Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Regulating the Emission of Tetraphenylethenes *through* Changing the Alkoxyl Linkage Length between Two Neighboring Phenyl Moieties

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Experimental Section

General Remarks. Tetrahydrofuran (THF) was distilled from sodium wire and benzophenone under nitrogen. Dichloromethane (DCM) was distilled from CaH2. Column chromatography was carried out on a silica gel column (Qingdao Haiyang, 200-300 mesh) with the indicated eluents. All the other reagents such as benzophenone, n-butyllithium in hexane (2.5 mol/L), 2,2'-dihydroxybenzophenone, diphenylmethane, methyl iodine, diiodomethane, 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, and triphenylethene were used as received.

^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer (1H: 400 MHz, 13C: 100 MHz) in $CDCl_3$. Spectra were referenced internally using the residual solvent resonances (δ = 7.28 for 1H NMR) relative to $SiMe_4$ (δ = 0 ppm). ^{13}C NMR spectra were referenced internally by using the solvent resonances (δ = 77.00 ppm for $CDCl_3$). Electronic absorption spectra were recorded on a Hitachi U-2900 spectrophotometer. Steady-state fluorescence spectra were recorded on a Hitachi F-7000 spectrophotometer and an Edinburgh Instruments FLS920 three-monochromator spectrophotometer. The emission spectra were corrected for the wavelength dependence of the sensitivity of the detection system. The absolute fluorescence quantum yields were measured with an integrating sphere. Fluorescence images were taken on a Nikon Eclipse Ti florescence microscope. ESI-MS spectrum was taken on a Thermo Fisher Q-Exactive mass spectrometer. Single-crystal X-ray diffraction analyses were performed on an Aglient SuperNova Atlas Dual diffractometer using CuKα radiation (λ = 1.54184 Å). Structure was solved by direct methods using SHELXTL and refined by full-matrix least-squares on F^2 using SHELX-97. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2×Ueq of the attached atom. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Number: **TPEOMe** 1820140, **TPEC1** 1820141, **TPEC2** 1820142, **TPEC3** 1820143, and **TPEC4** 1820144..

*Synthesis of **2,2'-Dimethyloxy-benzophenone**.* 2,2'-Dihydroxy-benzophenone (0.64 g, 3 mmol), K_2CO_3 (4.1 g, 30 mmol) and methyl iodine (1.7 g, 12 mmol) were dissolved in dry acetone (50 mL). The mixture was heated to reflux for 12 h under nitrogen. The resulting solution was filtered through a pad of Celite and evaporated to afford the crude product. The crude product was purified by silica gel column chromatography using hexane as eluent to give white solid in 90% yield (0.65 g). ^{1}H NMR (400 MHz, $CDCl_3$), (TMS, ppm): 7.53 (d, 2H, *J* = 7.6 Hz, ArH), 7.45 (t, 2H, *J* = 7.6 Hz, ArH), 7.01 (t, 2H, *J* = 7.2 Hz, ArH), 6.93 (t, 2H, *J* = 8.4 Hz, ArH), 3.68 (s, 6H, -OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$),δ: 195.28, 158.28, 132.53, 130.38, 130.26, 120.32, 111.44, 55.68. ESI-MS: Found an isotopic cluster peaking at m/z [M+Na^+] 265.14; Calculated for $C_{15}H_{14}O_3Na$, 265.08.

*Synthesis of **TPEOMe**.* To a solution of diphenylmethane (0.55 g, 3 mmol) in dry THF (30 mL), 1.0 mL of 2.5 M solution of *n*-butyllithium in hexane (2.5 mmol) was added at 0°C under nitrogen. The resulting orange-red solution was stirred for 45 min at this temperature. 2,2'-Dimethyloxy-benzophenone (0.54 g, 2.25 mmol) was then added and the reaction mixture warmed to room temperature and then stirred at 70°C for another 24 h. The reaction was quenched by adding 10% aqueous ammonium chloride solution. The organic layer was extracted with dichloromethane (3×50 mL), and the combined organic layers were washed with a saturated brine solution and dried over with anhydrous $MgSO_4$. The solvent was evaporated, and the resulting crude alcohol was dissolved in 80 mL of toluene in a 150 mL round-bottom flask fitted with a Dean-Stark trap. *p*-

