Supporting Information

Photochromic porous organic crystals constructed by the self-assembly of triarylethylene derivatives

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Experimental Procedure

General Methods

^{1}H Nuclear magnetic resonance (^{1}H NMR) spectra for the compounds were obtained on a Bruker Avance NEO 500 Nuclear Magnetic Resonance Spectrometer with DMSO-d_6 as solvent and tetramethylsilane (TMS) as the internal standard. High resolution mass spectra (MS) were recorded on a TSQ Fortis Triple Quadrupole Mass Spectrometer with Ultra HPLC & Q Exactive High Resolution Mass Spectrometer System. Thermogravimetric analysis was performed on a PerkinElmer Thermogravimetric Analyzer TGA 4000. Fourier transform infrared (FTIR) spectroscopy was conducted on a PerkinElmer Frontier FTIR spectrophotometer (4000–530 cm^{-1}) with a universal ATR accessory. Gas adsorption isotherms were collected using a Micromeritics 3Flex Accelerated Surface Area and Porosity Analyzer. Microscopic images were collected on a TESCAN MIRA LMS scanning electron microscope (SEM) and a FEI Talos F200s high-resolution transmission electron microscope (HR-TEM). Zeta potential measurements were performed on a Malvern Zetasizer Nano ZSE particle characterization system. UV-Vis absorption spectra, emission spectra and fluorescence lifetimes were obtained on a Hitachi U-3900H UV-vis spectrometer, an Edinburgh FS5 fluorescence spectrophotometer and a Hitachi F-7100 fluorescence spectrophotometer, respectively. Photochromic UV-vis absorption spectra were measured on an Ocean Optic QE 65Pro spectrometer. DFT calculations at B3LYP functional with 6-311G* basis set level were performed based on the single crystal structure using the Gaussian 09 software on the grounds of previous literatures.[1]

Crystal Structure Determination

Crystals suitable for X-ray diffraction were mounted on a MiTeGen dual-thickness micro-mount and placed under a cold stream of nitrogen (Oxford). Single-crystal X-ray diffraction measurements were recorded on a Bruker D8 VENTURE Duo FIXED-CHI X-Ray Diffractometer using a IμS micro-focus Mo-Kα radiation (λ = 0.71073 Å) with a Quazar multilayer optics. Data collection was conducted with the *APEX3* v2019.3-2click4 (Bruker Nano, 2019) program. Cell refinement and data reduction were performed with the *SAINT* V8.38A (Bruker AXS Inc., 2017) program. The structure was solved using *XT* 2014/5[2a] in the *APEX3* suite and refined with *SHELXL*2018/3.[2b] Hydrogen atoms were placed in idealised positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was refined by weighted least

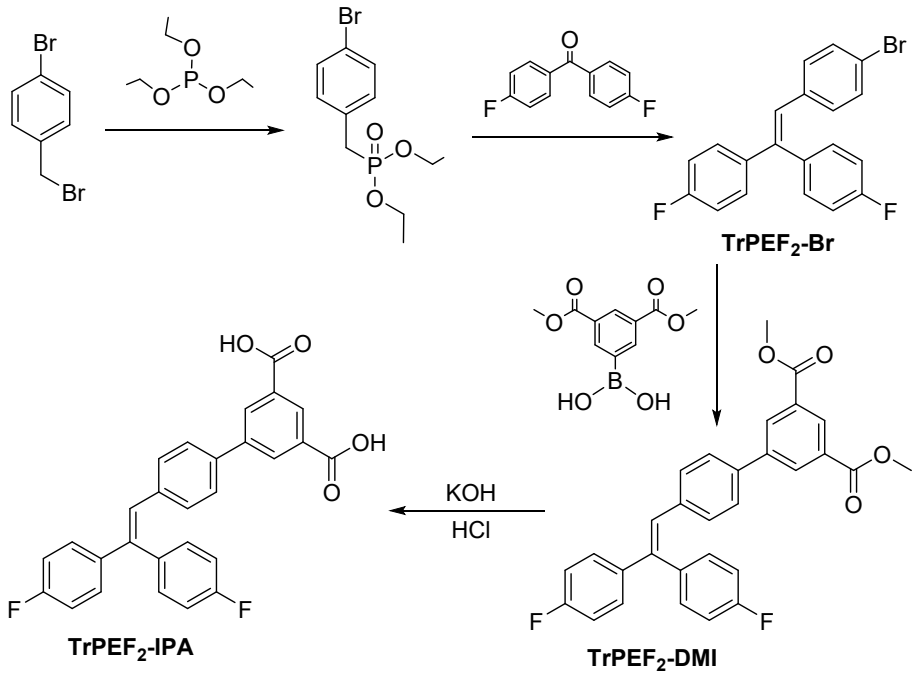
squares refinement on F^2 to convergence. All e.s.d.'s (except the e.s.d. in the dihedral angle between two least-square planes) are estimated using the full covariance matrix. The X-ray crystallographic data of **TrPEF$_2$-IPA** has been deposited at the Cambridge Crystallographic Data Centre (CCDC), under the deposition number CCDC 2179741. The data can be obtained free of charge from the Cambridge Crystallographic Data Center (https://www.ccdc.cam.ac.uk/structures/).

Materials

4-Bromobenzyl bromide, triethyl phosphite, 4,4'-difluorobenzophenone, potassium *tert*-butoxide (*t*-BuOK), 3-(methoxycarbonyl)phenyl boronic acid, tetrakis(triphenylphosphine)-palladium ($Pd(PPh_3)_4$), potassium carbonate, magnesium sulfate ($MgSO_4$) and potassium hydroxide (KOH) were purchased from Dieckmann (Hong Kong) Chemical Industry Company Limited. Ethanol, *n*-hexane, dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF), were purchased from Oriental Chemicals & Lab. Supplies Ltd. All other regents were commercially available and used as received.

Syntheses

The synthetic route of 4'-(2,2-bis(4-fluorophenyl)vinyl)-[1,1'-biphenyl]-3,5-dicarboxylic acid (**TrPEF$_2$-IPA**) is illustrated in Scheme S1. Diethyl (4-bromobenzyl)phosphonate was prepared according to a procedure reported in literature.[1]



Scheme S1. Synthetic route for **TrPEF$_2$-IPA**.

