

Supporting Information *for*

**Visible light-triggered gel-to-sol transition in halogen-bond-
based supramolecules**

Xun Tong,^a Yuan Qiu,^a Xiaoyu Zhao,^a Bijin Xiong,^a Rongzhen Liao,^{*a}

Haiyan Peng,^a Yonggui Liao^{*ab} and Xiaolin Xie^{ab}

^a Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China. E-mail: rongzhen@mail.hust.edu.cn, ygliao@mail.hust.edu.cn

^b National Anti-counterfeit Engineering Research Center, Huazhong University of Science and Technology, Wuhan 430074, China

1. General analyses

The UV-vis measurements were carried out upon a xenon lamp (Perfect Light, PLS-SXE300) through a filter at 450 ± 13 nm and 21 mW cm^{-2} for trans-cis photoisomerization, as well as through a filter at 550 ± 13 nm and 22 mW cm^{-2} for cis-trans photoisomerization.

The T_{GS} was determined by falling ball method. A certain concentration of gel formed in a 5 mL sample bottle (approximately 10 mm in diameter). A steel ball with a diameter of 1 mm was placed on the surface of the gel and heated slowly until the steel ball fell into the bottom of the vial. The corresponding temperature is T_{GS} .

All calculations were performed with the Gaussian 16 software package.¹ The geometries were optimized at the M06-2X/def2-SVP level in the gas phase. More accurate energies were obtained by single-point calculations at the M06-2X/def2-TZVPP level. Frequency calculations were performed at the same level of theory as geometry optimization to verify the nature of all stationary points (no imaginary frequency). In order to reduce the computational cost, a methoxy group was used to replace the decyloxy group in Azopy-C₁₀.

2. Syntheses and Characterization

Synthesis of Azopy

The synthesis of Azopy was according to the literature.² (42% yield)

Synthesis of 4-Decyloxybenzoic Acid

Bromodecane (14.80 g, 66.91 mmol) was added to the solution of 4-hydroxybenzoic acid (10.00 g, 72.40 mmol), KOH (7.4 g, 131.88 mmol) and KI (0.17 g, 1 mmol) in MeOH (50 mL). The reaction mixture was stirred and refluxed for 18 h. Then, the solvent was evaporated under low pressure and then poured into deionized water. The pH was adjusted to 3-4 with 1 M HCl. The resultant precipitates were filtered and recrystallized from methanol, and then dried in a vacuum oven. White solid was obtained in 72% yield (14.5 g). [¹H NMR (400 MHz, DMSO-*d*₆, δ): 10.35 (s, 1H), 7.80 (d, *J* = 8.6, 2H), 6.85 (d, *J* = 8.6, 2H), 4.20 (t, *J* = 6.4, 2H), 1.90–0.66 (m, 19H).]

Synthesis of Azopy-C_n

The synthesis of Azopy-C_n was based on the reference.³ ¹H NMR spectrum of Azopy-C₁₀ was shown in Fig. S1. (56% yield)

Synthesis of 2,3,5,6-Tetrafluoro-4-iodobenzeneamine

The synthesis of 2,3,5,6-tetrafluoro-4-iodobenzeneamine was according to the reference.⁴ (87% yield)

Synthesis of BTFIPD

The synthesis of BTFIPD was based on the reference.⁵ ¹H NMR and ¹⁹F NMR spectra of BTFIPD before and after green light irradiation were shown in Fig. S2. (*cis* (18%) and *trans* (9%) yield)

