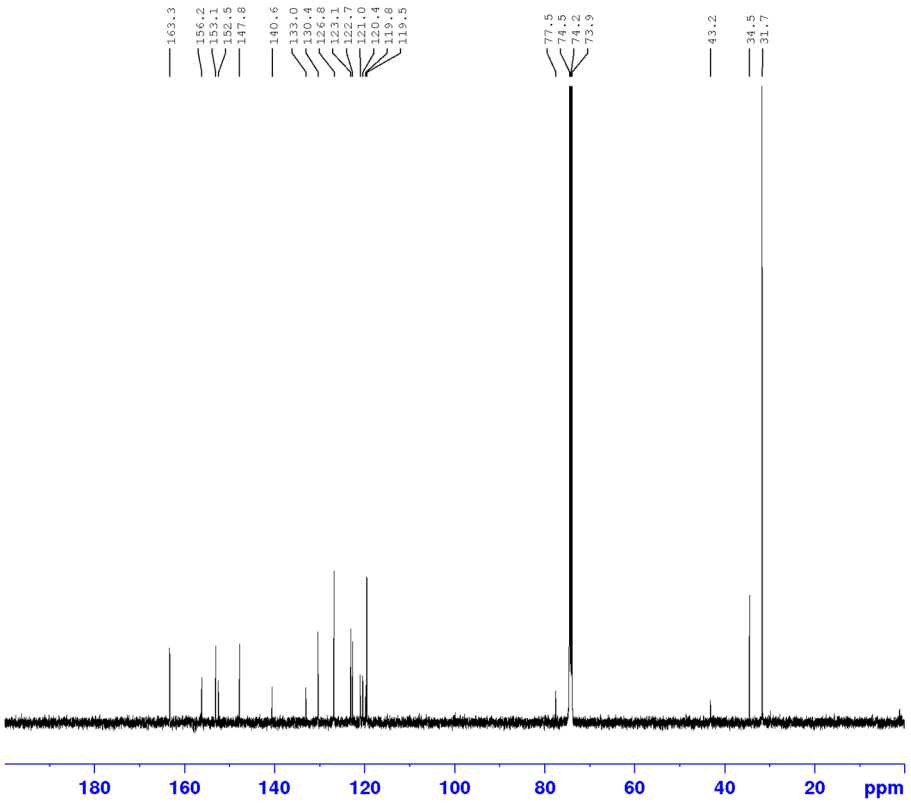


Fig. S2. ^{13}C-NMR spectrum of **APC** (101 MHz, $C_2D_2Cl_4$, 360K).

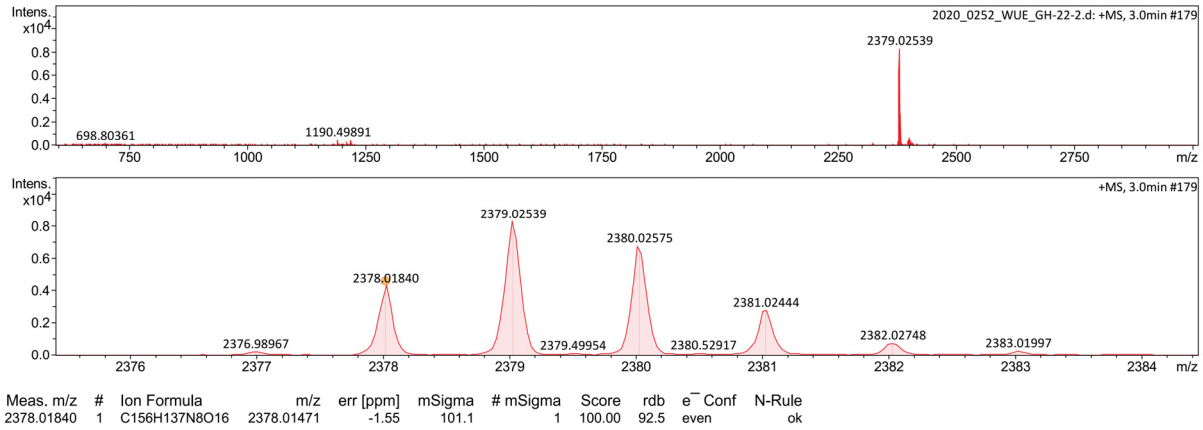


Fig. S3. HR-ESI mass spectrum of **APC**, $CHCl_3$/MeCN = 1:1.

