Supporting Information

Switching excitons between the emissive and photochromic pathways in triphenylethylene system

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CONTENT

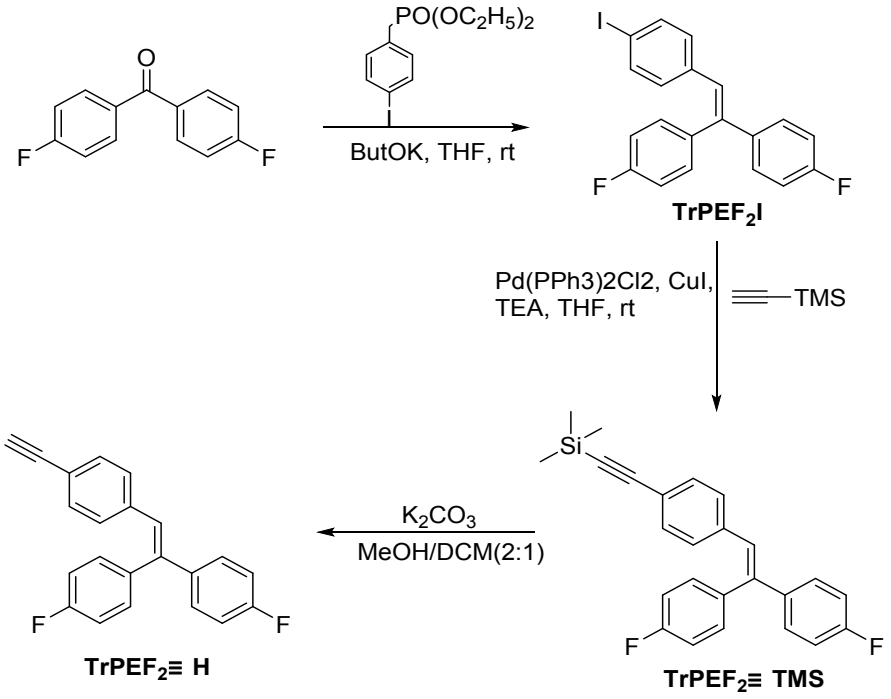
Experimental Procedures

General Methods

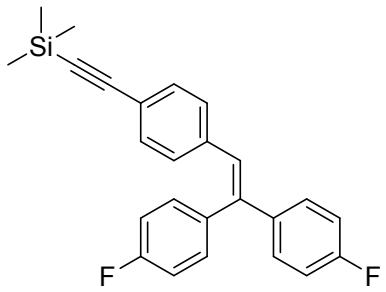
^{1}H NMR, ^{13}C NMR spectra for the materials were performed on a Bruker Avance NEO 500 Nuclear Magnetic Resonance Spectrometer with Chloroform-*d* as solvent and tetramethylsilane (TMS) as the internal standard. High resolution Mass spectra (MS) were recorded on an Exactive GC high resolution mass spectrometer. PXRD data were obtained on a Bruker X-ray diffractometer (D8 Advance) by using an Cu Kα (λ= 0.154184 nm) X-ray source in the circumstances of 40 kV and 30 mA, with a speed of 10° (2θ) per 1 min. Single-crystal X-ray analyses were collected using an Bruker D8 Venture X-ray Single Crystal Diffractometer with a (Cu) X-ray source. UV-vis absorption spectra and photoluminescence (PL) spectra were obtained on an Ocean Optic QE 65Pro spectrometer with Ocean Optic reflection probes R600-125F, respectively. TD-DFT calculations at B3LYP functional with 6-311G* basis set level were performed based on single crystal structure in Gaussian 09 software on the grounds of previous literatures[1, 2].

Materials and syntheses

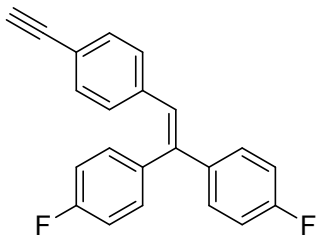
The compounds $TrPEF_2$≡TMS and $TrPEF_2$≡H were synthesized according to the synthetic routes described in Scheme S1. The details of the synthetic procedure for $TrPEF_2I$ was according to previous literature[3] All the final compounds were characterized by ^{1}H NMR spectroscopy, high-resolution EI mass spectroscopy. All regents and solvents were purchased from Aladdin, Titan or Adamas, and were used as received.



Scheme S1 Synthetic routes for $TrPEF_2I$, $TrPEF_2$≡TMS and $TrPEF_2$≡H

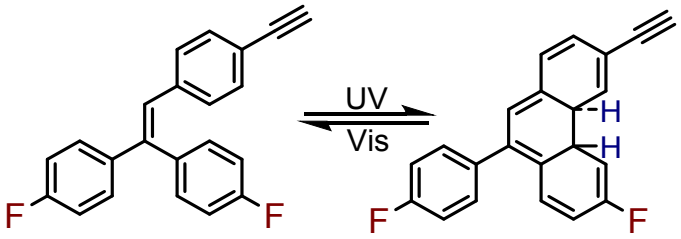


TrPEF$_2$≡TMS: To a mixture of TrPEF$_2$I (2.50 g, 5.98 mmol), CuI (56.92 mg) and Pd(PPh$_3$)$_2$Cl$_2$ (350 mg, 0.5 mmol) in degassed THF (40 ml) and Et$_3$N (10 ml) under an argon atmosphere was added trimethylsilylacetylene (8.97 mmol) in a dropwise manner. The resulting mixture was stirred at ambient temperature for 20 hours. The mixture was then filtered, and the filtrate was poured into water and extracted with CH_2Cl_2. Further purification was done by column chromatography on silica gel with hexane as eluent. Solvent removal yielded a light white solid. Yield: 1.82 g (78 %). ^{1}H NMR (500 MHz, CD_3Cl, 298 K, relative to Me_4Si): δ = 0.23 (s, 9H), 6.85 (s, 1H), 6.93 (d, 7.8 Hz, 2H), 6.69-7.03 (m, 4H), 7.11-7.14 (m, 2H), 7.24-7.28 (m, 4H); High solution EI-MS: m/z found: 388.1449 $[M]^+$; calcd for $C_{25}H_{22}F_2Si$: 388.1459.



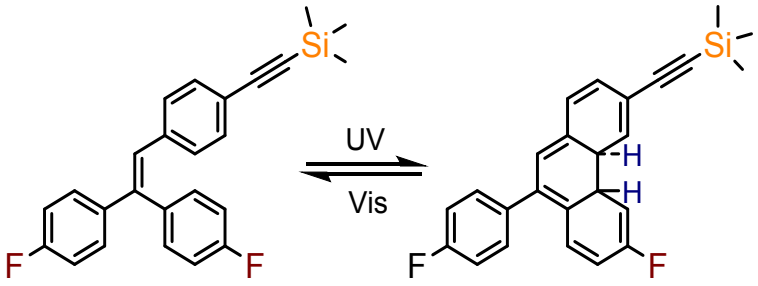
TrPEF$_2$≡H: To a solution of TrPEF$_2$≡TMS (1.00 g, 2.57 mmol) in methanol/CH_2Cl_2 (30 ml, v/v = 2:1) was added K_2CO_3 (1.07 g, 7.72 mmol) and stirred at room temperature for 12 h. The resulting mixture was added to water and extracted with ethyl ether. The solvent was removed and the residue was further purified by silica gel column chromatography. Solvent removal yielded a light white solid. Yield: 0.65 g (80 %). ^{1}H NMR (500 MHz, CD_3Cl, 298 K, relative to Me_4Si): δ = 3.07 (s, 1H), 6.86 (s, 1H), 6.95 (d, 8.0 Hz, 2H), 6.99-7.04 (m, 6H), 7.12-7.15 (m, 2H), 7.24-7.28 (m, 2H); High solution EI-MS: m/z found: 316.1054 $[M]^+$; calcd for $C_{22}H_{14}F_2$: 316.1064.