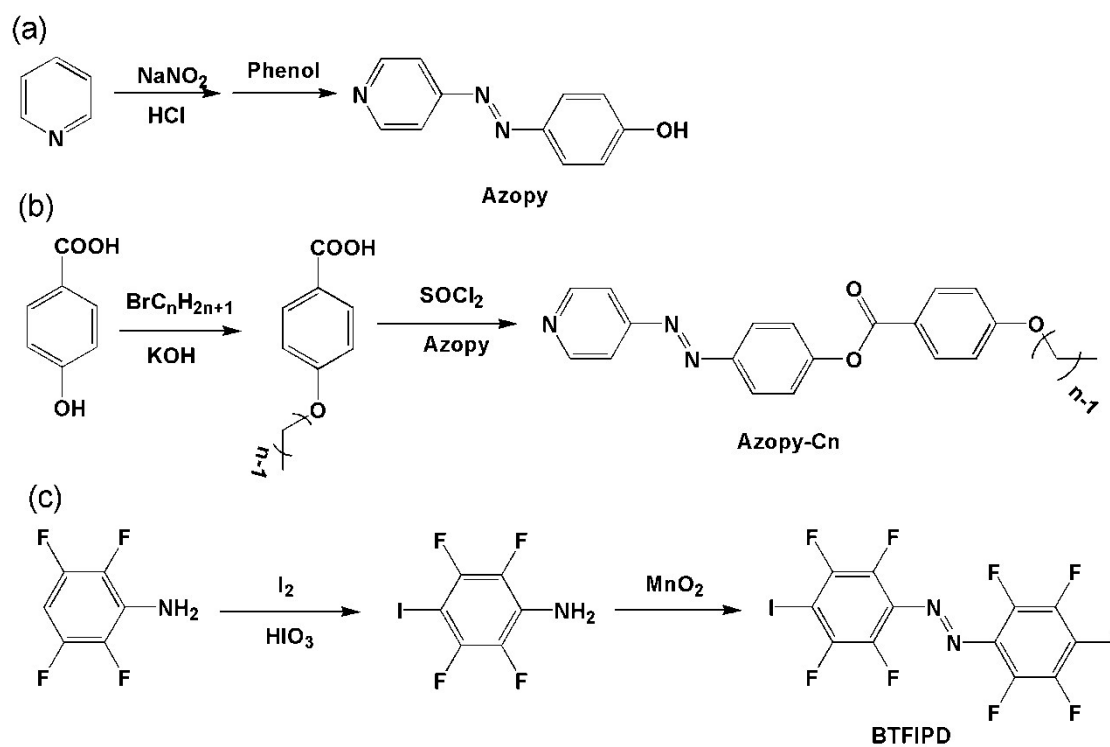
3. Figures and Tables

Table S1. Gelation property of Azopy-C₁₀•BTFDD in various solvents

Solvent	phase ^a	CGC (wt%)	Solvent	phase ^b	CGC (wt%)
ethyl acetate	S		petroleum ether	P	
dichloromethane	S		ethanol	P	
methanol	P		THF	G	6%
trichloromethane	P		acetonitrile	P	
1,2-dichloroethane	P		pyridine	G	14%
DMF	PG		deionized water	P	
toluene	P		acetone	S	
cyclohexane	P		ether	P	

^a S = solution; PG = partial gel; G = gel; P = precipitation

^b The critical gelation concentrations (CGC) were obtained at room temperature by tube inversion method.



Scheme S1 Synthetic routes of Azopy-C_n (n = 8, 10, 12) and BTFIPD.

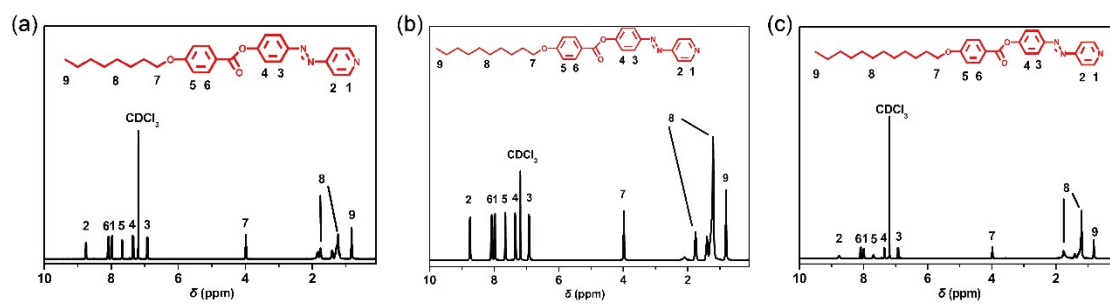


Fig. S1 ^1H NMR spectra of Azopy- C_8 , Azopy- C_{10} , and Azopy- C_{12} in CDCl_3 .