S3. Supporting spectroscopic data

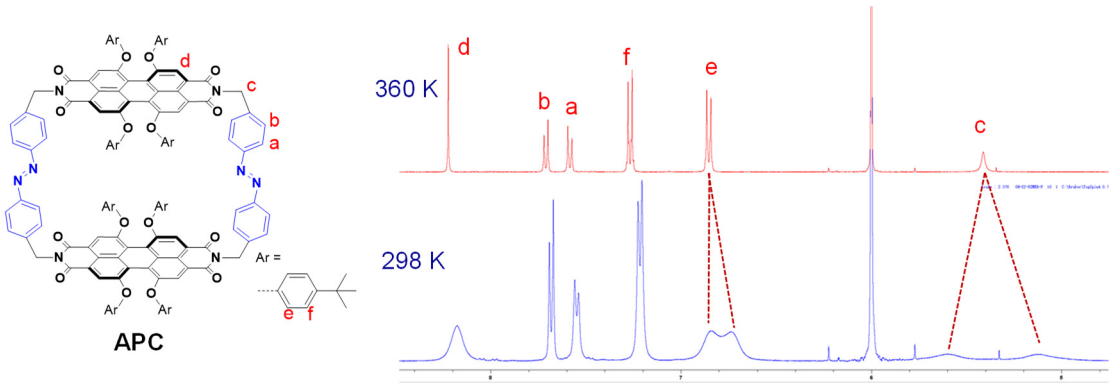


Fig. S4. ^{1}H-NMR spectra of **APC** at different temperatures, 400 MHz, $C_2D_2Cl_4$. The broadening of some protons at 298 K in attributed to the barrier for the interconversion of *P*/*M*-atropoisomers of tetraphenoxy-PBIs.[4]

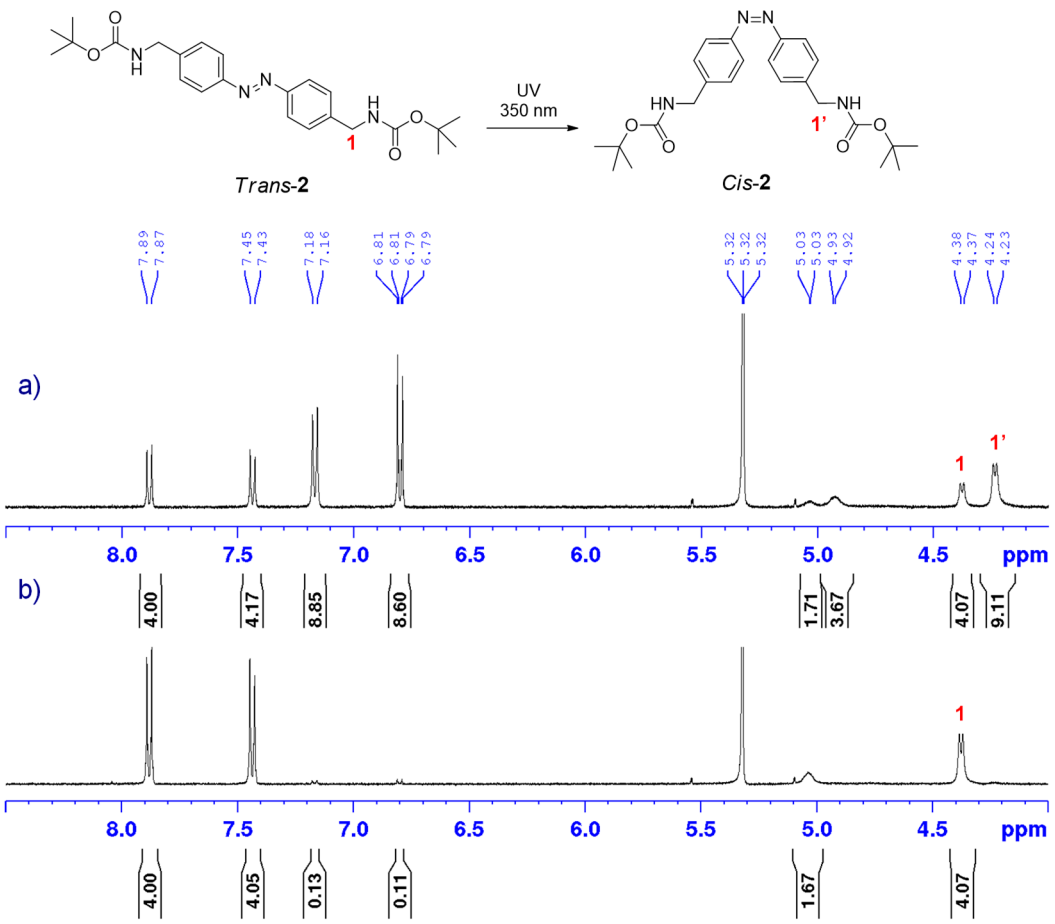
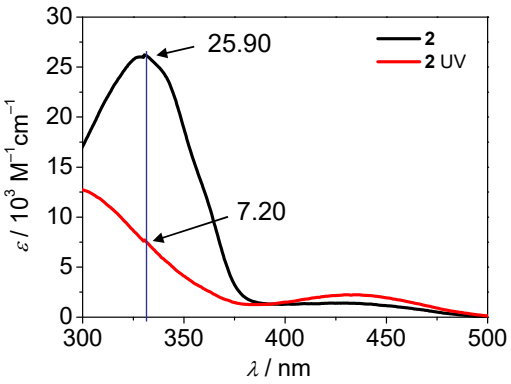