Supplementary Information



$TrPEF_2$≡H **$TrPEF_2$≡ H(c)**

Scheme S2 Schematic diagram of photochromic mechanism of $TrPEF_2$≡H



$TrPEF_2$≡TMS **$TrPEF_2$≡TMS(c)**

Scheme S3 Schematic diagram of photochromic mechanism of $TrPEF_2$≡TMS

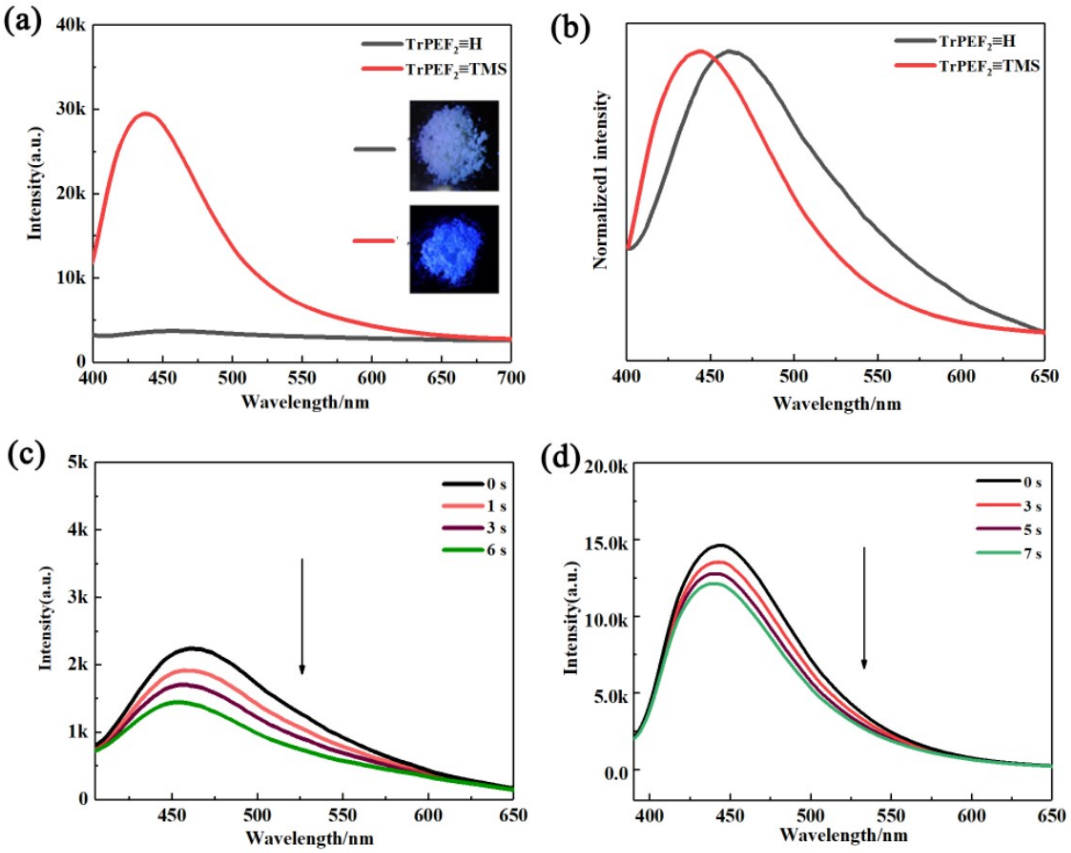


Figure S1 (a) Emission spectra of $TrPEF_2$≡H and $TrPEF_2$≡TMS in powder states, the inset shows the photographs of the $TrPEF_2$≡H and $TrPEF_2$≡TMS upon 365 nm UV irradiation. (b) Normalized emission spectra of $TrPEF_2$≡H and $TrPEF_2$≡TMS in powder states. Emission spectra of (c) $TrPEF_2$≡H and (d) $TrPEF_2$≡TMS respond to UV irradiation time.

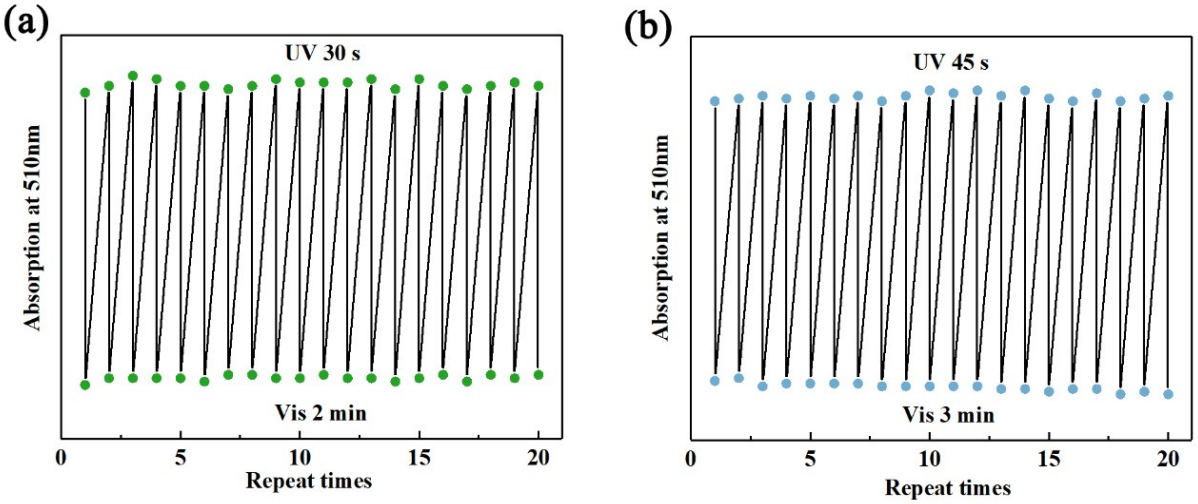


Figure S2 (a) Recycling of the photochromic and recovery processes of compound $TrPEF_2$≡TMS in powder state as a function of exposure time, irradiating under the UV-light (365 nm) and white-light for 30 seconds and 2 minutes, respectively. (b) Recycling of the photochromic and recovery process of compound $TrPEF_2$≡H in powder state as a function of exposure time, irradiating under the UV-light (365 nm) and white-light for 45 seconds and 3 minutes, respectively.