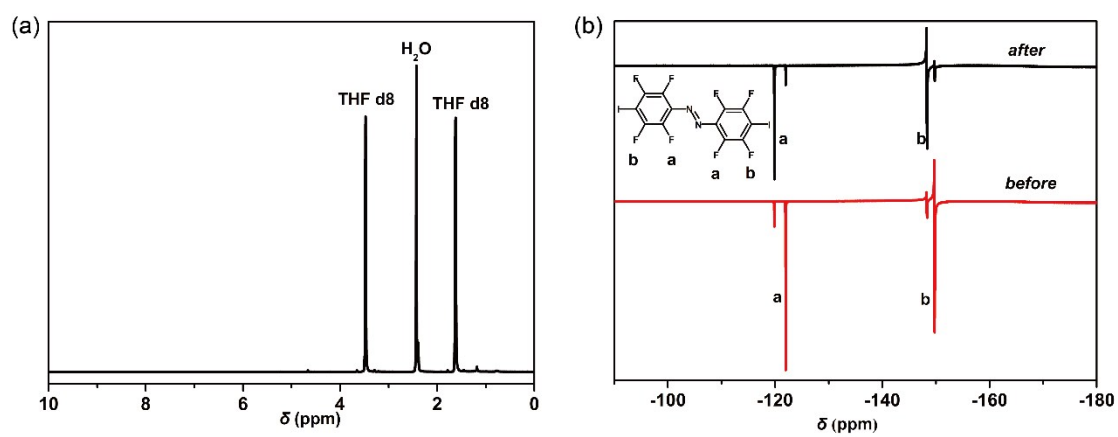


Fig. S2 (a) ^1H NMR spectrum and (b) ^{19}F NMR spectra of BTfIPD before (bottom) and after (top) green light irradiation for 10 min in THF d8.

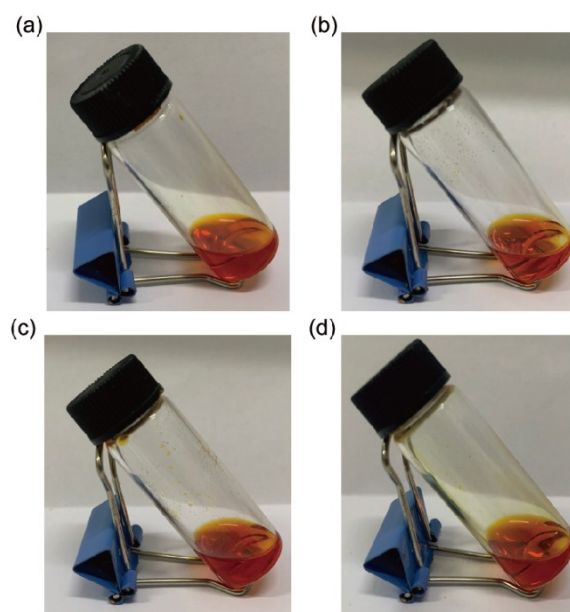


Fig. S3 Photos of pure BTfIPD in (a) THF and (b) pyridine; pure Azopy- C_{10} in (c) THF and (d) pyridine.