Fig. S5. ^{1}H-NMR spectra of reference azobenzene **2**, a) after and b) before UV irradiation. 298 K, CD_2Cl_2, 400 MHz. [**2**] = 1x 10^{-3} M.

According to the NMR signal change of protons 1, the *trans* → *cis* transformation ratio of reference compound **2** is about Integral(1') / (Integral (1) + Integral (1')) = 9.11 / (9.11 + 4.07) = 69.1 %.

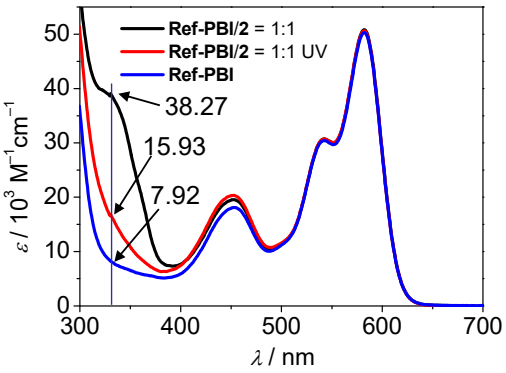


Absorption at 333 nm
Trans-**2** : 25.90
PSS-**2** : 7.20

Conversion:
(25.90-7.20)/25.9 = 72.2 %

Fig. S6. UV-vis absorption spectra of compound **2** before (black line) and after (red line) UV irradiation. DCM, 298 K, 5.0 x 10^{-6} M.

According to the absorption change of *trans*-azobenzene at 330 nm, the *trans* → *cis* transformation ratio is calculated to be (25.90-7.20) / 25.9 = 72.2 %, which is consistent with the ratio derived from NMR spectra.



Absorption at 333 nm
Trans-**2** : 38.27
PSS-**2** : 15.93
Ref-PBI: 7.92

Conversion:
(38.27-15.93)/(38.27-7.92) = 73.6%

Fig. S7. UV-vis spectra of mixture of **Ref-PBI** and azobenzene **2**, [**Ref-PBI**] = [**2**] = 2.5 x 10^{-6} M in DCM, 298 K. Black line: absorption spectrum of **Ref-PBI/2** mixture, Red line: absorption spectrum of **Ref-PBI/2** mixture after UV irradiation for 1 min. Blue line: absorption spectrum of **Ref-PBI**.

We further measured the UV-vis absorption spectra of a 1:1 mixture of **Ref-PBI** and azobenzene **2**. According to the absorption change of compound **2**, the *trans* → *cis* transformation ratio is determined as (38.27-15.93) / (38.27-7.92) = 73.6%, which is consistent with the result obtained for individual azobenzene **2**.