Synthesis of $TrPEF_2$-Br

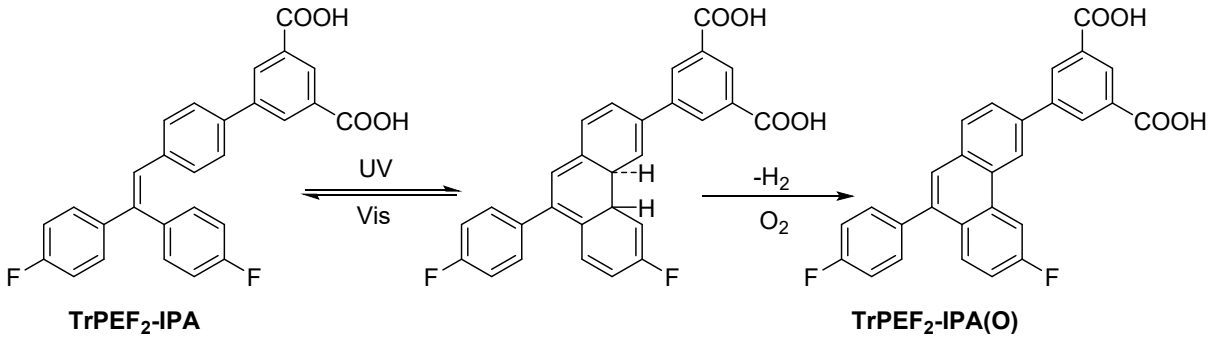
The compound was synthesised according to a modified literature procedure.[1] To a two-necked round-bottomed flask containing 4,4'-difluorobenzophenone (2.74 g, 12.54 mmol) and diethyl (4-bromobenzyl)phosphonate (3.50 g, 11.40 mmol) was added degassed THF (70 mL) under an argon atmosphere. After cooling to 0 °C, *t*-BuOK (3.84 g, 34.19 mmol) was added. Upon stirring for 4 hours under an argon atmosphere, the mixture was poured into ethanol/deionised water (250 ml, 3:2 v/v), and stirred for another 1 hour. The white precipitate which formed was collected by filtration. The precipitate was dissolved in CH_2Cl_2 and washed 3 times with water. The organic layer was dried over anhydrous $MgSO_4$. After evaporation of the filtrate, the residue was purified by recrystallization via vapor diffusion of hexane into a concentrated dichloromethane solution of the product to give **$TrPEF_2$-Br** (3.50 g, 82.7 %) as a white powder.

Synthesis of $TrPEF_2$-DMI

A mixture **$TrPEF_2$-Br** (1.00 g, 2.69 mmol), 3-(methoxycarbonyl)phenyl boronic acid (961.69 mg, 4.04 mmol) and potassium carbonate (1.61 g, 11.63 mmol) was dissolved in tetrahydrofuran/deionised water (50 mL, 4:1 v/v). The reaction mixture was stirred at room temperature under nitrogen for 30 min, and then $Pd(PPh_3)_4$ (93.39 mg, 61 mmol) was added. The resulting solution was heated at 85 °C for 24 h. After the reaction was completed, the mixture was poured into water and extracted 3 times with dichloromethane. The organic layer was dried over anhydrous $MgSO_4$. After removing the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (dichloromethane/n-hexane, 1:5 v/v) to obtain **$TrPEF_2$-DMI** (1.03 g, 78.9 %) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ (TMS, ppm): 8.43 (d, J = 3.5 Hz, 1H), 8.38 (d, J = 2 Hz, 2H), 7.63–7.30 (d, J = 10.5 Hz, 2H), 7.38–7.35 (m, 2H), 7.31–7.19 (m, 6H), 7.16–7.15 (m, 2H). EI-MS: m/z found: 507.13515 $[M+Na]^+$; calcd for $C_{30}H_{22}F_2O_4$: 507.13784.

Synthesis of $TrPEF_2$-IPA

To a solution of **$TrPEF_2$-DMI** (0.60 g, 1.44 mmol) in THF/H_2O (20 mL, 1:1 v/v) was added KOH (2.08 g, 37.15 mmol). The resulting mixture was refluxed for 1 d. After cooling to room temperature, the pH value of the mixture was adjusted to 1.0 by adding 1 M HCl, and then the reaction mixture was filtered to afford **$TrPEF_2$-IPA** as a white solid. Yield: 0.51 g (90.2 %). ^{1}H NMR (500 MHz, DMSO-d_6) δ (TMS, ppm): 13.38 (s, 2H), 8.43 (s, 1H), 8.43 (s, 2H), 7.60–7.58 (d, J = 10.5 Hz, 2H), 7.37–7.34 (d, J = 7 Hz, 2H), 7.28–7.19 (m, 6H), 7.16–7.14 (m, 3H). EI-MS: m/z found: 456.11230 $[M]^-$; calcd for $C_{28}H_{18}F_2O_4$: 456.11732.



Scheme S2. Cyclization reaction in the photochromism process of **TrPEF$_2$-IPA**, and the subsequent dehydrogenation to form **TrPEF$_2$-IPA(O)**.

Synthesis of dehydrogenated photoisomer TrPEF$_2$-IPA(O)

A mixture of TrPEF$_2$-IPA (100.0 mg, 0.22 mmol) in THF(10 ml) was irradiated with UV-light in a vial under oxygen for 12 h. The mixture was dissolved in 20 ml dichloromethane and washed with $MgSO_4$ aqueous solution for 3 times. The mixture was further purified by column chromatography with ethyl acetate/n-hexane as eluent. A white solid named TrPEF$_2$-IPA(O) was obtained. Yield: 80.0 mg (80.35 %). ^{1}H NMR (500 MHz, DMSO-d_6) δ (TMS, ppm): 13.48 (s, 2H), 9.19 (s, 1H), 9.07–9.05 (d, J = 12 Hz, 2H), 8.46 (s, 2H), 8.54 (s, 1H), 8.17–8.15 (d, J = 8.5 Hz, 1H), 8.06–8.04 (d, J = 8.5 Hz, 1H), 7.84–7.81 (m, 2H), 7.61–7.58 (m, 2H), 7.54–7.51 (m, 1H), 7.42–7.39 (m, 2H).

Dye Adsorption

TrPEF$_2$-IPA (15 mg) was soaked in an aqueous solution (20 mL) of methylene blue (MB; 18 mg L^{-1}) or rhodamine B (RhB; 15 mg L^{-1}). The mixture was magnetically stirred at room tepmperature in the dark for 48 h. Sample was extracted from the stirred suspension and centrifuged to remove the adsorbent. A clear supernatant was obtained for UV/vis absorption measurements.

Table S1. Photophysical properties of **TrPEF$_2$-IPA**.

Sample	State	Fluorescence		Photochromism
		λ_F (nm)	τ_F (ns)	λ_P (nm)
TrPEF$_2$-IPA	Powder	445	2.1	462
	In THF	444	–	502

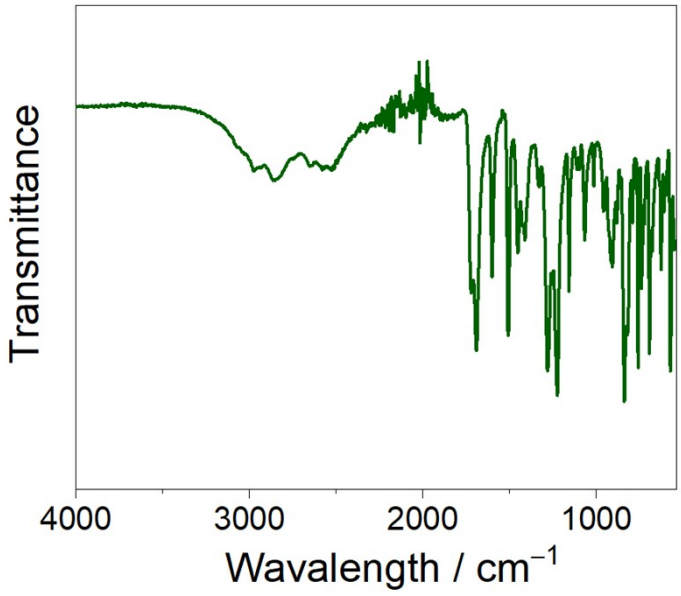


Figure S1. FTIR spectrum of **TrPEF$_2$-IPA**.