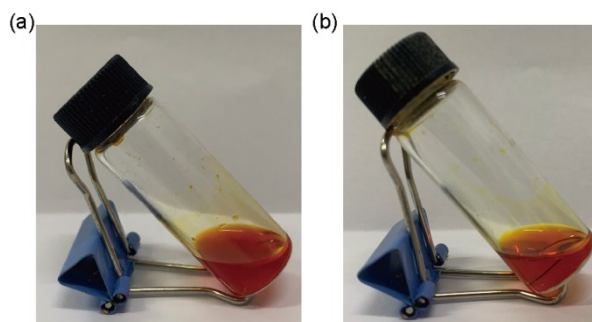


Fig. S4 Photos of Azopy-C₁₂•BTFIPD and Azopy-C₈•BTFIPD in THF.

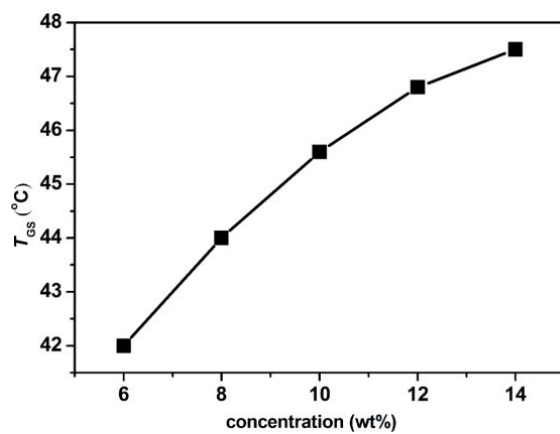


Fig. S5 Gel-sol transition diagram of gels at different concentrations tested by falling ball method.

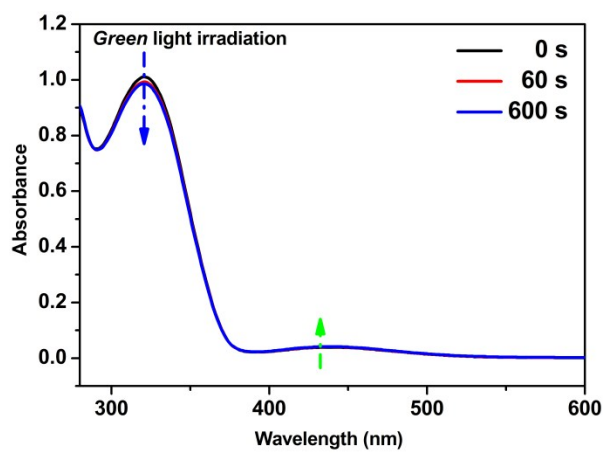


Fig. S6 UV-Vis absorption spectra of pure Azopy-C₁₀ irradiated by green light (550 nm, 22 mW cm⁻²). The concentration is 8×10^{-5} mol L⁻¹ in THF.