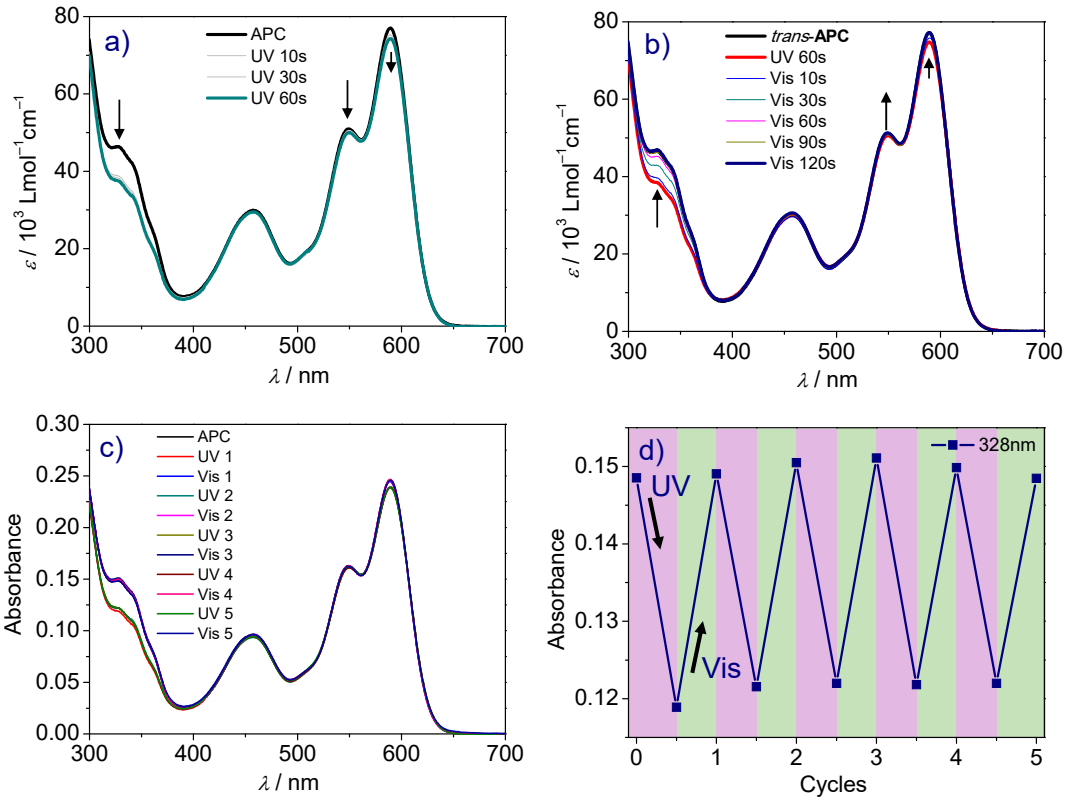


Fig. S8. UV-vis absorption spectra of cyclophane **APC** in $CHCl_3$ a) after different UV light irradiation times, b) after different visible light irradiation times following UV irradiation for 60 seconds, c) upon alternating UV (1 min) and visible light (3 min) irradiation. d) Change of absorption intensity of **APC** at 328 nm upon alternating UV (1 min) and visible light irradiation (3 min). [**APC**] = 3.7 x10^{-5} M in $CHCl_3$, 298 K. UV light source: RPR-3500A lamp (350 nm wavelength); visible light source: white light lamp NARVA (type LT 80WT5/840 HQ).

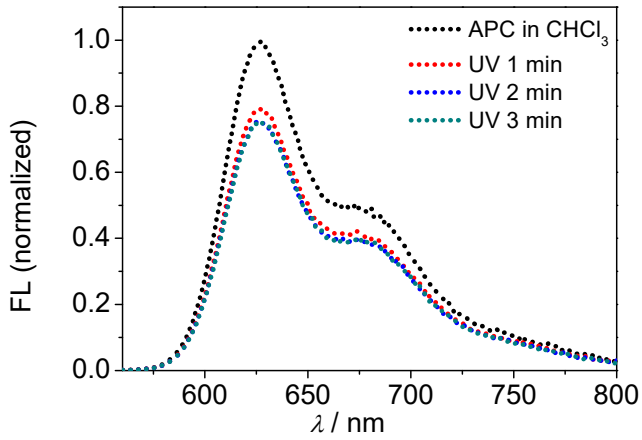
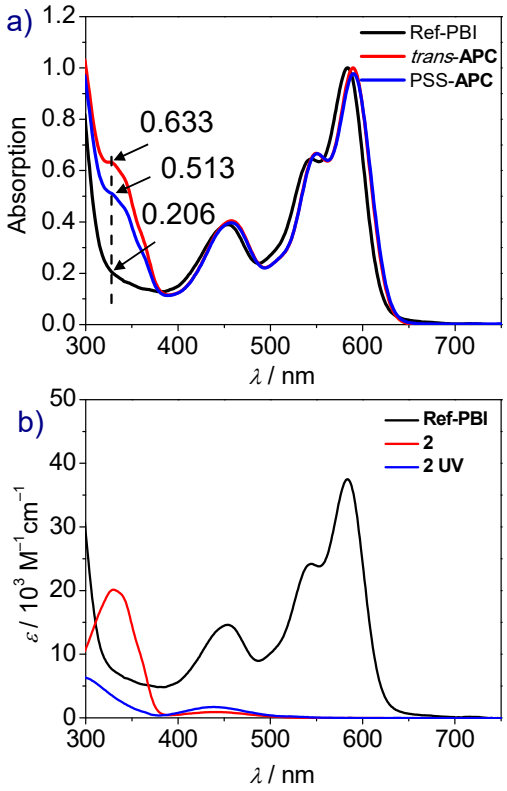


Fig. S9. Time-dependent fluorescence spectra of cyclophane **APC** after different UV irradiation times in chloroform at 298 K; conc. 1 x 10^{-6} M.