Toluenesulphonic acid (52 mg, 0.3 mmol) was added, and the mixture was refluxed for 4 h and cooled to room temperature. The toluene layer was washed with 10% aqueous NH_4Cl solution and dried over with anhydrous $MgSO_4$. After evaporating the solvent, the crude product was purified by silica gel column chromatography using hexane/dichloromethane (DCM) (95/5, v/v) as eluent to give white solid in 40% yield (0.35 g). ^{1}H NMR (400 MHz, $CDCl_3$), (TMS, ppm): 7.11-7.06 (m, 14H, ArH), 6.74 (t, 2H, *J* = 7.6 Hz, ArH), 6.69 (d, 2H, *J* = 8.0 Hz, ArH), 3.44 (s, 6H, -OMe). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 151.17, 143.60, 142.61, 133.29, 132.76, 132.03, 130.47, 127.70, 127.05, 126.13, 119.97, 111.21, 55.34. ESI-MS: Found an isotopic cluster peaking at m/z [M+Na$^+$] 415.15; Calculated for $C_{28}H_{24}O_2Na$, 415.17.

Synthesis of ***α,α′-dihydroxy TPE****.* The solution of **TPEOMe** (392 mg, 1 mmol) in dry DCM (20 mL) was cooled to -65 °C under a nitrogen atmosphere. A 1.0 M solution of BBr_3 (4.0 mL, 4.0 mmol) was added via syringe. The resulting mixture was kept at -65 °C for 20 minutes and then allowed to warm to room temperature for 12 h. The reaction mixture was poured into water (100 mL) and stirred for another 1 h under nitrogen. Then the reaction mixture was extracted with DCM and dried over with anhydrous $MgSO_4$. For compound α,α'-dihydroxy TPE is readily to be oxide in the air, the obtained product was not purified further (338 mg, 93%).

Synthesis of ***TPEC1****.* The α,α'-dihydroxy TPE (364 mg, 1 mmol), K_2CO_3 (1.38 g, 10 mmol) and diiodomethane (402 mg, 1.5 mmol) were dissolved in dry acetone (50 mL). The mixture was heated to reflux for 12 h under nitrogen. The resulting solution was filtered and evaporated to afford the crude product. The crude product was purified by silica gel column chromatography using hexane/DCM (80/20, v/v) as eluent to give white solid in 60% yield (226 mg). ^{1}H NMR (400 MHz, $CDCl_3$), (TMS, ppm): 7.25 (d, 4H, *J* = 7.2 Hz, ArH), 7.17 (t, 4H, *J* = 6.8 Hz, ArH), 7.10 (t, 4H, *J* = 7.2 Hz, ArH), 7.06 (t, 2H, *J* = 7.6 Hz, ArH), 6.94 (d, 2H, *J* = 8.0 Hz, ArH), 6.85 (t, 2H, *J* = 7.2 Hz, ArH), 6.15 (s, 2H, -OCH_2-). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.29, 142.76, 141.08, 135.27, 131.31, 130.66, 129.05, 128.15, 127.79, 126.63, 123.02, 120.35, 94.26. ESI-MS: Found an isotopic cluster peaking at m/z [M+CH_3OH+Na$^+$] 431.09; Calculated for $C_{68}H_{78}O_{10}Na$, 431.16.

Synthesis of ***TPEC2****.* The same synthetic procedure described in **TPEC1** was performed for compound **TPEC2**, and the crude product was purified by silica gel column chromatography using hexane/DCM (85/15, v/v) as eluent to give white solid in 30% yield (117 mg). ^{1}H NMR (400 MHz, $CDCl_3$), (TMS, ppm): 7.13-7.09 (m, 14H, ArH), 6.92 (t, 2H, *J* = 7.2 Hz, ArH), 6.89 (d, 2H, *J* = 8.8 Hz, ArH), 4.36 (s, 4H, -OCH_2-). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 157.23, 142.72, 142.22, 136.26, 132.75, 131.08, 130.29, 128.35, 127.42, 126.47, 123.61, 121.92, 74.58. ESI-MS: Found an isotopic cluster peaking at m/z [M+Na$^+$] 413.16; Calculated for $C_{28}H_{22}O_2Na$, 413.15.