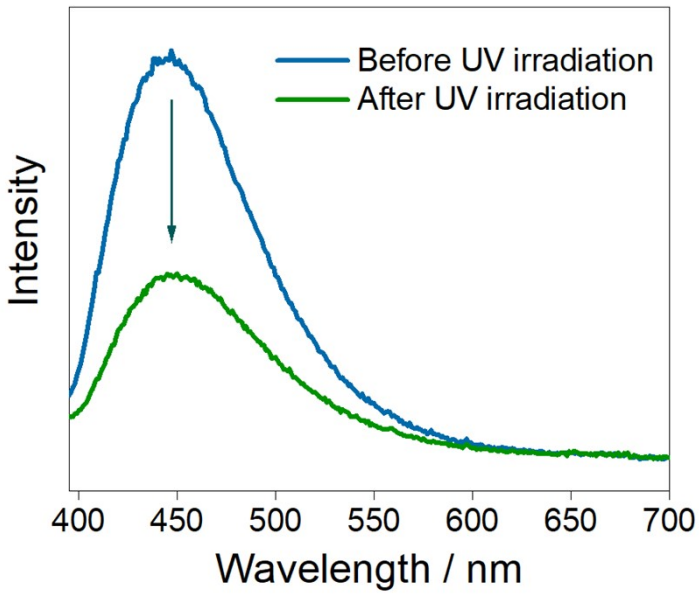


Figure S2. Changes in the emission spectrum of **TrPEF$_2$-IPA** after prolonged persistent UV light irradiation at 365 nm in the solid state at room temperature.

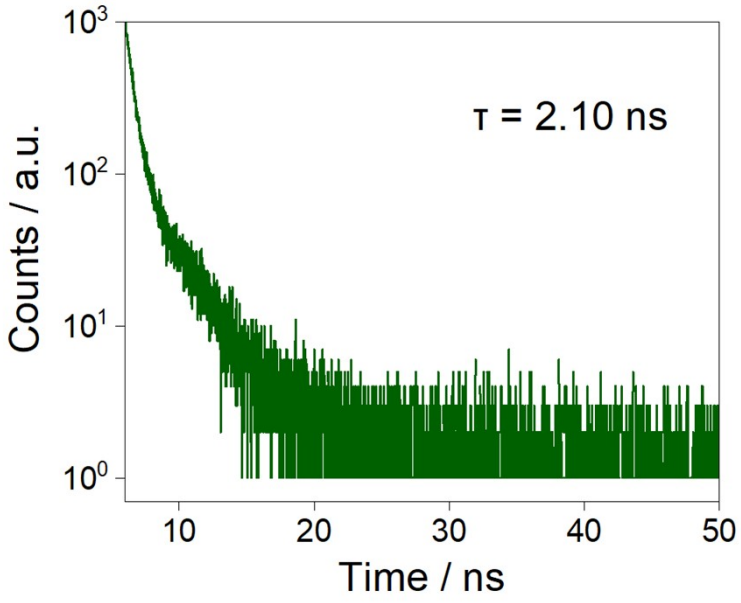


Figure S3. Time-resolved decay curve of **TrPEF$_2$-IPA** upon photoexcitation at 365 nm in the solid state at room temperature.

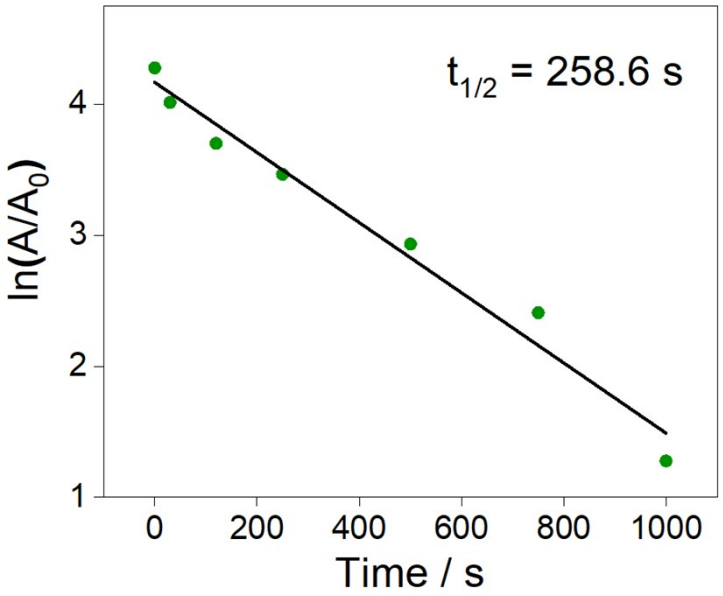


Figure S4. The half-life period of **TrPEF$_2$-IPA** in THF solution under prolonged visible light irradiation at room temperature.

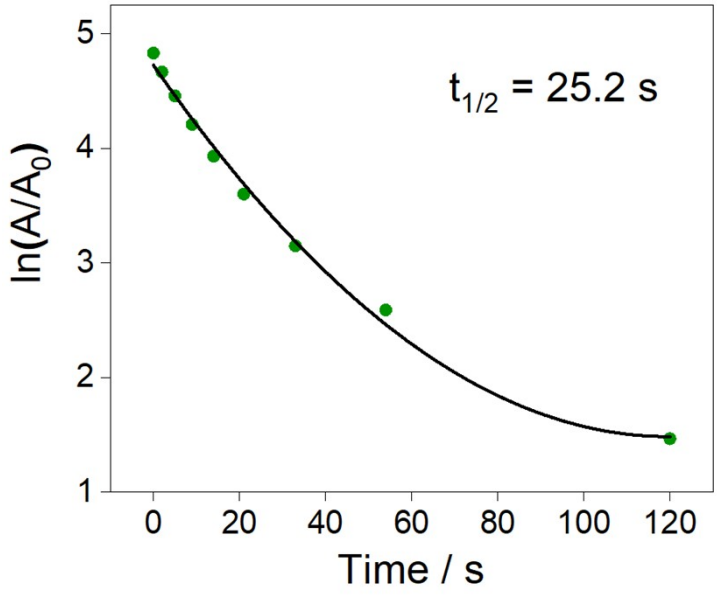


Figure S5. The half-life period of the photochromic **TrPEF$_2$-IPA** in the solid state under prolonged visible light irradiation at room temperature.