Absorption at 328 nm
APC : 0.633
PSS-**APC** : 0.513
PBI moieties ~ 0.206

Conversion:
(0.633-0.513)/(0.633-0.206) ~ 28 %

Fig. S10. a) UV/Vis absorption spectra used for determination of *trans* → *cis* isomerization ratio at photo-stationary state under UV irradiation of cyclophane **APC** in chloroform at 298 K; [**APC**] = 3.7 x 10^{-5} M. Red line: absorption of *trans*-**APC**, blue line: absorption of PSS-**APC**, black line: normalized absorption of **ref-PBI**, [**ref-PBI**] = 5 x 10^{-6} M in chloroform at 298 K. The absorption spectrum of **ref-PBI** was normalized according to the absorption maximum of **APC** at 589 nm. b) UV-vis absorption spectra of **ref-PBI** and azobenzene **2**, [**ref-PBI**] = [**2**] = 5 x 10^{-6} M in chloroform at 298 K.

Due to the interchromophoric interactions and probably some residual of solvent molecules in the cyclophane, the molar extinction coefficient of **APC** at 328 nm (46.40 x 10^3 M^{-1} cm^{-1}, Fig. S8a) is obviously smaller than that of the sum of two equivalents of individual azobenzene **2** and **ref-PBI** at 328 nm (2*21.1 + 2*7.3) *10^3 $M^{-1}cm^{-1}$ = 56.8*10^3 $M^{-1}cm^{-1}$ (Fig. S10 b). To obtain the absorption contribution of azobenzene in **APC** at 328 nm, we need to subtract the absorption contribution of PBI moieties at 328 nm. Considering the azobenzene chromophores do not show absorption in the range of the absorption maximum of **APC** (λ_{max} = 589 nm), we can roughly get the absorption contribution of PBI moieties in **APC** at 328 nm from the normalized absorption spectrum of **ref-PBI** (Fig. S10a, black line). Accordingly, the absorption of the PBI moieties is 0.206 and the absorption contribution of *trans*-azobenzene moieties is 0.633 – 0.206 = 0.427. After UV irradiation, the change of *trans*-azobenzene absorption is 0.633 – 0.513 = 0.12. Hence, the *trans* → *cis* isomerization ratio can be estimated as 0.12/0.427 = 28 %, which is in good consistent with the value calculated from the NMR data (Fig. S11).

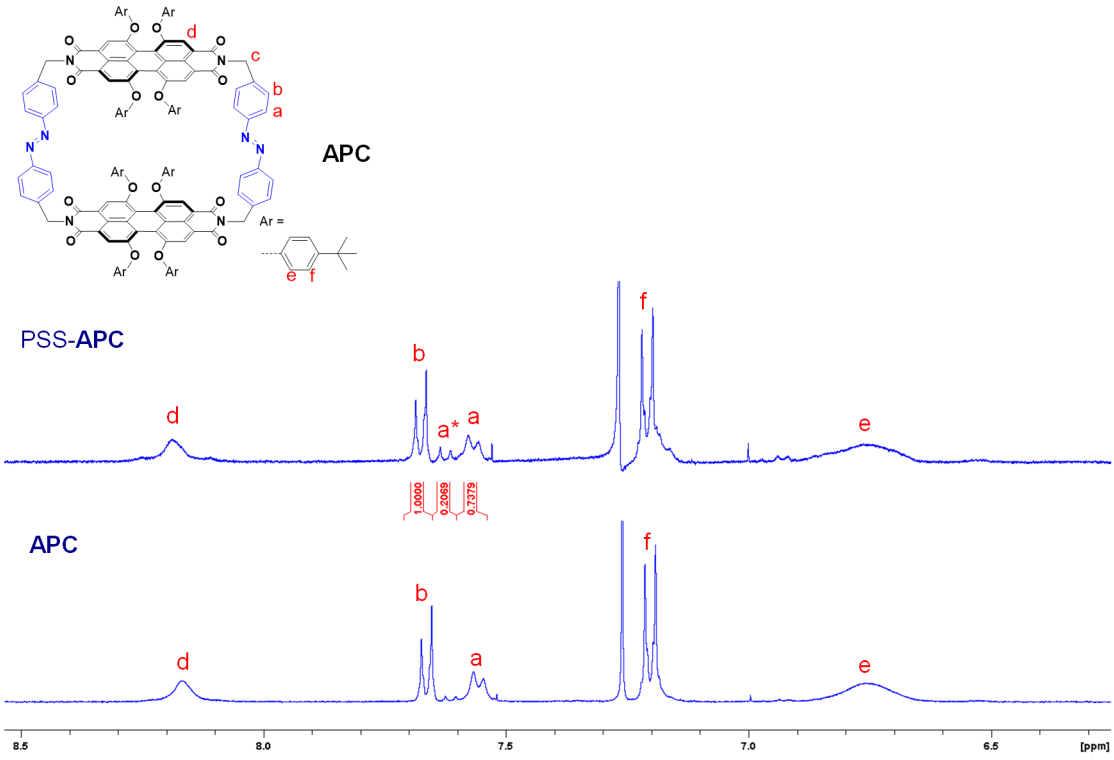
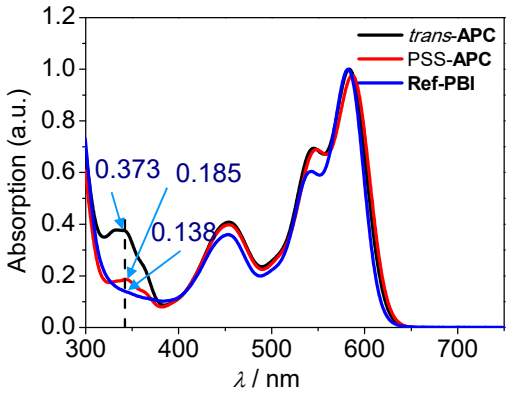