Synthesis of ***TPEC3****.* The same synthetic procedure described in **TPEC1** was performed for **TPEC3**, and the crude product was purified by column chromatography on silica gel using hexane/DCM (80/20, v/v) as the eluent to obtain **TPEC3** (67%, yield) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$), (TMS, ppm): 7.13-7.07 (m, 14 H, ArH), 6.87 (s, 2H, ArH), 6.85 (s, 2H, ArH), 4.39 (s, 4H, -OCH_2-), 2.09-2.03 (m, 2H, -CH_2-). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 157.40, 142.71, 142.57, 135.40, 134.13, 131.05, 130.23, 127.91, 127.27, 126.17, 122.06, 119.08, 71.13, 29.66. ESI-MS: Found an isotopic cluster peaking at m/z [M+Na$^+$] 427.17; Calculated for $C_{29}H_{24}O_2Na$, 427.17.

Synthesis of ***TPEC4****.* The same synthetic procedure described in **TPEC1** was performed for **TPEC4**, and the crude product was purified by column chromatography on silica gel using hexane/DCM (80/20, v/v) as the eluent to obtain **TPEC4** (92%, yield) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$), □ (TMS, ppm): 7.08-7.04 (m, 14H, ArH), 6.79 (t, 2H, *J* = 7.2 Hz, ArH), 6.75 (d, 2H, *J* = 8.0 Hz, ArH), 4.33 (s, 2H, -OCH_2-), 4.11 (s, 2H, -

OCH_2-), 1.97 (s, 2H, -CH_2-), 1.97 (s, 2H, -CH_2-). ^{13}C NMR (100 MHz, $CDCl_3$), δ : 156.03, 142.97, 142.17, 134.52, 134.03, 131.09, 130.48, 127.58, 127.10, 126.04, 120.71, 115.31, 69.96, 26.97. ESI-MS: Found an isotopic cluster peaking at m/z [M+H^+] 419.17; Calculated for $C_{30}H_{26}O_2$, 419.20.