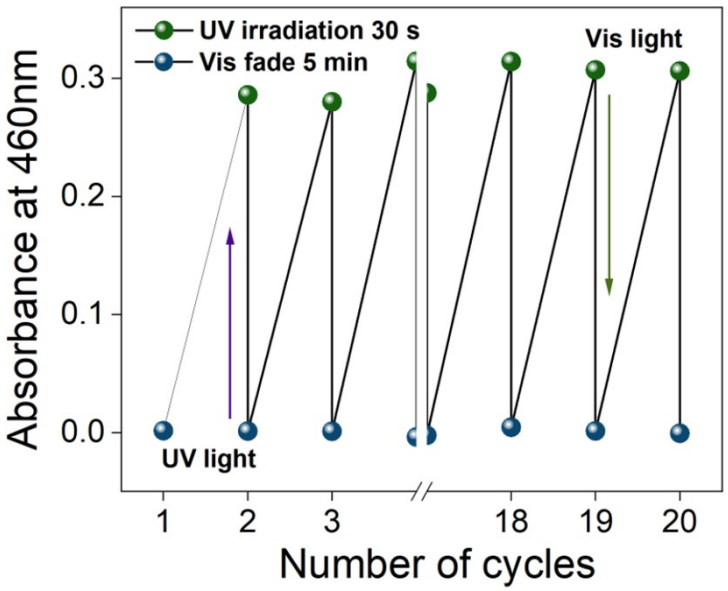


Figure S6. Absorption switching of **TrPEF$_2$-IPA** in THF solution at 460 nm after 20 cycles of alternate UV and visible light irradiation at room temperature.

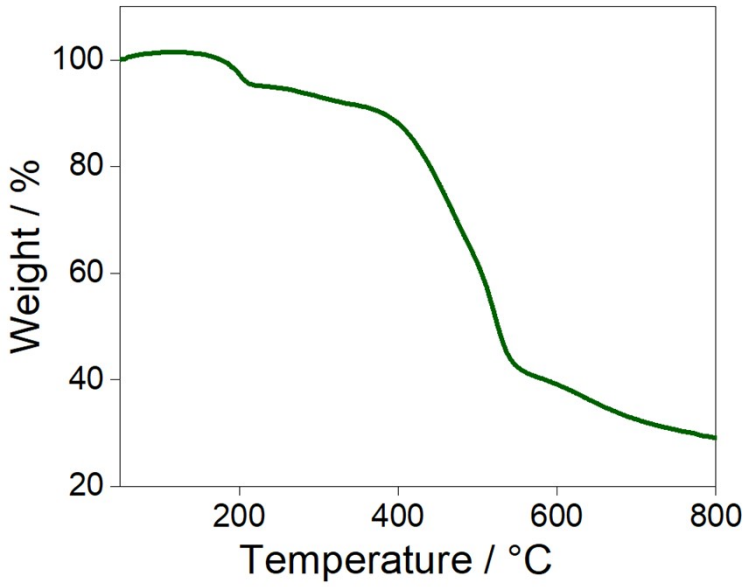


Figure S7. Thermogravimetric analysis profile of **TrPEF$_2$-IPA**.

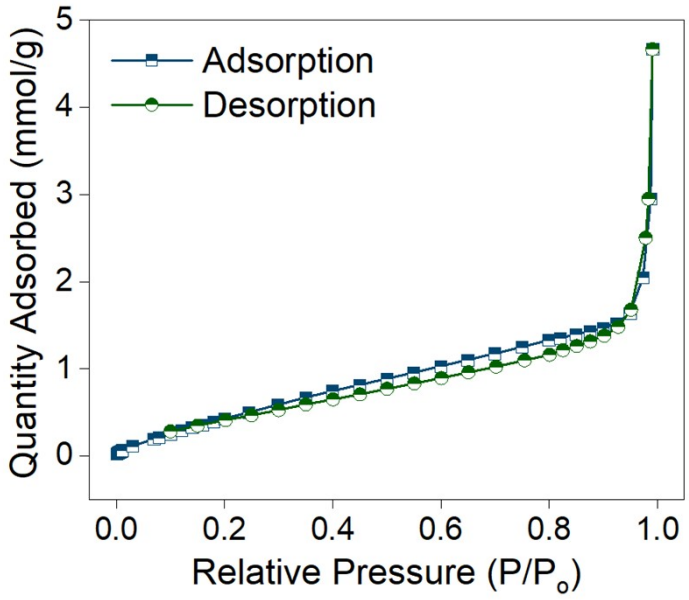


Figure S8. Nitrogen sorption isotherm of activated **TrPEF$_2$-IPA**.

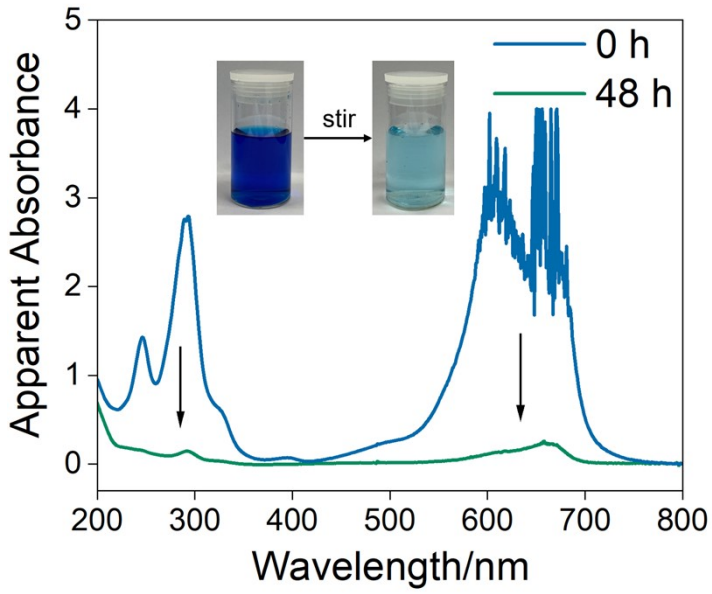


Figure S9. Changes in the UV/vis absorption spectra of the supernatant of an aqueous solution of MB after the adsorption by **TrPEF$_2$-IPA** for 48 h. Insets show photographs of the corresponding colour changes.

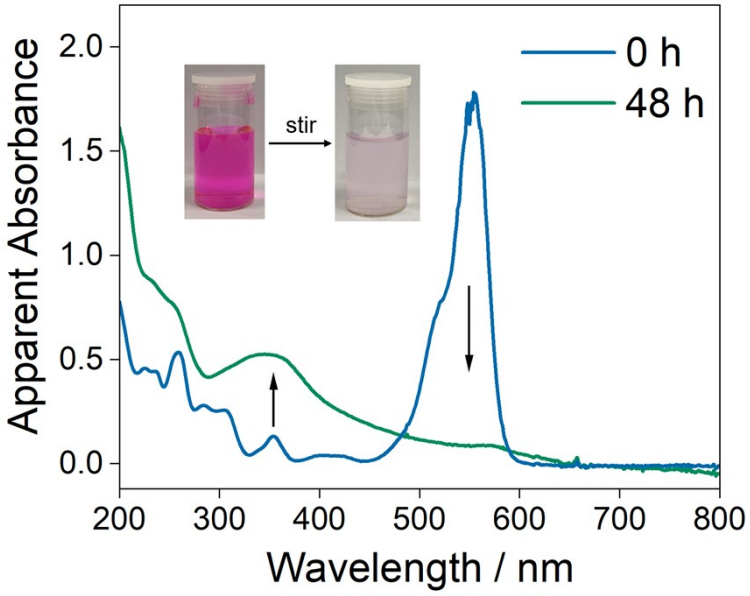


Figure S10. Changes in the UV/vis absorption spectra of the supernatant of an aqueous solution of RhB after the adsorption by **TrPEF$_2$-IPA** for 48 h. Insets show photographs of the corresponding colour changes.