Fig. S11. NMR spectra of cyclophane **APC** and PSS-**APC** in $CDCl_3$, 298 K, 400 MHz.

After UV irradiation, the aromatic protons **a** in close proximity to the N=N bond showed changes from which the trans → cis isomerization ratio can be calculated to be Integral(**a***) / (Integral(**a***) + Integral(**a**)) = 22.0 %, where **a*** is the corresponding azobenzene proton **a** after UV irradiation (i.e. of *cis*-Azo).



Absorption at 333 nm
APC : 0.373
PSS-**APC** : 0.185
PBI moieties ~ 0.138

Conversion:
(0.373-0.185)/(0.373-0.138) ~ 80 %

Fig. S12. UV-vis absorption spectra of **APC** and PSS-**APC**. [**APC**] = 8.6 x 10^{-6} M in DCM, 298 K. [**ref-PBI**] = [**2**] = 5.0 x 10^{-6} M in DCM.

Following the same procedure as applied to the data shown in Fig. S10, the *trans* → *cis* transformation ratio of **APC** in dichloromethane was calculated to be 80 %.

Table S1. Fluorescence quantum yield (FLQY) of *trans*-**APC** and photo-stationary PSS-**APC** after UV irradiation for different excitation wavelengths.

	trans-**APC**	PSS-**APC**
λ_{Ex} = 510 nm	16 %	7 %
λ_{Ex} = 350 nm	16 %	10 %

Notes: photo-stationary state was obtained by UV irradiation for 5 min. FLQY was measured by using an integrating sphere, 298 K, [**APC**] = $1*10^{-6}$ M, DCM.

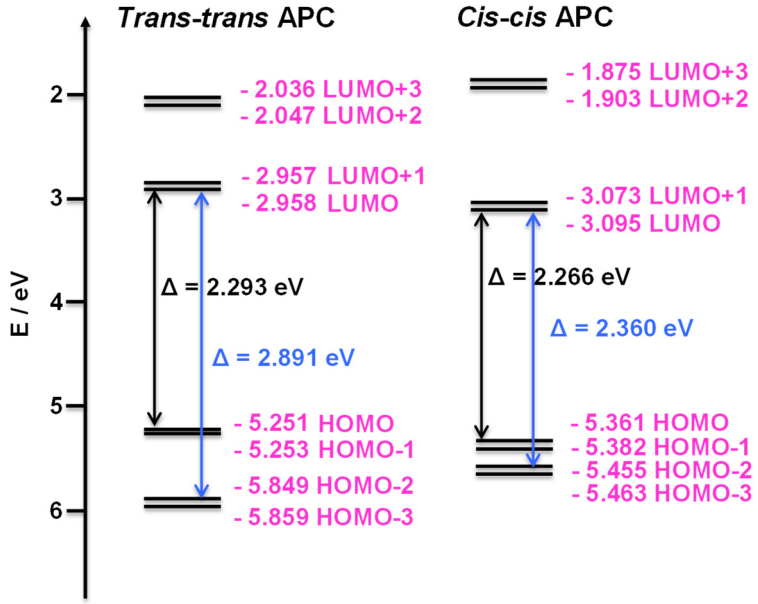


Fig. S13. Illustration of energy levels of *trans-trans* **APC** and *cis-cis* **APC**. The values were obtained from DFT calculations (Gaussian 09, B3LYP 6-31G(d,p) level).