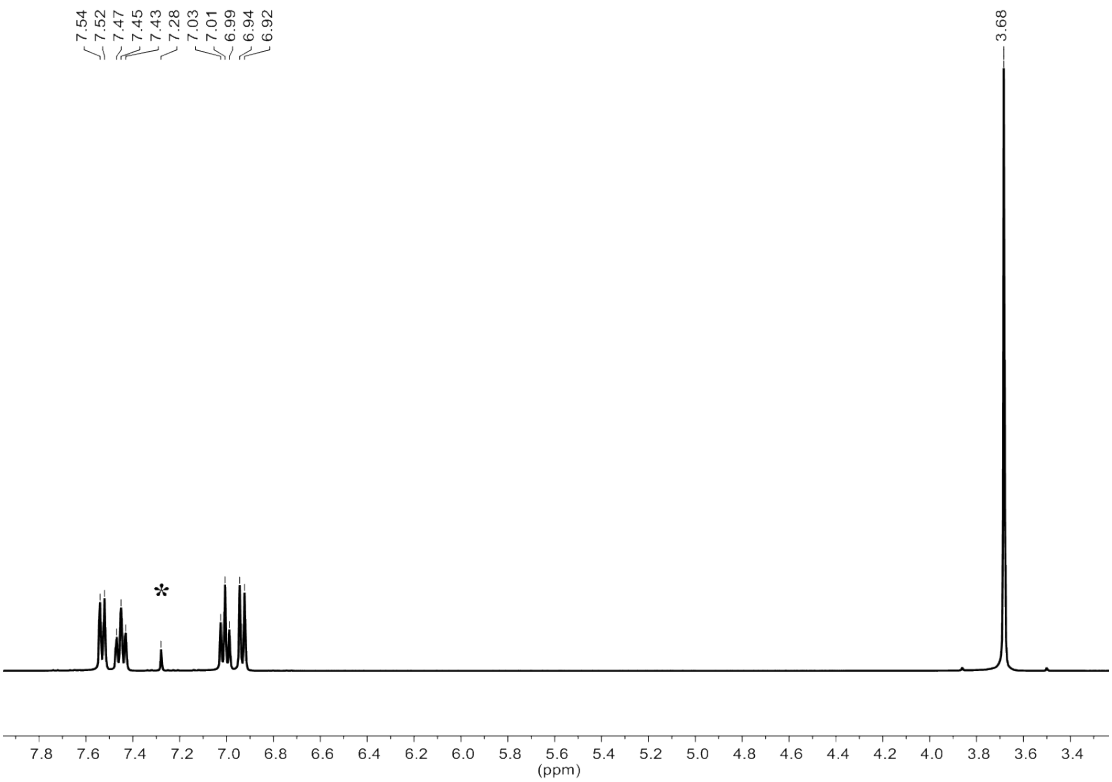


Fig. S1. ^{1}H NMR spectrum of compound 2,2'-dimethyloxy-benzophenone in $CDCl_3$. The residual solvent signals are marked with asterisks.

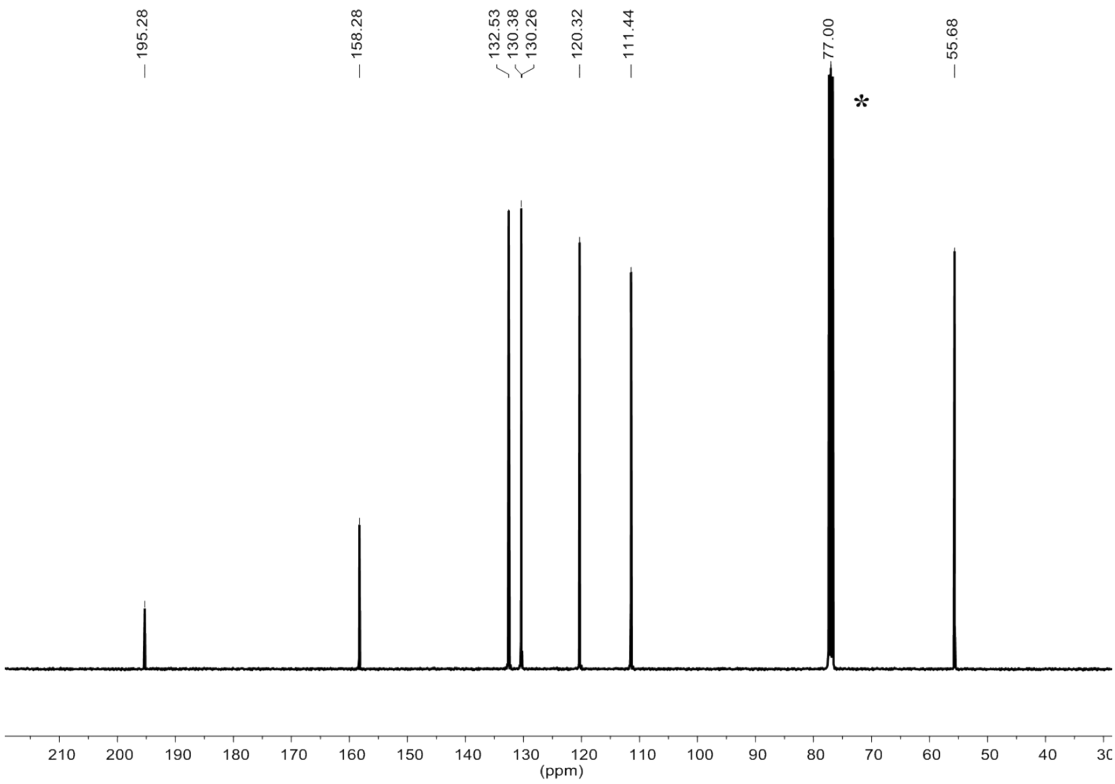


Fig. S2. ^{13}C NMR spectrum of compound 2,2'-dimethyloxy-benzophenone in $CDCl_3$. The residual solvent signals are marked with asterisks.