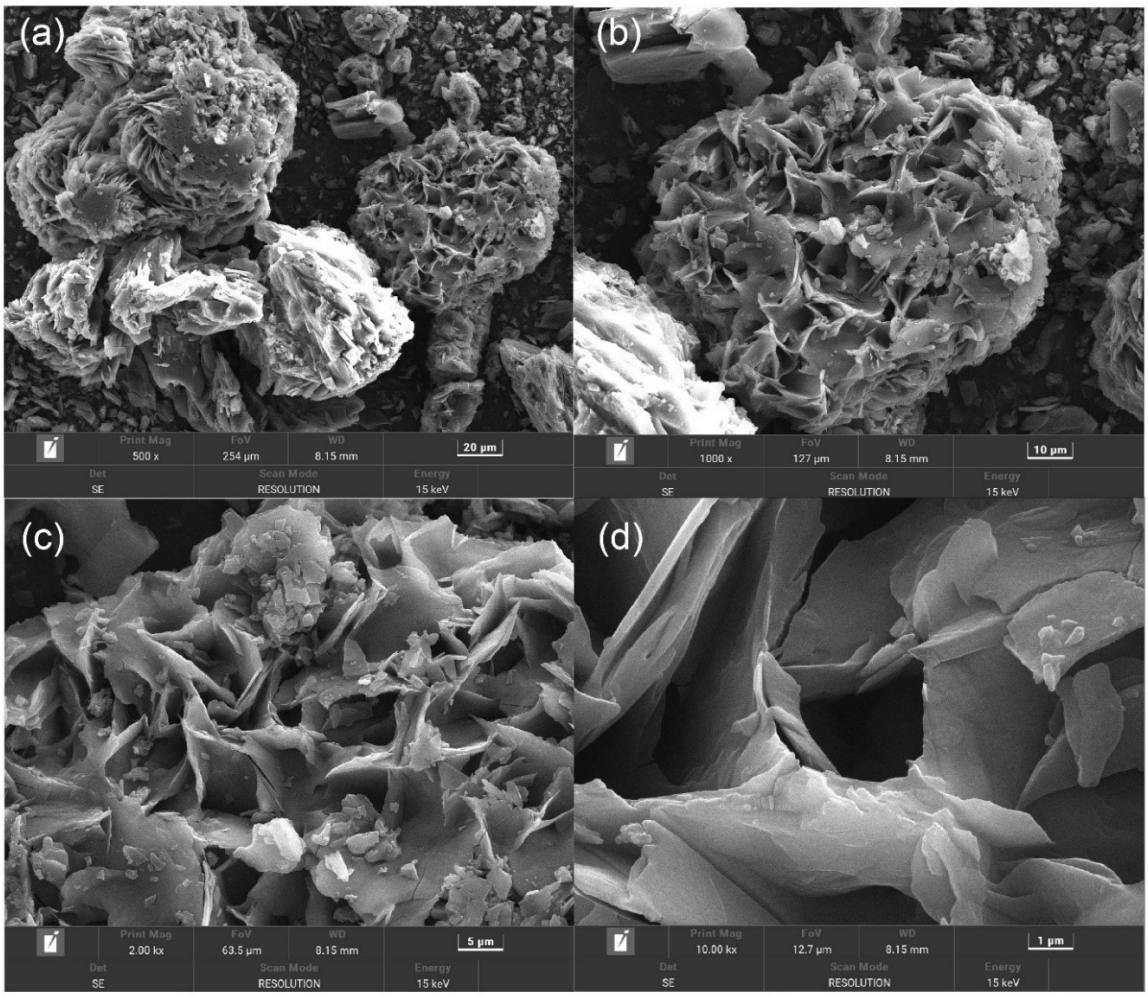


Figure S11. Scanning electron micrographs of **TrPEF$_2$-IPA** at different magnifications.

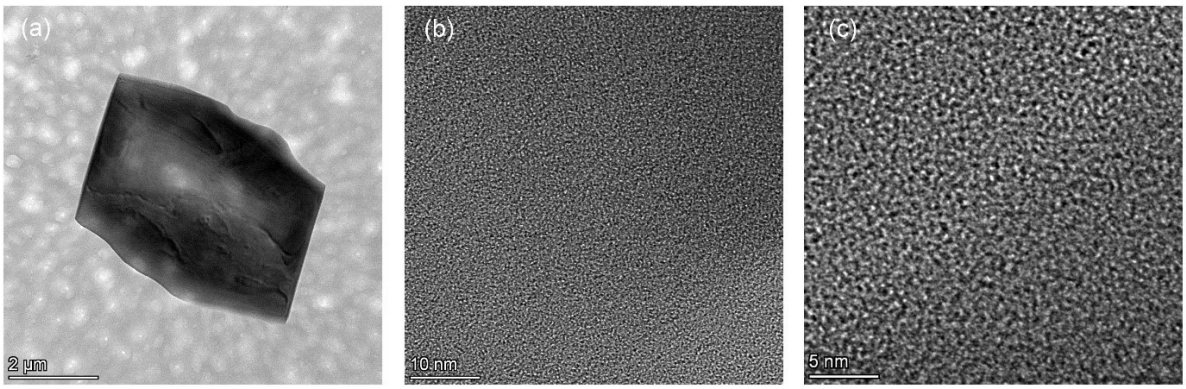


Figure S12. High-resolution transmission electron micrographs of **TrPEF$_2$-IPA** at different magnifications.

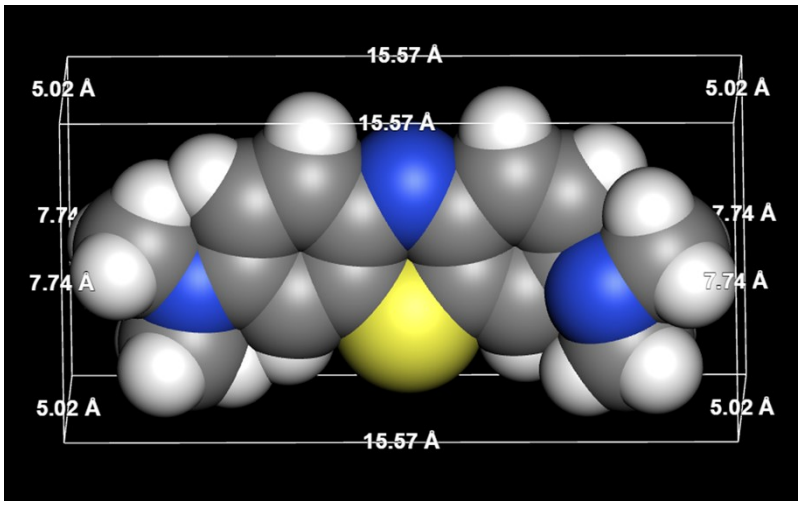


Figure S13. Modelled structure of methylene blue (MB) showing its dimensions.