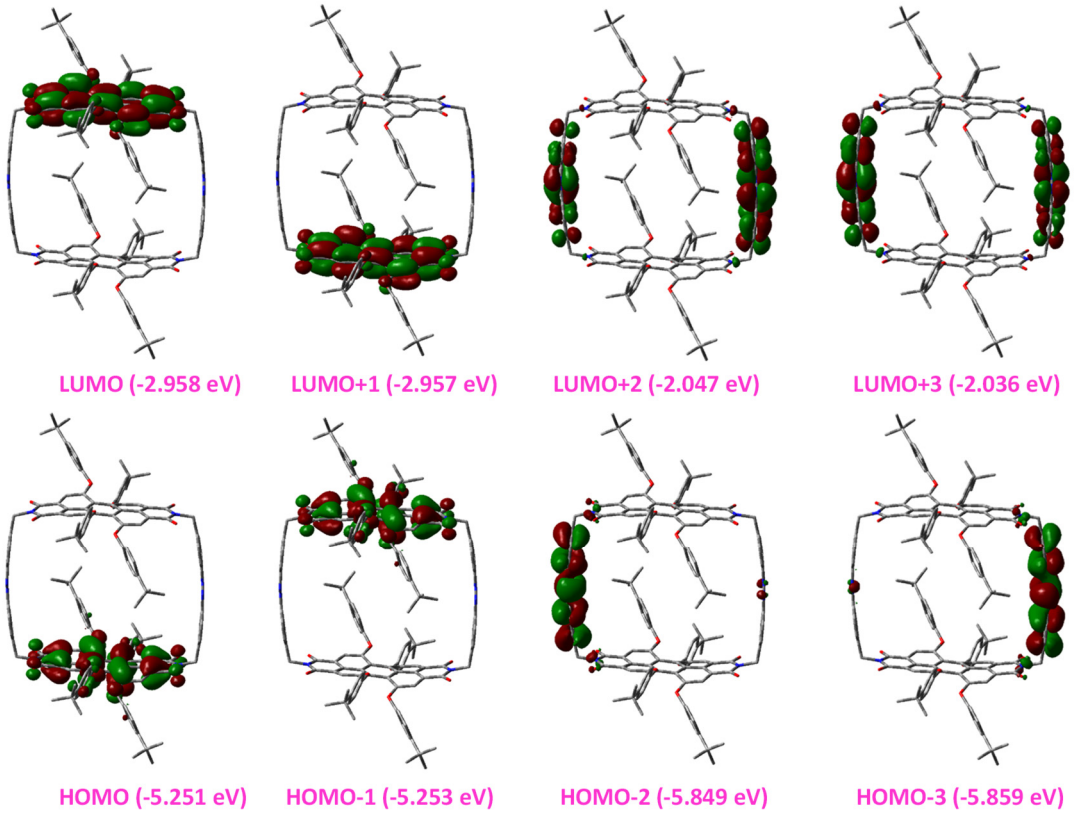


Fig. S14. Illustration of molecular orbitals of *trans*-*trans* **APC** (B3LYP 6-31G(d,p) level). All hydrogen atoms are omitted for clarity.