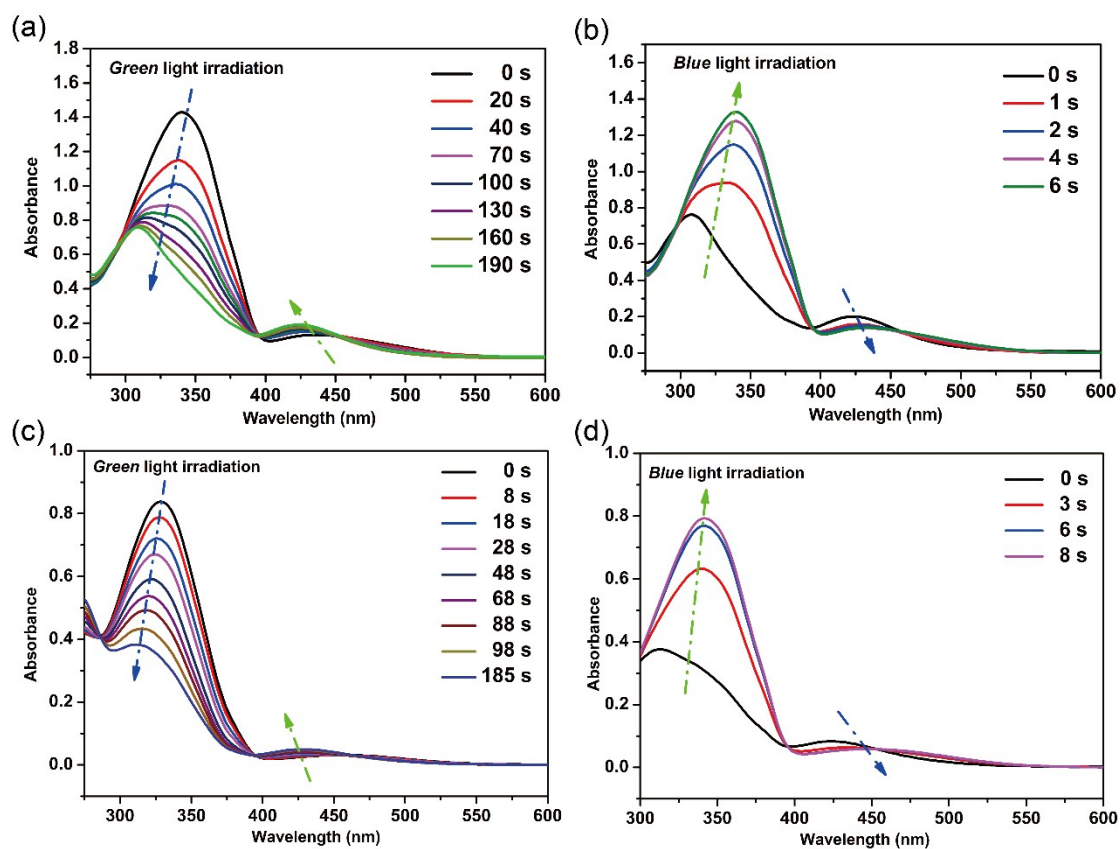


Fig. S7 UV-Vis absorption spectra of (a, b) pure BTFIPD and (c, d) Azopy-C₁₀•BTFIPD (at a molar ratio of 2:1) irradiated by (a, c) green light (550 nm, 22 mW cm⁻²) and (b, d) then blue light (450 nm, 21 mW cm⁻²). The concentrations are 8×10^{-5} mol L⁻¹ in THF.

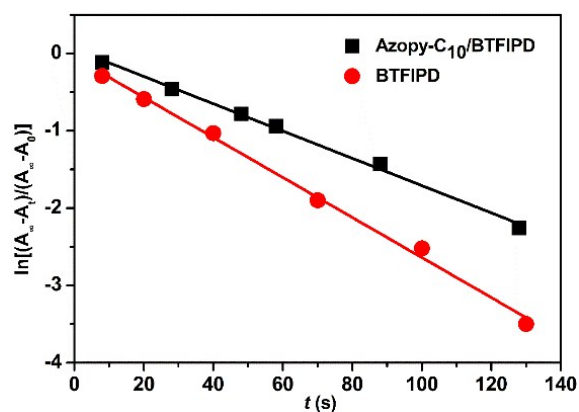


Fig. S8 Kinetic curves of *trans-cis* isomerization for BTFIPD (circles) and Azopy-C₁₀•BTFIPD (squares) in THF.