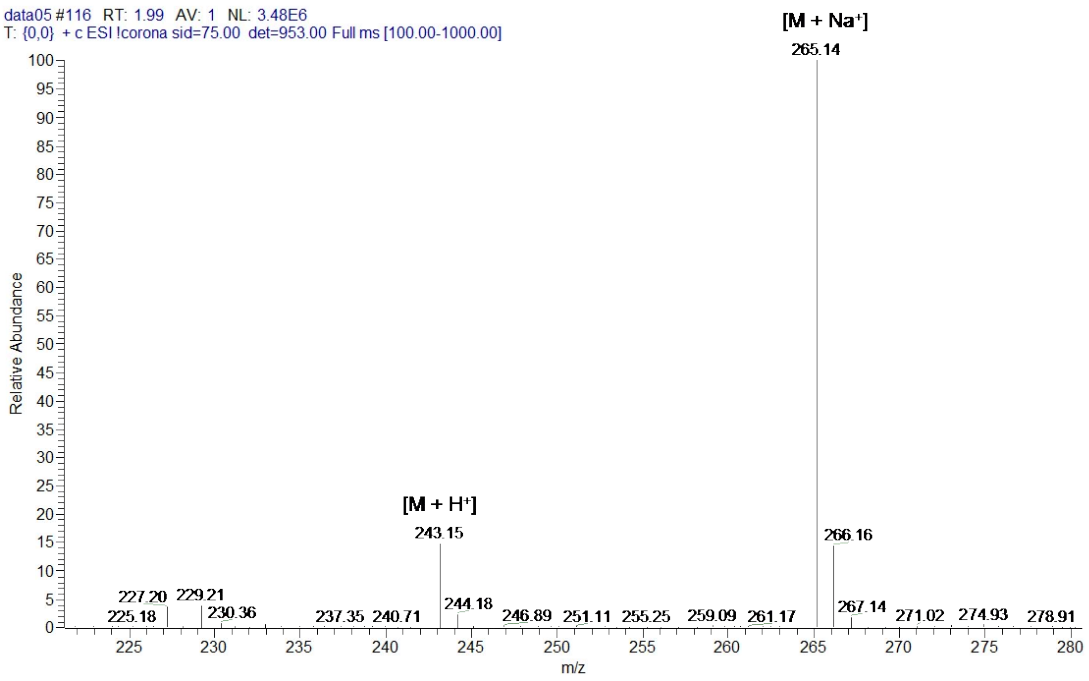


Fig. S3. ESI-MS spectrum of compound 2,2'-dimethyloxy-benzophenone.