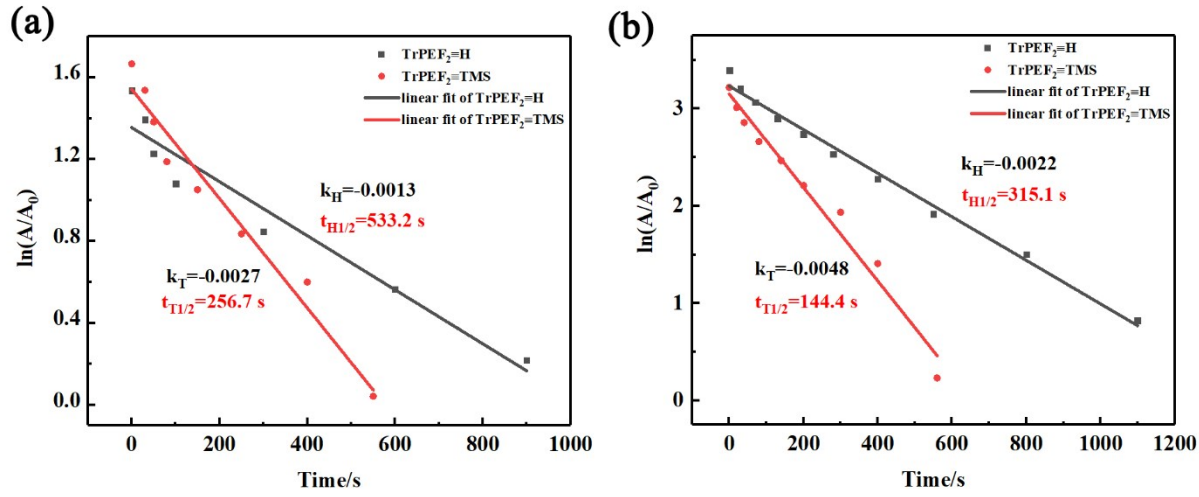


Figure S3 First-order kinetic plots for decoloring of $TrPEF_2$≡TMS and $TrPEF_2$≡H (a) in solutions and (b) in films at the wavelength of 460 nm. ($A=A_0 \exp(-kt)$, A_0 is the absorbance before irradiation (t = 0), and A is the absorbance at the moment of irradiation time)

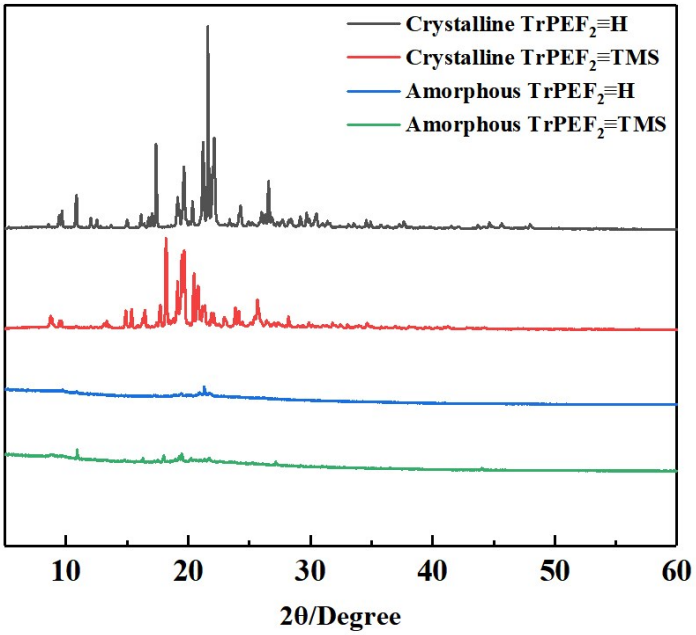


Figure S4 pXRD spectra of $TrPEF_2$≡H and $TrPEF_2$≡TMS in solid state.

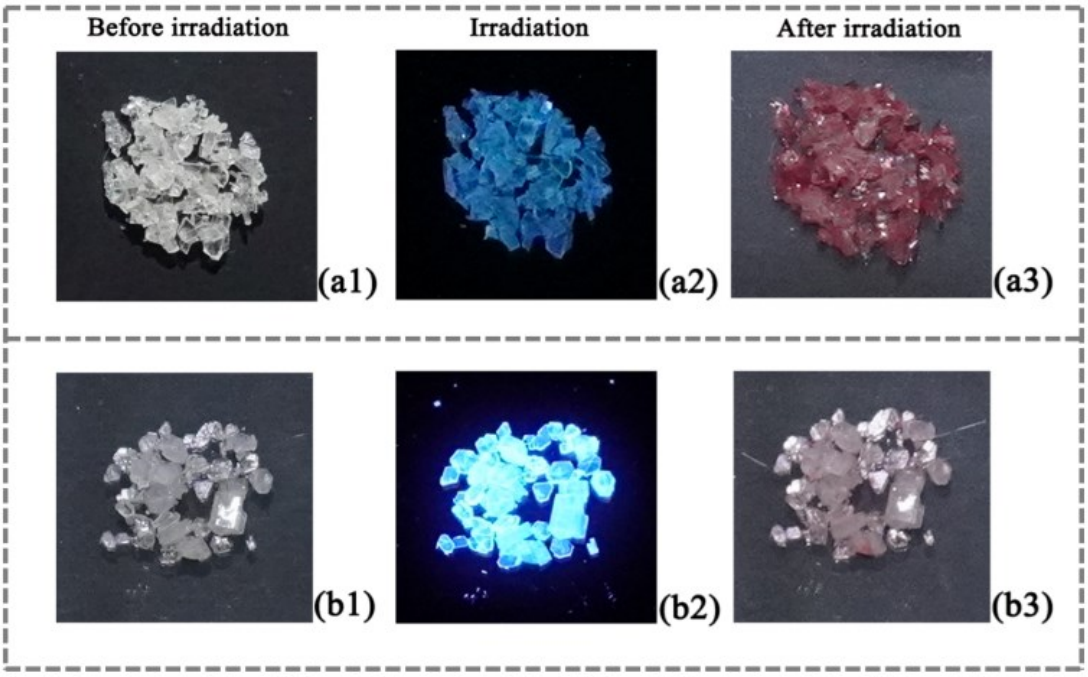


Figure S5 Photographs of $TrPEF_2$≡H (a1) before irradiation, (b1) under irradiation and (c1) after irradiation; and of $TrPEF_2$≡TMS (a2) before irradiation, (b2) under irradiation and (c2) after irradiation. Excitation source was 365 nm under ambient conditions.

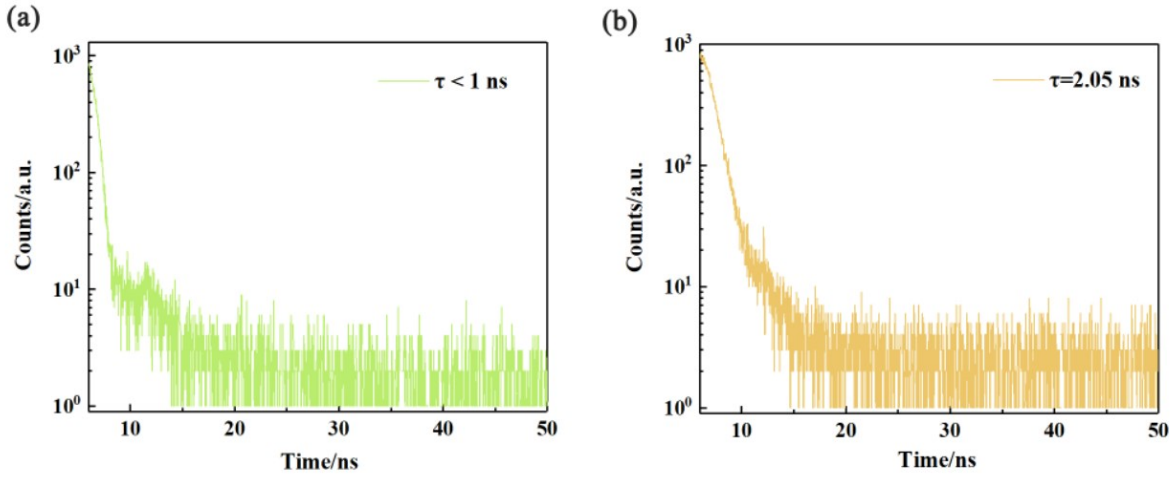


Figure S6 The fluorescence decays of (a) $TrPEF_2{\equiv}H$ and (b) $TrPEF_2{\equiv}TMS$ in solid states under 365 nm excitation at room temperature.