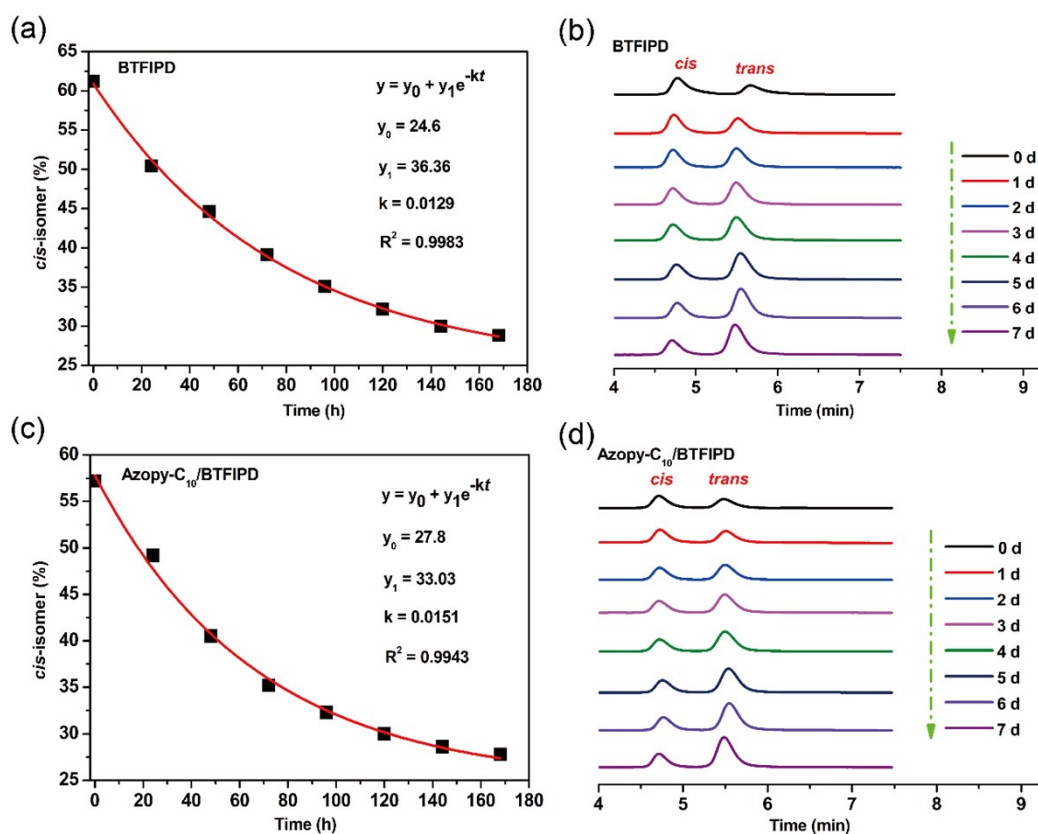


Fig. S9 HPLC measurement was conducted after irradiating the samples with 22 mW cm^{-2} of 550 nm light for 20 min. Plot of *cis* content versus time for (a) BTFIPD and (c) Azopy-C₁₀•BTFIPD in dark at 25 °C. HPLC traces of photostationary state samples in THF in dark at 25 °C for (b) BTFIPD and (d) Azopy-C₁₀•BTFIPD.