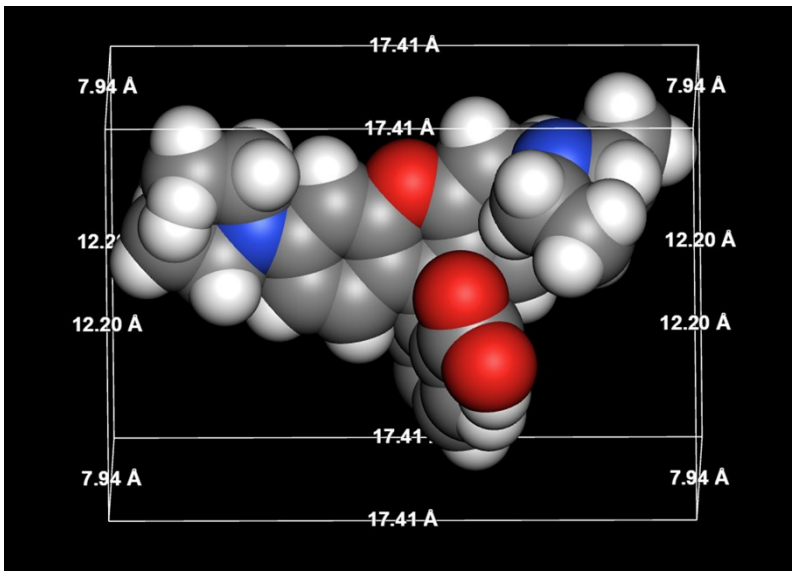


Figure S14. Modelled structure of rhodamine B (RhB) showing its dimensions.

Table S2. Surface charges and pH values of **TrPEF$_2$-IPA**, MB, RhB, **TrPEF$_2$-IPA**/MB mixture and **TrPEF$_2$-IPA**/RhB mixture in water.

	TrPEF$_2$-IPA	**Methylene Blue (MB)**	**Rhodamine B (RhB)**	**TrPEF$_2$-IPA/MB**	**TrPEF$_2$-IPA/RhB**
Surface charge	–33 mV	–13.6 mV	–16.8 mV	–20.8 mV	–20.3 mV
pH value	5.98	5.73	5.90	6.61	6.25

Single crystal data

Table S3. Crystal data and structural refinement for the single crystal of **TrPEF$_2$-IPA**.

Formula	$C_{28}H_{18}F_2O_4 \cdot C_2H_6O$	**Z**	2
Formula weight	502.49	μ / mm^{-1}	0.10
Temperature / K	192.99	**F(000)**	524
Crystal system	triclinic	**Crystal size / mm^3**	0.16 × 0.16 × 0.12
Space group	*P*-1	**Radiation**	MoKα (λ = 0.71073 Å)
a / Å	9.6027(19)	**Reflections collected / independent / observed**	29719 / 5752 / 3084
b / Å	9.943(2)		
c / Å	14.283(3)	D_x / g cm^{-3}	1.291
α / °	95.747(7)	R_{int}	0.083
β / °	98.450(7)	**Goodness-of-fit on F^2**	1.016
γ / °	104.466(5)	R_1,[a] wR_2[b] [$I \geq 2\sigma(I)$]	R_1 = 0.0536, wR_2 = 0.1107
Volume / Å^3	1292.8(5)	R_1, wR_2 [all data]	R_1 = 0.1330, wR_2 = 0.1364

[a] $R_1 = \Sigma||F_o| - |Fc||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[^2(F_o)^2 + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

Table S4. Bond lengths for the single crystal of **TrPEF$_2$-IPA**.

Atom	Atom	Length / Å	Atom	Atom	Length / Å
F1	C26	1.365(2)	C10	C11	1.392(3)
F2	C20	1.369(2)	C11	C12	1.402(3)
O1	C7	1.217(2)	C16	C17	1.496(3)
O2	C7	1.314(2)	C16	C23	1.497(3)
O3	C8	1.323(2)	C17	C22	1.398(3)
O4	C8	1.209(2)	C17	C18	1.404(3)
C1	C2	1.394(3)	C18	C19	1.397(3)
C1	C6	1.396(2)	C19	C20	1.364(3)
C1	C7	1.495(3)	C20	C21	1.375(3)
C2	C3	1.402(2)	C21	C22	1.389(3)
C3	C4	1.395(2)	C23	C24	1.394(3)
C3	C9	1.492(3)	C23	C28	1.398(3)
C4	C5	1.399(3)	C24	C25	1.383(3)
C5	C6	1.393(3)	C25	C26	1.380(3)
C5	C8	1.494(3)	C26	C27	1.371(3)
C9	C10	1.397(3)	C27	C28	1.385(3)
C9	C14	1.400(3)			

Table S5. Bond angles for the single crystal of **TrPEF$_2$-IPA**.

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
C2	C1	C6	119.97(17)	C11	C12	C15	119.52(17)
C2	C1	C7	118.23(17)	C16	C15	C12	128.83(18)
C6	C1	C7	121.75(17)	C15	C16	C17	119.31(17)
C1	C2	C3	121.55(17)	C15	C16	C23	122.39(18)
C4	C3	C2	117.57(17)	C17	C16	C23	118.20(16)
C4	C3	C9	121.33(16)	C22	C17	C18	117.75(19)
C2	C3	C9	121.10(16)	C22	C17	C16	121.58(18)
C3	C4	C5	121.57(17)	C18	C17	C16	120.64(18)
C6	C5	C4	119.92(17)	C19	C18	C17	120.7(2)
C6	C5	C8	118.80(17)	C20	C19	C18	119.1(2)
C4	C5	C8	121.28(17)	C19	C20	F2	118.8(2)
C5	C6	C1	119.42(17)	C19	C20	C21	122.4(2)
O1	C7	O2	123.96(18)	F2	C20	C21	118.8(2)
O1	C7	C1	121.64(19)	C20	C21	C22	118.5(2)
O2	C7	C1	114.40(17)	C21	C22	C17	121.5(2)
O4	C8	O3	123.51(19)	C24	C23	C28	118.46(18)
O4	C8	C5	123.96(18)	C24	C23	C16	121.10(17)
O3	C8	C5	112.53(18)	C28	C23	C16	120.44(17)
C10	C9	C14	117.73(18)	C25	C24	C23	121.0(2)
C10	C9	C3	121.19(17)	C26	C25	C24	118.4(2)
C14	C9	C3	121.07(17)	F1	C26	C27	118.8(2)
C11	C10	C9	121.36(18)	F1	C26	C25	118.3(2)
C10	C11	C12	120.66(18)	C27	C26	C25	122.87(19)
C13	C12	C11	117.77(18)	C26	C27	C28	118.1(2)
C13	C12	C15	122.66(18)	C27	C28	C23	121.26(19)