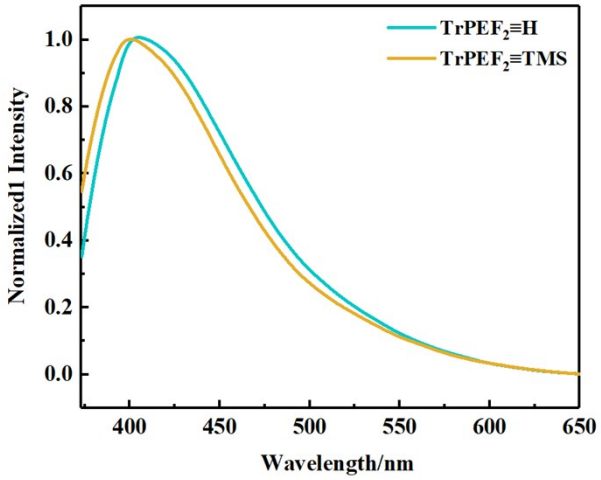


Figure S7 Emission spectra of $TrPEF_2{\equiv}H$ and $TrPEF_2{\equiv}TMS$ doped PMMA films with the doping concentration of 5 wt%. Excitation at 365 nm.

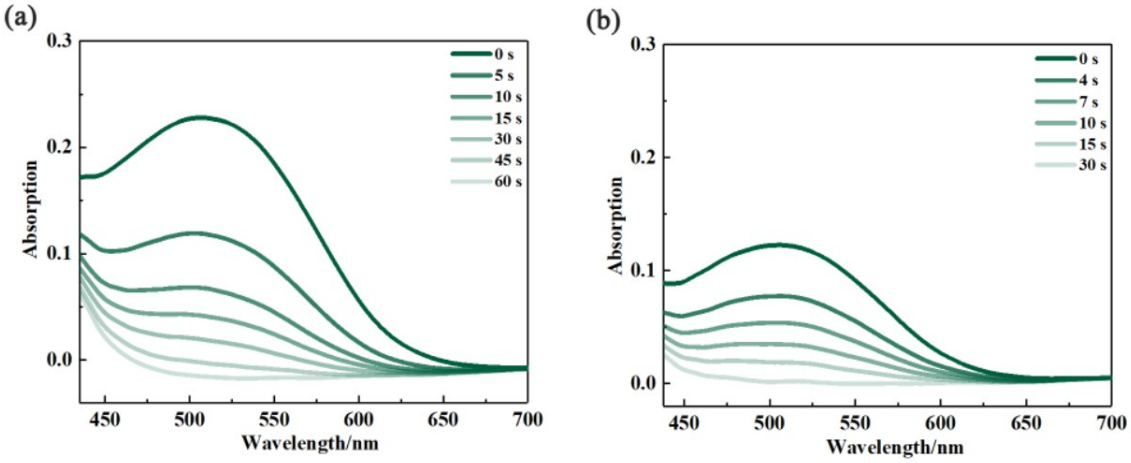


Figure S8 Time dependent UV-vis absorption spectra of compound (a) $TrPEF_2{\equiv}H$ and (b) $TrPEF_2{\equiv}TMS$ powders during the photochromic bleaching process.

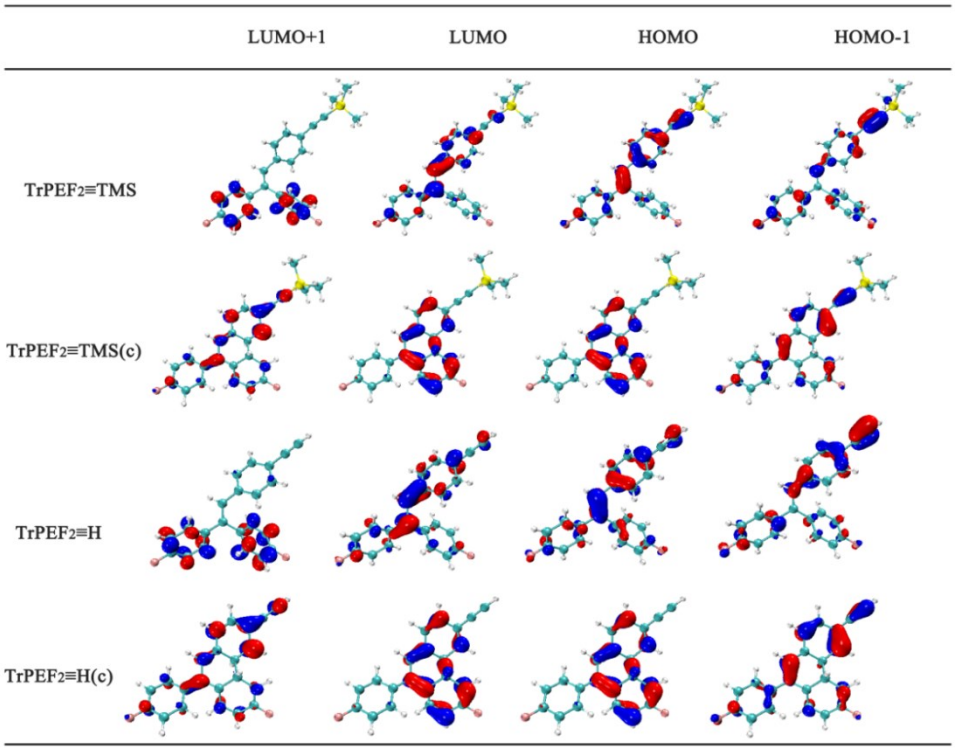


Figure S9 HOMOs and LUMOs of E-products of $TrPEF_2$≡TMS, $TrPEF_2$≡TMS(c), $TrPEF_2$≡H and $TrPEF_2$≡H(c) calculated with B3LYP/6-311+G(d,p) level.

Table S1 Calculated HOMO, LUMO distributions, energy levels, energy gap and oscillator strength (f value) for $TrPEF_2$≡TMS, $TrPEF_2$≡TMS(c), $TrPEF_2$≡H and $TrPEF_2$≡H(c).

Sample	E_{LUMO+1}(eV)	E_{LUMO}(eV)	E_{HOMO}(eV)	E_{HOMO-1}(eV)	Eg(eV)	oscillator strength (f value)
$TrPEF_2$≡TMS	-1.05	-1.84	-5.89	-6.94	4.05	1.0032
$TrPEF_2$≡TMS(c)	-1.22	-2.55	-4.43	-5.80	1.88	0.0714
$TrPEF_2$≡H	-1.08	-1.90	-6.01	-7.13	4.11	0.6594
$TrPEF_2$≡H(c)	-1.22	-2.58	-4.47	-5.88	1.89	0.0696

Single crystal data of $TrPEF_2$≡TMS and $TrPEF_2$≡H

Single-crystal X-ray analyses for $TrPEF_2$≡TMS and $TrPEF_2$≡H were performed on an Oxford Diffraction Gemini S Ultra X-ray single-crystal diffractometer with graphite-monochromatized Cu-Kα

radiation (λ = 1.54184 Å). The structure was solved with Olex2 v1.2 program and expanded using Fourier techniques. Non-H atoms of this compound was further refined with anisotropic thermal parameters. The hydrogen atoms were added in idealized positions and refined with fixed geometry according to their carrier atoms.