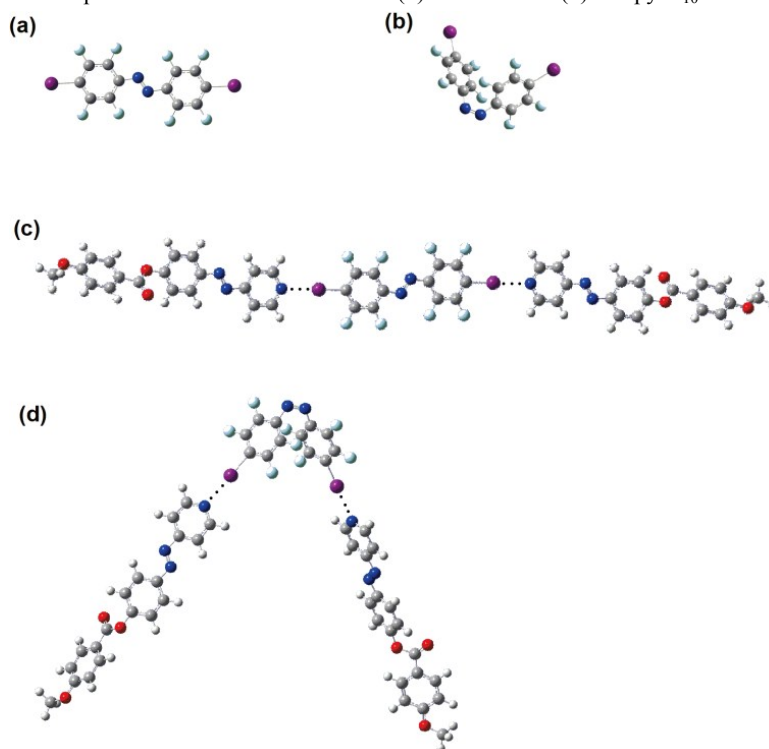


Fig. S10 The optimized molecular structures for (a) *trans* BTFIPD, (b) *cis* BTFIPD, (c) Azopy-C₁₀•(*trans*)BTFIPD complex and (d) Azopy-C₁₀•(*cis*)BTFIPD complex which are obtained from Gaussian16 calculation at the M062X/def2-SVP level.

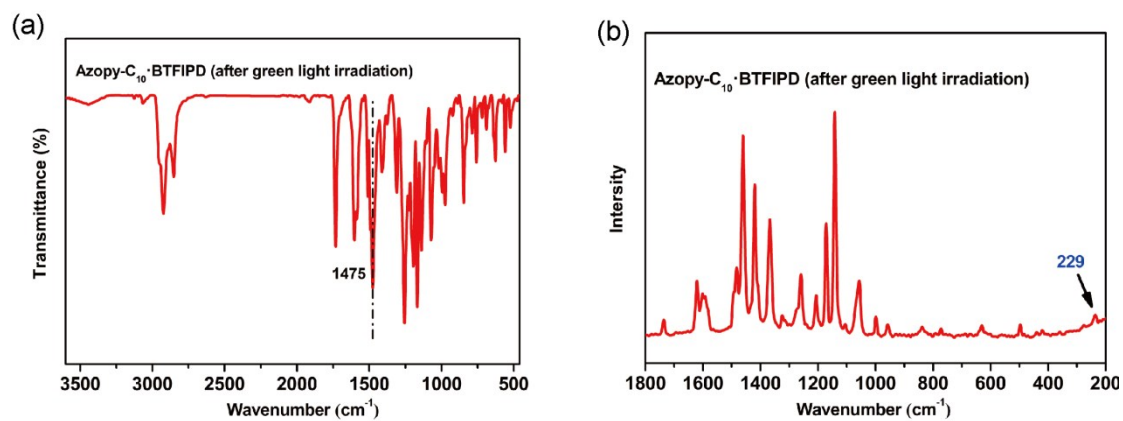


Fig. S11 (a) FT-IR and (b) Raman spectra of Azopy-C₁₀•BTFIPD supramolecules after green light irradiation.

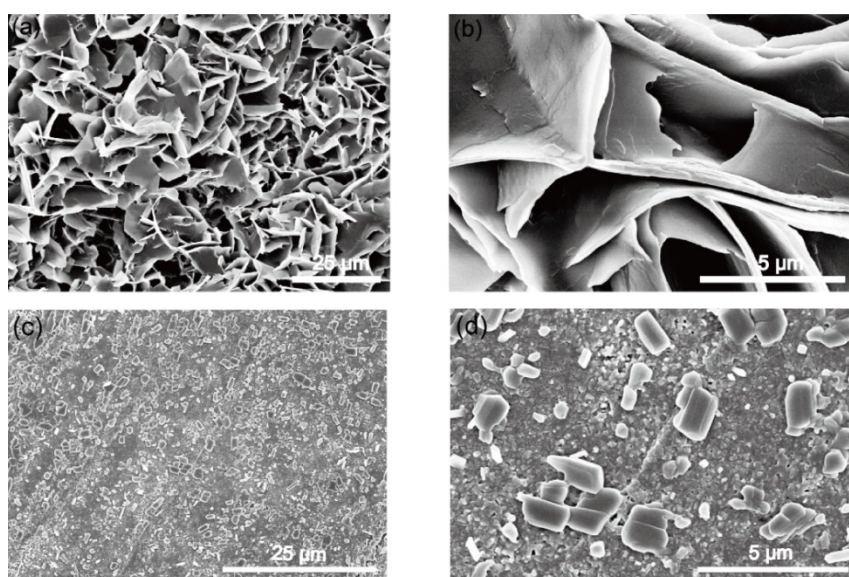


Fig. S12 SEM images of (a, b) pure Azopy-C₁₀ and (c, d) pure BTFIPD assemblies formed in THF.