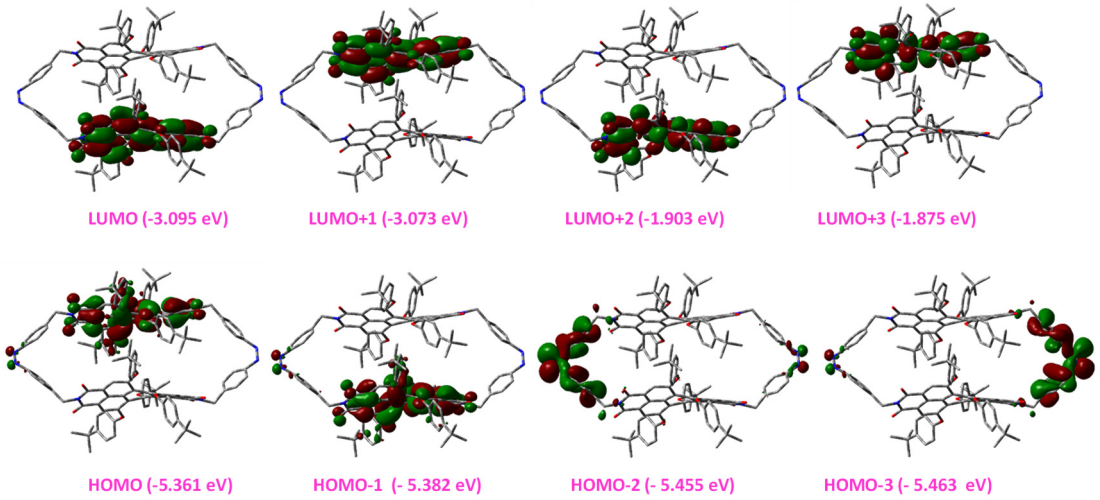


Fig. S15. Illustration of molecular orbitals of *cis*-*cis* **APC** (B3LYP 6-31G(d,p) level). All hydrogen atoms are omitted for clarity.

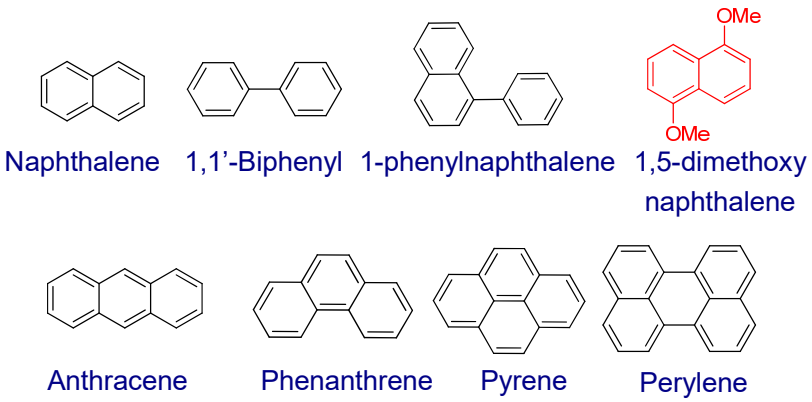


Fig. S16. Guest molecules utilized for host-guest studies.

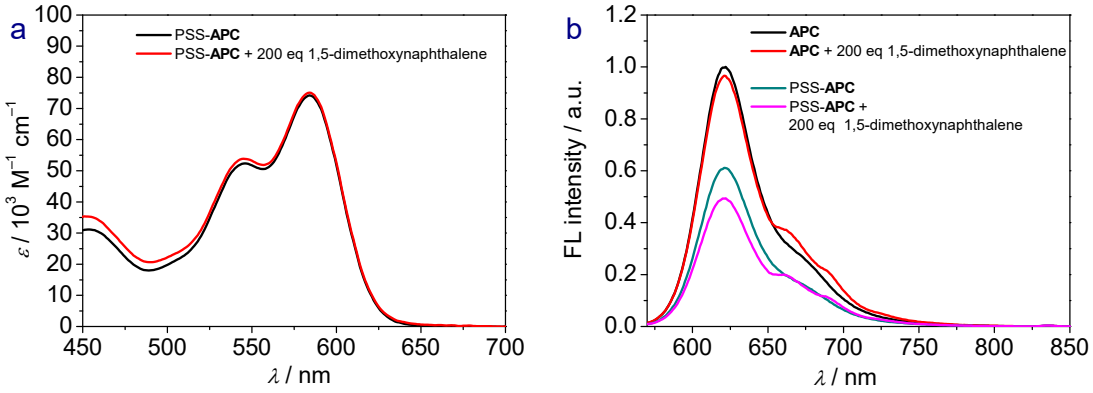


Fig. S17. UV-vis and FL spectra of **APC** and PSS-**APC** for titration experiments. a) UV-vis spectra of PSS-**APC** and PSS-**APC**/1,5-dimethoxynaphthalene. b) FL spectra of **APC** and PSS-**APC** before and after adding 200 eq. of 1,5-dimethoxynaphthalene. [**APC**] = $1*10^{-5}$ M in DCM, 298 K.

S4. Reference

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W.

Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16 Rev. C.01.

2. Y. R. Choi, G. C. Kim, H. G. Jeon, J. Park, W. Namkund and K. Jeong, Azobenzene-based chloride transporters with light-controllable activities, *Chem. Commun*. 2014, **50**, 15305–15308.
3. D. Dotcheva, M. Klapper and K. Müllen, Soluble polyimides containing perylene units, *Macromol. Chem. Phys*. **1994**, *195*, 1905–1911.
4. P. Osswald, F. Würthner, Effects of Bay Substituents on the Racemization Barriers ofPerylene Bisimides: Resolution of Atropo-Enantiomers, *J. Am. Chem. Soc.* **2007**, *129*, 14319–14326.