Table S2. Crystal data for $TrPEF_2{\equiv}H$;

Formula	$C_{22}H_{14}F_2$	***γ*/°**	95.6220(10)°
Formula weight	316.33	**Volume/Å^3**	1646.92(9)
Temperature/K	150.0	**ρ_{calc}/g cm^{-3}**	1.2758
Crystal system	triclinic	**μ/mm^{-1}**	0.724
Space group	*P-1*	**F(000)**	658.2
a/Å	9.6755(3)	**Crystal size/mm^3**	0.5 × 0.2 × 0.1
b/Å	10.4719(3)	**Reflections collected**	30043
c/Å	17.0175(5)	**D_x/g cm^{-3}**	1.276
***α*/°**	97.5810(10)°	**Unique (R_{int})**	0.1374
***β*/°**	90103.5160(10)°		

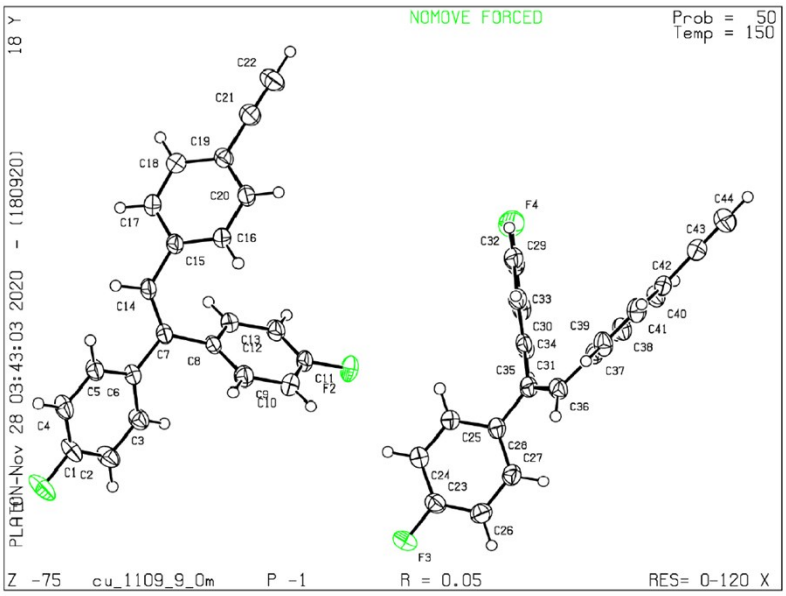


Figure S10 Single crystal structure of $TrPEF_2{\equiv}H$.

Table S3 Bond distances (Å) for $TrPEF_2{\equiv}H$

Atom	Atom	Length/Å	Atom	Atom	Length/Å

F3	C23	1.3591(16)	C35	C36	1.347(2)
F2	C11	1.3601(14)	C3	C2	1.383(2)
F1	C1	1.3625(16)	C12	C11	1.373(2)
F4	C29	1.3569(17)	C14	C15	1.4709(19)
C8	C13	1.3955(18)	C9	C10	1.3914(19)
C8	C7	1.4947(16)	C15	C17	1.397(2)
C8	C9	1.3915(19)	C42	C41	1.3980(19)
C13	C12	1.3898(18)	C42	C43	1.4348(19)
C34	C35	1.4904(19)	C5	C4	1.381(2)
C34	C33	1.3974(19)	C33	C32	1.384(2)
C34	C31	1.3977(19)	C18	C17	1.378(2)
C28	C35	1.4846(18)	C18	C19	1.399(2)
C28	C27	1.3977(19)	C26	C27	1.386(2)
C28	C25	1.4011(19)	C26	C23	1.376(2)
C6	C7	1.4865(18)	C30	C31	1.388(2)
C6	C3	1.4016(18)	C30	C29	1.375(2)
C6	C5	1.4008(18)	C39	C41	1.382(2)
C40	C38	1.3781(19)	C24	C23	1.379(2)
C40	C42	1.3983(19)	C24	C25	1.3842(19)
C7	C14	1.3482(19)	C4	C1	1.377(2)
C38	C37	1.4021(18)	C11	C10	1.375(2)
C20	C16	1.378(2)	C21	C19	1.435(2)
C20	C19	1.398(2)	C21	C22	1.184(2)
C16	C15	1.4070(18)	C32	C29	1.378(2)
C37	C36	1.4707(18)	C2	C1	1.376(2)
C37	C39	1.3994(19)	C43	C44	1.183(2)

Table S4 Bond Angles (°) for $TrPEF_2{\equiv}H$

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C7	C8	C13	119.46(12)	C43	C42	C40	120.04(13)
C9	C8	C13	118.61(12)	C43	C42	C41	121.23(13)

C9	C8	C7	121.92(12)	C4	C5	C6	121.83(13)
C12	C13	C8	121.47(13)	C32	C33	C34	121.50(13)
C33	C34	C35	120.73(12)	C19	C18	C17	120.05(13)
C31	C34	C35	120.98(12)	C23	C26	C27	118.37(13)
C31	C34	C33	118.29(13)	C29	C30	C31	118.52(14)
C27	C28	C35	121.57(12)	C30	C31	C34	120.90(14)
C25	C28	C35	120.36(12)	C41	C39	C37	121.33(13)
C25	C28	C27	118.05(13)	C26	C27	C28	121.34(13)
C3	C6	C7	121.25(11)	C25	C24	C23	118.40(13)
C5	C6	C7	121.18(11)	C1	C4	C5	118.15(13)
C5	C6	C3	117.54(12)	C18	C17	C15	122.01(13)
C42	C40	C38	120.46(13)	C26	C23	F3	118.87(12)
C6	C7	C8	117.79(11)	C24	C23	F3	118.59(12)
C14	C7	C8	121.83(12)	C24	C23	C26	122.54(13)
C14	C7	C6	120.30(11)	C12	C11	F2	118.15(14)
C37	C38	C40	121.35(12)	C10	C11	F2	118.75(13)
C19	C20	C16	121.10(12)	C10	C11	C12	123.09(12)
C15	C16	C20	120.76(13)	C24	C25	C28	121.27(13)
C36	C37	C38	122.08(12)	C22	C21	C19	177.75(15)
C39	C37	C38	117.65(13)	C18	C19	C20	118.52(13)
C39	C37	C36	120.25(12)	C21	C19	C20	120.68(13)
C28	C35	C34	117.03(11)	C21	C19	C18	120.79(13)
C36	C35	C34	122.56(13)	C29	C32	C33	118.04(14)
C36	C35	C28	120.32(12)	C1	C2	C3	118.52(13)
C2	C3	C6	121.36(13)	C39	C41	C42	120.39(13)
C11	C12	C13	117.68(13)	C44	C43	C42	179.85(17)
C35	C36	C37	127.38(13)	C11	C10	C9	118.41(13)
C15	C14	C7	128.28(12)	C30	C29	F4	119.05(14)
C10	C9	C8	120.69(13)	C32	C29	F4	118.21(14)
C14	C15	C16	122.92(12)	C32	C29	C30	122.74(14)