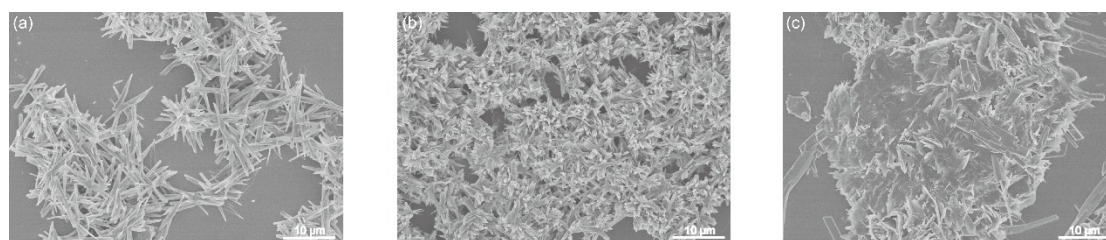


Fig. S13 SEM images of Azopy-C₁₀•BTFIPD supramolecules formed in THF after UV light irradiation for (a) 0 min, (b) 30 min, and (c) 180 min.

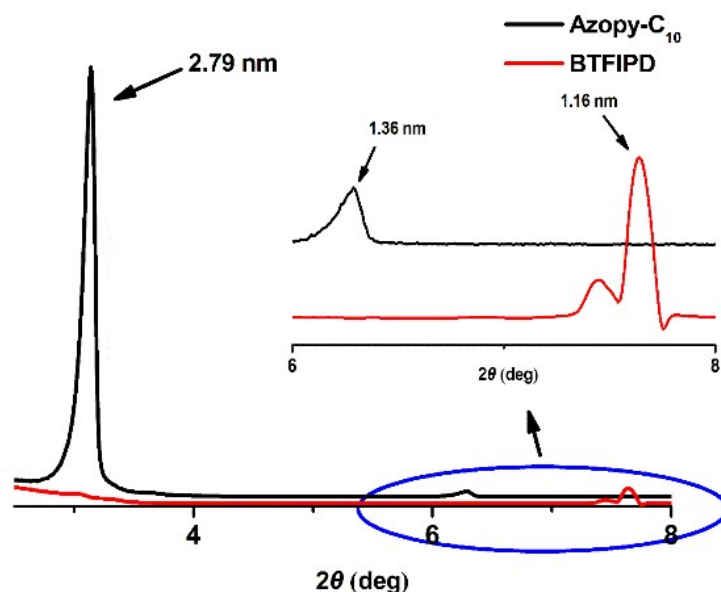


Fig. S14 XRD patterns of pure Azopy-C₁₀ (top) and pure BTFIPD (bottom).

References

- 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, D. Williams-Young, 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, Inc., Wallingford CT, 2016.
- 2 L. Cui and Y. Zhao, *Chem. Mater.*, 2004, **16**, 2076-2082.
- 3 H. Hu, Y. Qiu, J. Wang, D. Zhao, H. Wang, Q. Wang, Y. Liao, H. Peng and X. Xie, *Macromol. Rapid Commun.*, 2018, **40**, 1800629.
- 4 L. V. Politanskaya, V. D. Shteingarts and E. V. Tretyakov, *J. Fluorine Chem.*, 2016, **188**, 85-98.
- 5 O. S. Bushuyev, A. Tomberg, T. Friscic and C. J. Barrett, *J. Am. Chem. Soc.*, 2013, **135**, 12556-12559.