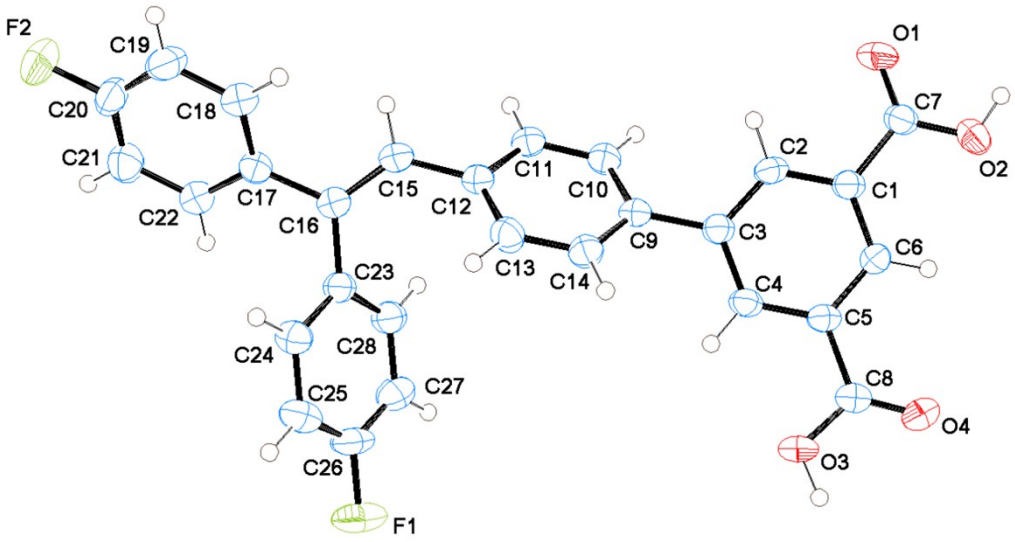


Figure S15. Molecular structure of an independent molecule of **TrPEF$_2$-IPA** with the atomic numbering scheme. Solvent molecules are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Characterization of the compounds

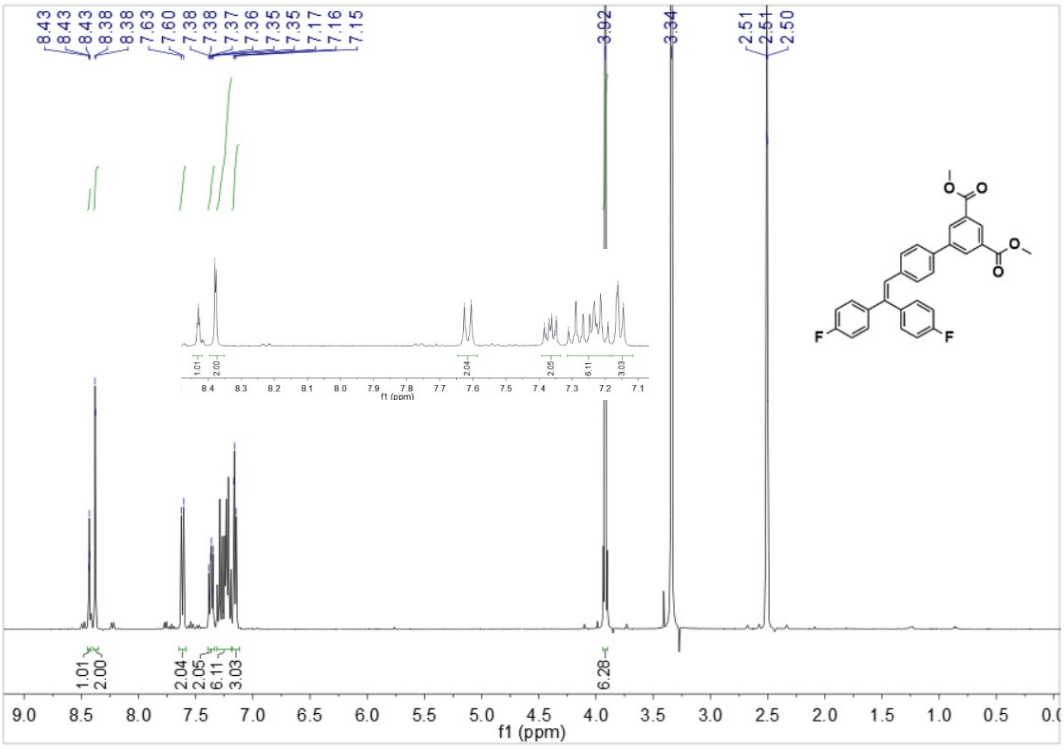


Figure S16. ^{1}H NMR spectrum of **TrPEF$_2$-DMI** in DMSO-d_6.

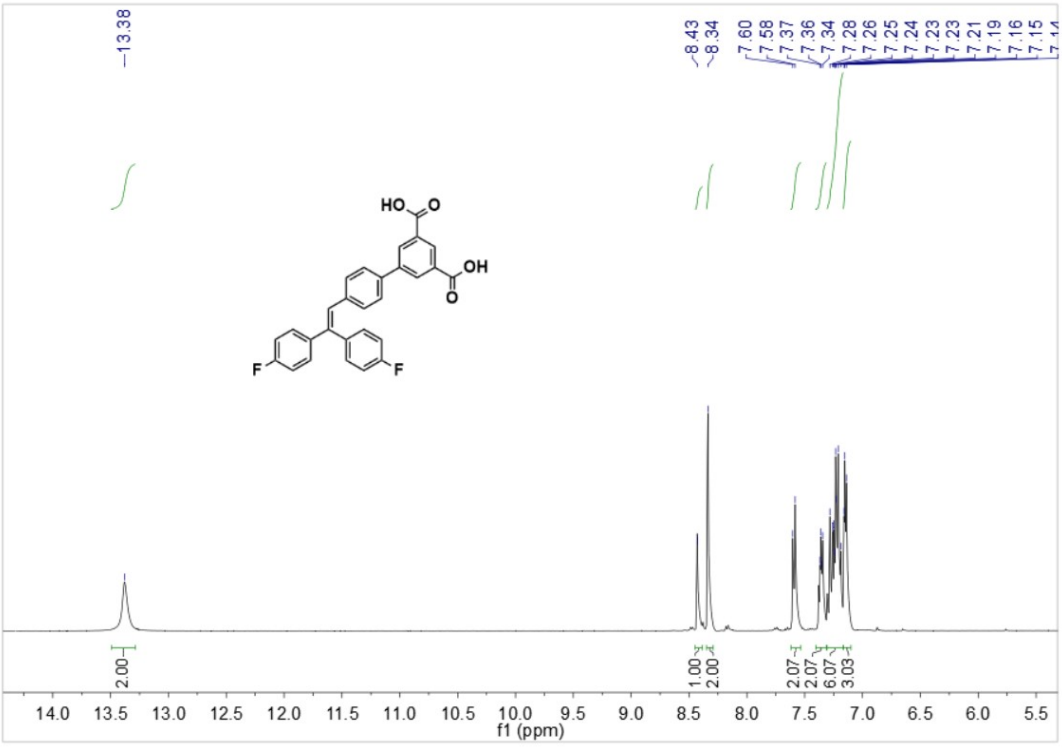


Figure S17. ^{1}H NMR spectrum of **TrPEF$_2$-IPA** in DMSO-d_6.