C17	C15	C16	117.47(13)	C4	C1	F1	118.91(13)
C17	C15	C14	119.60(12)	C2	C1	F1	118.51(13)
C41	C42	C40	118.73(13)	C2	C1	C4	122.58(14)

Table S5 Crystal data for $TrPEF_2$≡TMS;

Formula	$C_{25}H_{22}F_2Si$	**γ/°**	90°
Formula weight	388.52	**Volume/Å^3**	2118.49(14)
Temperature/K	150.0	**ρ_{calc}/g cm^{-3}**	1.218
Crystal system	monoclinic	**μ/mm^{-1}**	1.176
Space group	*P*21	**F(000)**	816.0
a/Å	9.2475(4)	**Crystal size/mm^3**	0.5 × 0.2 × 0.1
b/Å	11.3110(4)	**Reflections collected**	26712
c/Å	20.2758	**D_x/g cm^{-3}**	1.218
α/°	90°	**Unique (R_{int})**	0.1479
β/°	92.685(2)°		

Table S6 Bond distances (Å) for $TrPEF_2$≡TMS

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Si1	C21	1.8481(16)	C17	C19	1.396(2)
Si1	C22	1.8549(17)	C6	C7	1.4903(19)
Si1	C23	1.8572(17)	C6	C4	1.402(2)
Si1	C24	1.8575(17)	C6	C5	1.396(2)
F2	C1	1.3612(17)	C7	C8	1.4905(19)
F1	C00Q	1.3638(18)	C8	C10	1.393(2)
C13	C14	1.474(2)	C1	C3	1.378(2)
C13	C7	1.347(2)	C1	C2	1.374(2)
C14	C15	1.4004(19)	C4	C2	1.387(2)
C14	C16	1.399(2)	C12	C00Q	1.372(2)
C15	C17	1.384(2)	C19	C20	1.436(2)
C9	C8	1.393(2)	C20	C21	1.206(2)
C9	C12	1.389(2)	C5	C3	1.393(2)
C18	C16	1.377(2)	C10	C11	1.384(2)

C18	C19	1.401(2)	C11	C00Q	1.370(3)

Table S7 Bond Angles (°) for $TrPEF_2{\equiv}TMS$

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C21	Si1	C22	109.30(8)	C9	C8	C7	120.90(12)
C21	Si1	C23	107.32(7)	C9	C8	C10	118.78(14)
C21	Si1	C24	106.27(8)	C10	C8	C7	120.17(13)
C22	Si1	C23	110.67(9)	F2	C1	C3	118.91(14)
C22	Si1	C24	111.62(8)	F2	C1	C2	118.41(14)
C23	Si1	C24	111.44(9)	C2	C1	C3	122.68(14)
C7	C13	C14	129.35(13)	C2	C4	C6	121.13(14)
C15	C14	C13	118.69(12)	C00Q	C12	C9	118.10(15)
C16	C14	C13	123.88(13)	C18	C19	C20	119.23(13)
C16	C14	C15	117.39(13)	C17	C19	C18	118.30(13)
C17	C15	C14	121.77(13)	C17	C19	C20	122.46(13)
C12	C9	C8	120.83(14)	C21	C20	C19	176.25(15)
C16	C18	C19	121.03(13)	C20	C21	Si1	172.85(13)
C15	C17	C19	120.24(13)	C3	C5	C6	121.20(14)
C4	C6	C7	119.40(13)	C1	C3	C5	118.21(14)
C5	C6	C7	122.37(13)	C1	C2	C4	118.48(14)
C5	C6	C4	118.21(14)	C11	C10	C8	120.89(15)
C18	C16	C14	121.20(13)	C00Q	C11	C10	118.35(15)
C13	C7	C6	120.56(13)	F1	C00Q	C12	118.34(16)
C13	C7	C8	124.32(13)	F1	C00Q	C11	118.62(15)
C6	C7	C8	114.93(11)	C11	C00Q	C12	123.04(15)

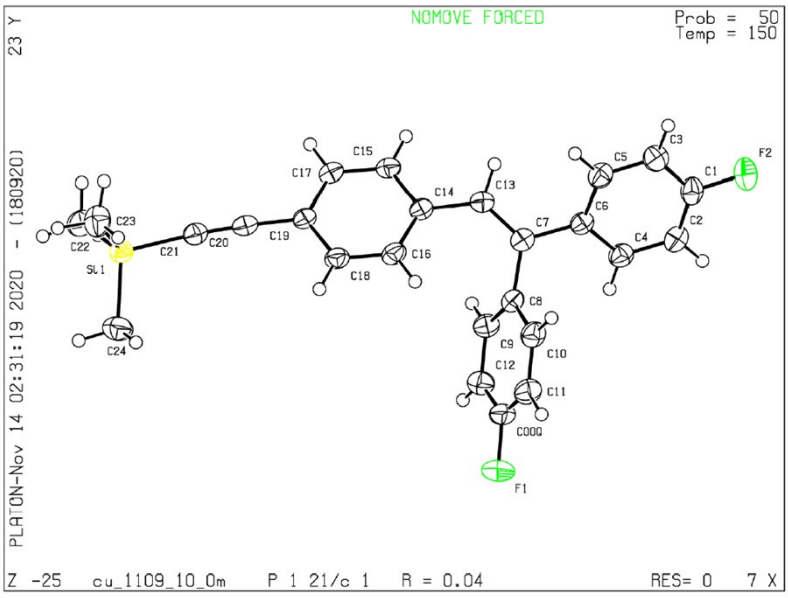


Figure S11 Single crystal structure of $TrPEF_2$≡TMS.

Characterization of chemical structure

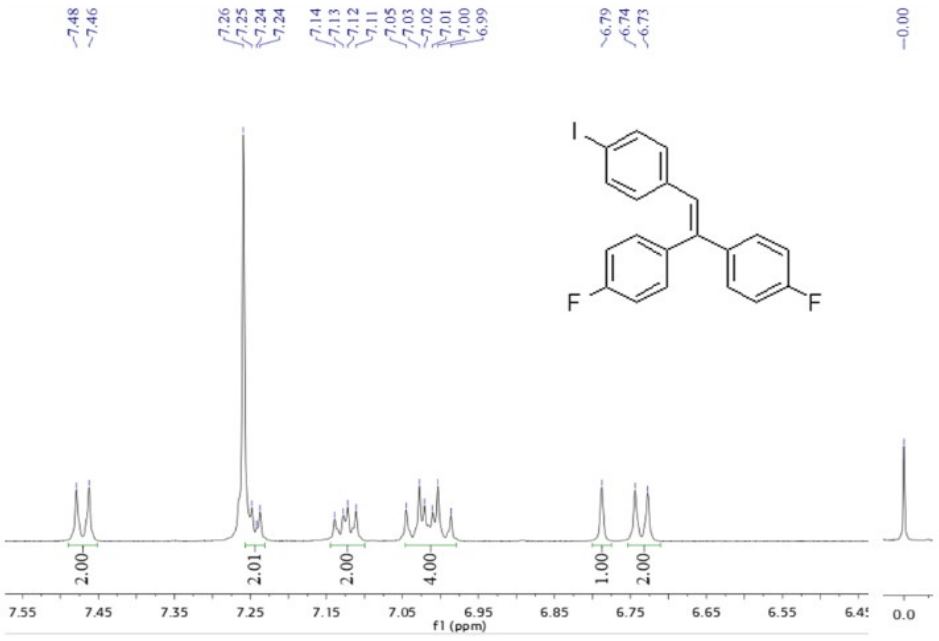


Figure S12 ^1H NMR spectrum of $TrPEF_2I$ (in Chloroform-*d*).

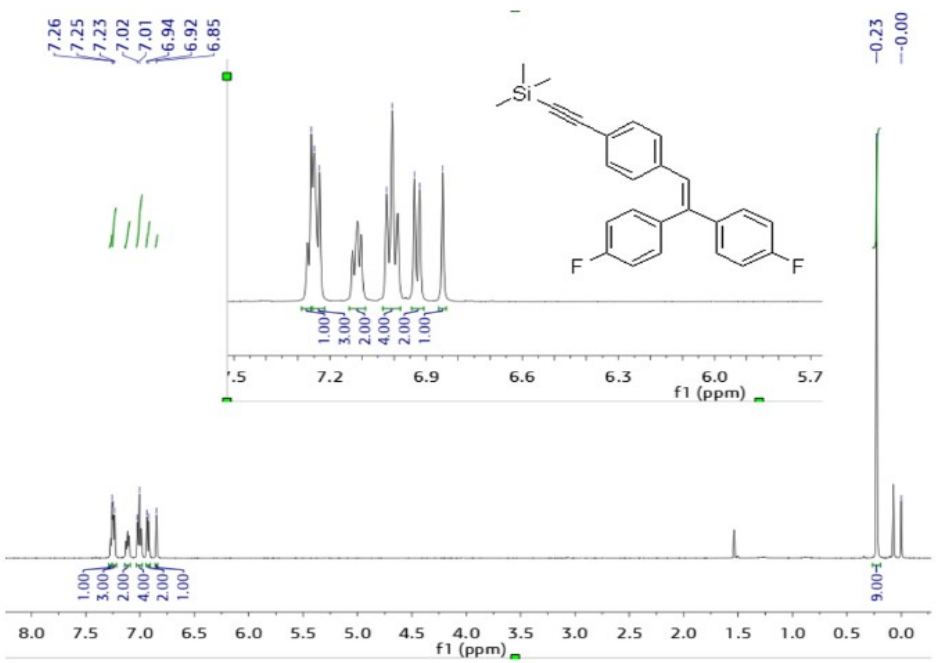


Figure S13 ^{1}H NMR spectrum of $TrPEF_2$≡TMS(in Chloroform-*d*).

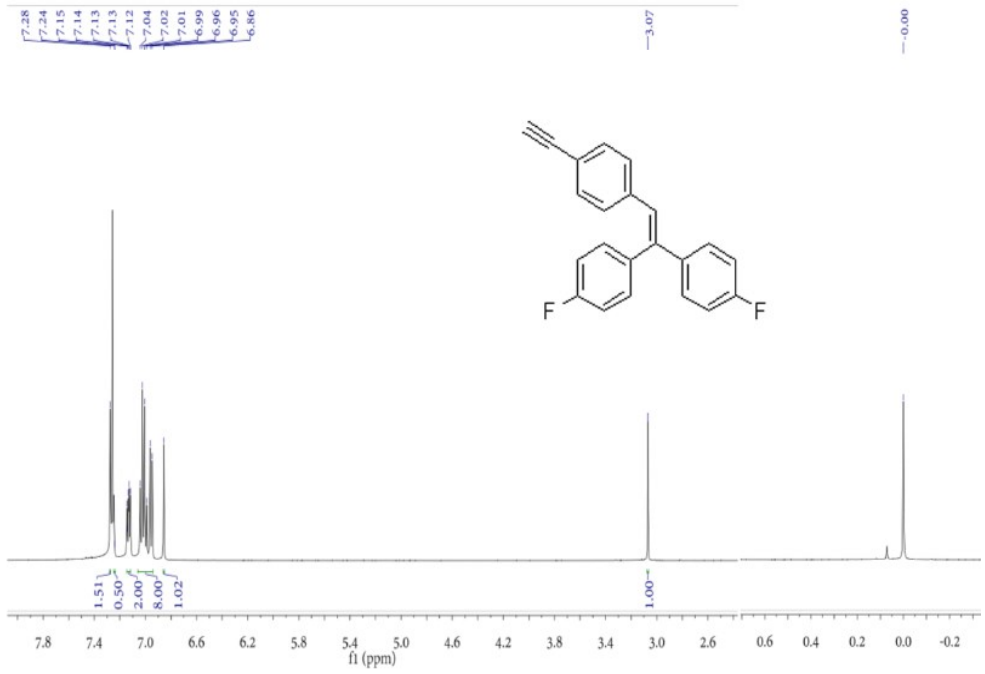


Figure S14 ^{1}H NMR spectrum of $TrPEF_2$≡H (in Chloroform-*d*).

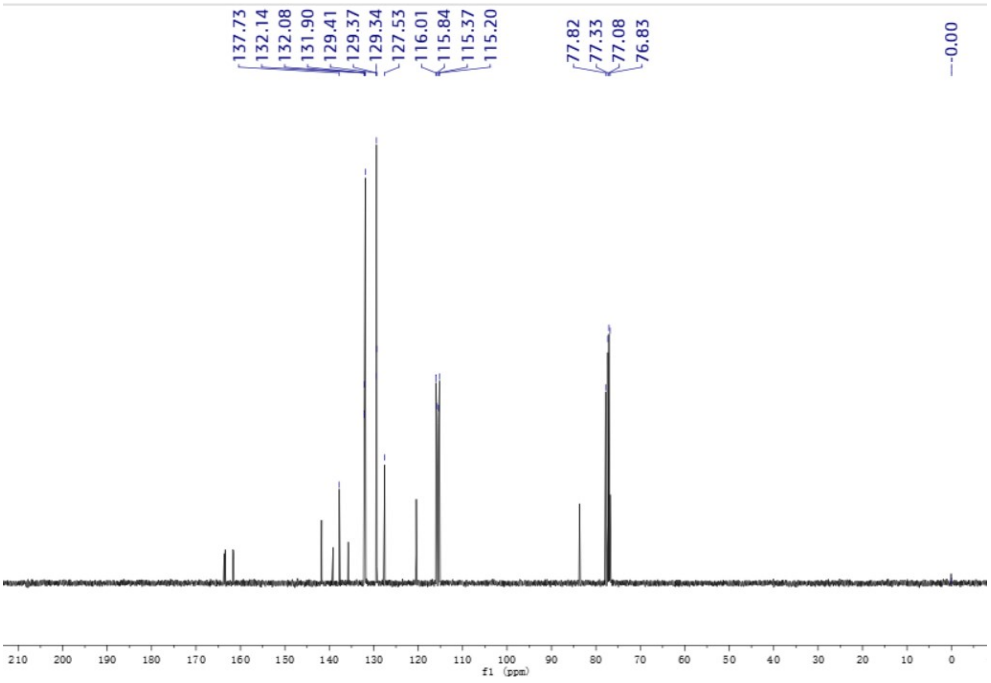


Figure S15 ^{13}C NMR spectrum of TrPEF$_2$≡H (in Chloroform-*d*).