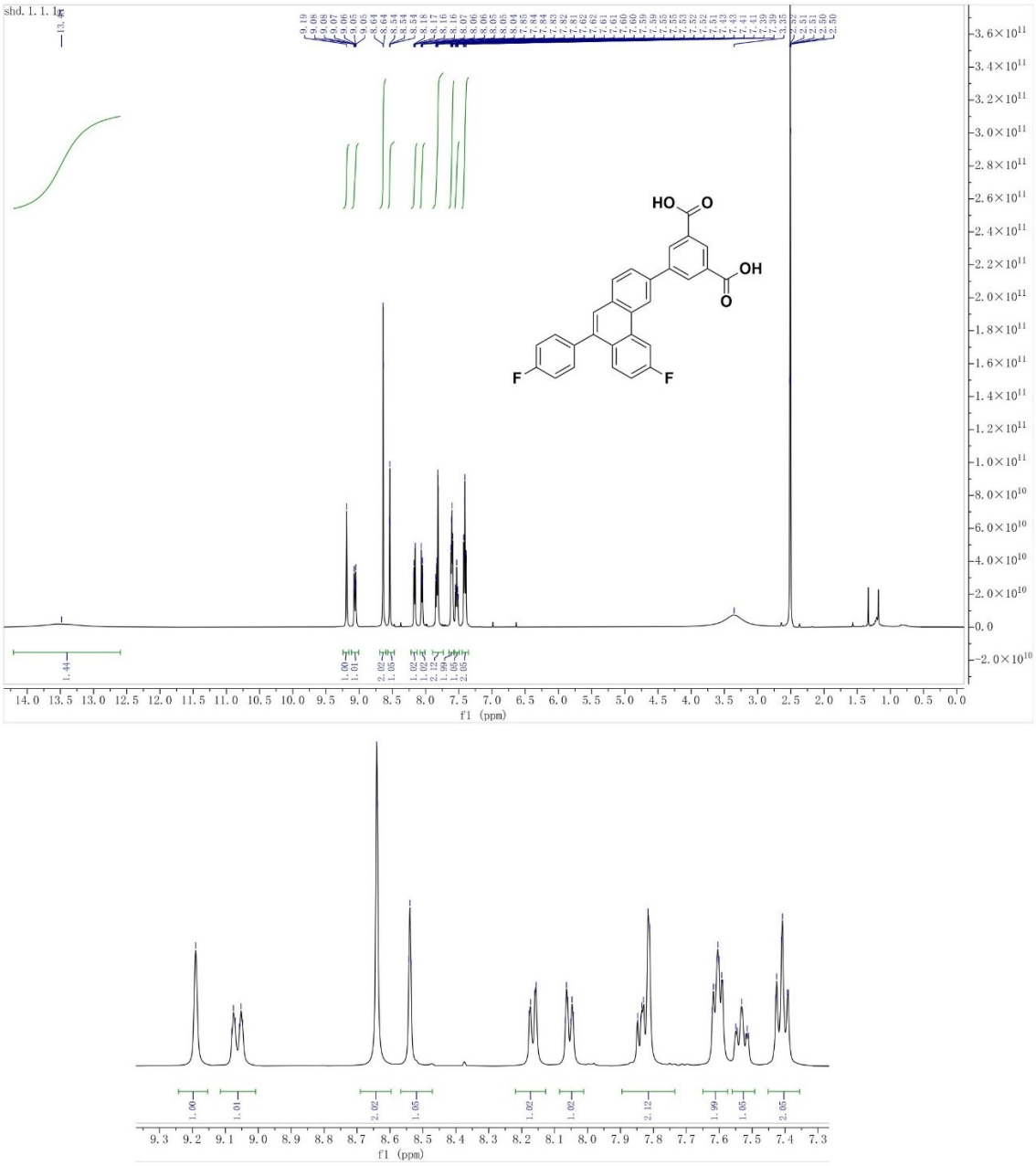


Figure S18. ^{1}H NMR spectrum of **TrPEF$_2$-IPA(O)** (in DMSO-d_6).

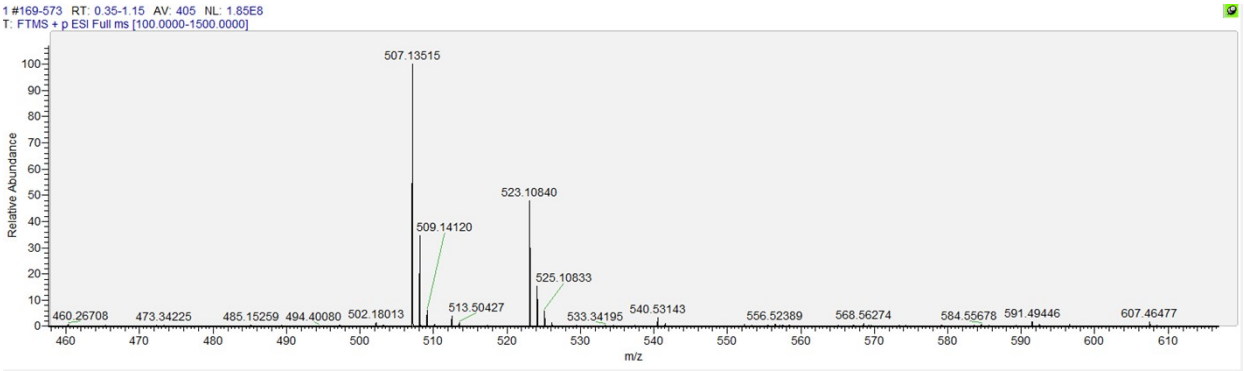


Figure S19. High resolution mass spectrum of **TrPEF$_2$-DMI**.

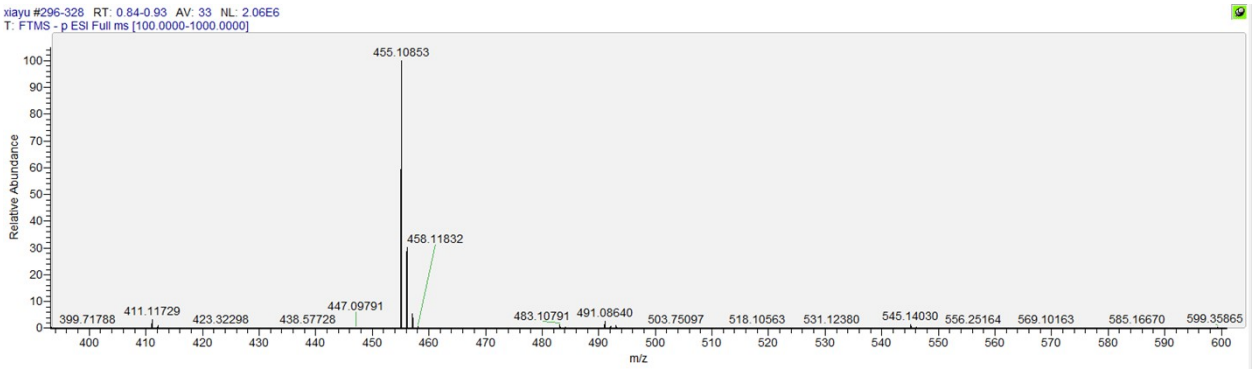


Figure S20. High resolution mass spectrum of **TrPEF$_2$-IPA**.

References

1 a) R. Baker, R. J. Sims, *Synthesis* **1981**, 2, 117; b) D. Ou, T. Yu, Z. Yang, T. Luan, Z. Mao, Y. Zhang, S. Liu, J. Xu, Z. Chi, M. R. Bryce, *Chem. Sci.* **2016**, 7, 5302; c) Tian Lu, Feiwu Chen, *J. Comput. Chem.* **2012,** 33, 580-592.

2 a) G. M. Sheldrick, *Acta Cryst.* **2015**, A71, 3; b) G. M. Sheldrick, *Acta Cryst.* **2015**, C71, 3.