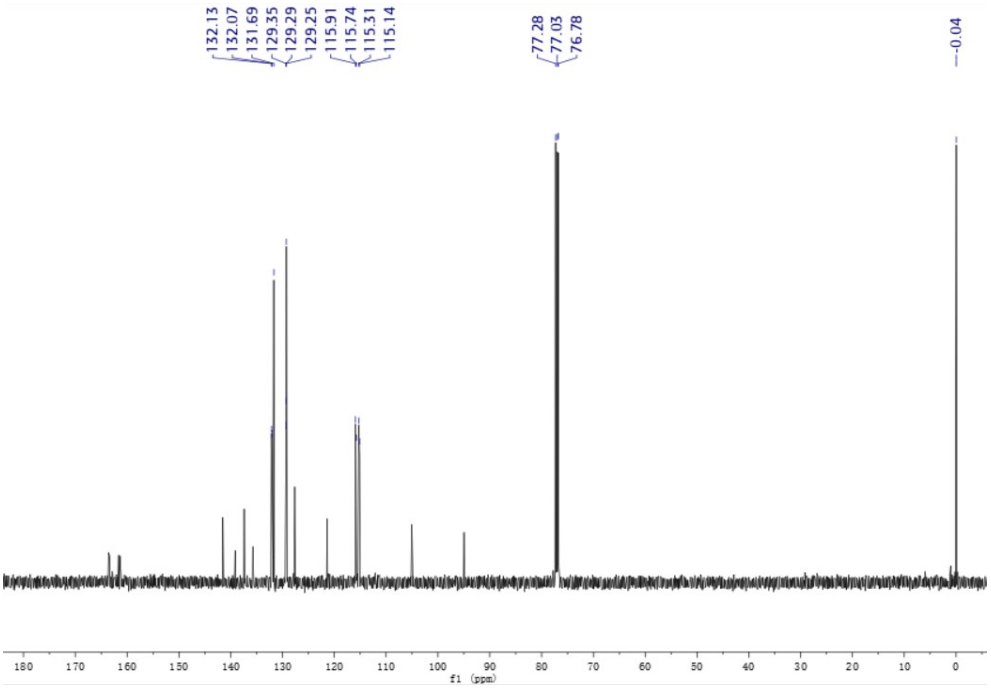


Figure S16 ^{13}C NMR spectrum of TrPEF$_2$≡TMS (in Chloroform-*d*).

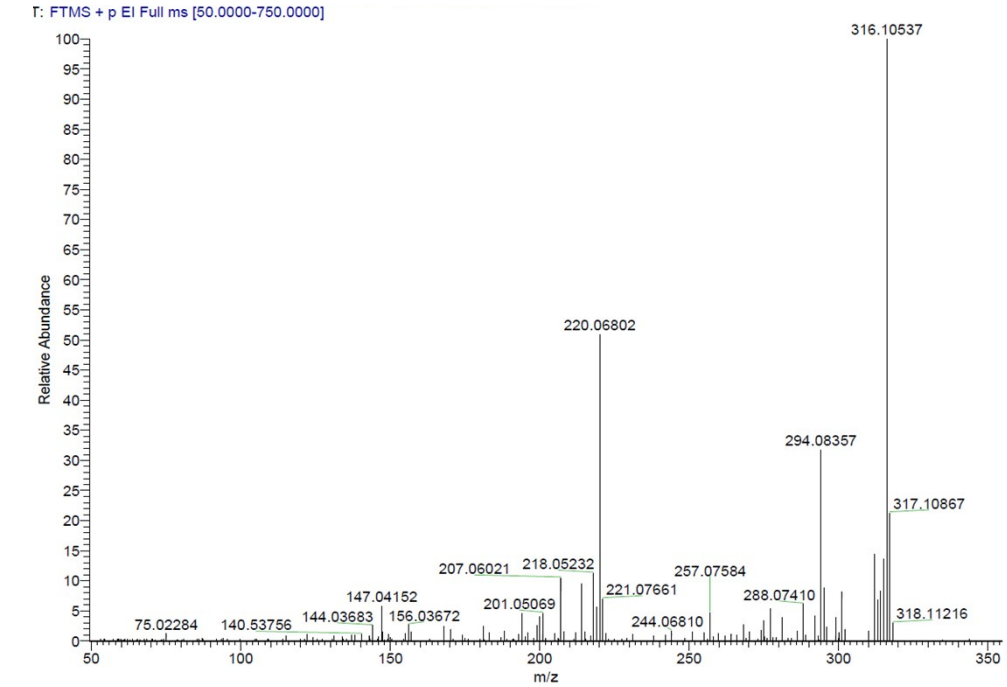


Figure S17 High resolution EI mass spectrum of compound $TrPEF_2{\equiv}H$.

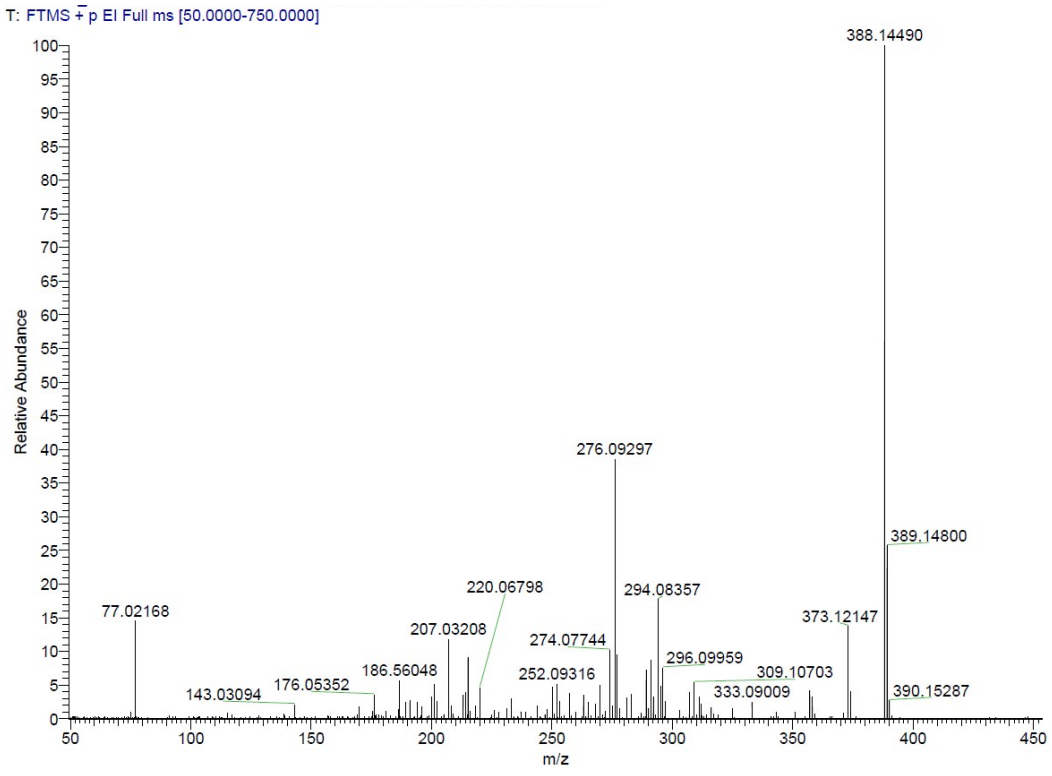


Figure S18 High resolution EI mass spectrum of compound $TrPEF_2{\equiv}TMS$.

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