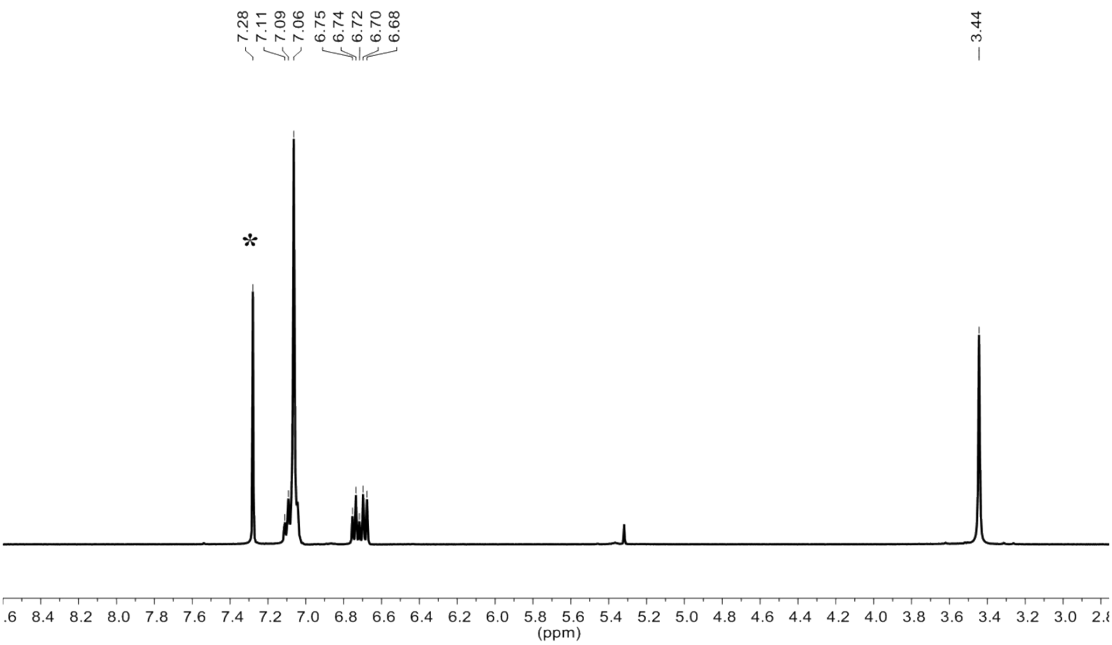


Fig. S4. ^{1}H NMR spectrum of **TPEOMe** in $CDCl_3$. The residual solvent signals are marked with asterisks.

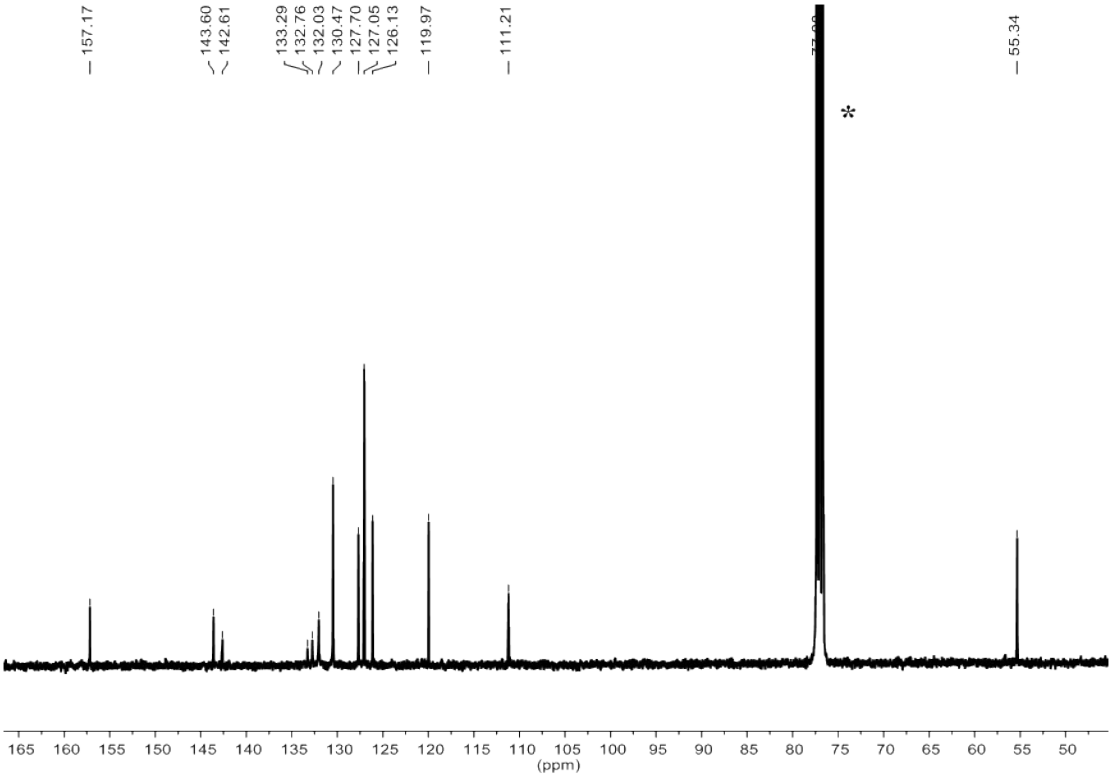


Fig. S5. ^{13}C NMR spectrum of **TPEOMe** in $CDCl_3$. The residual solvent signals are marked with asterisks.

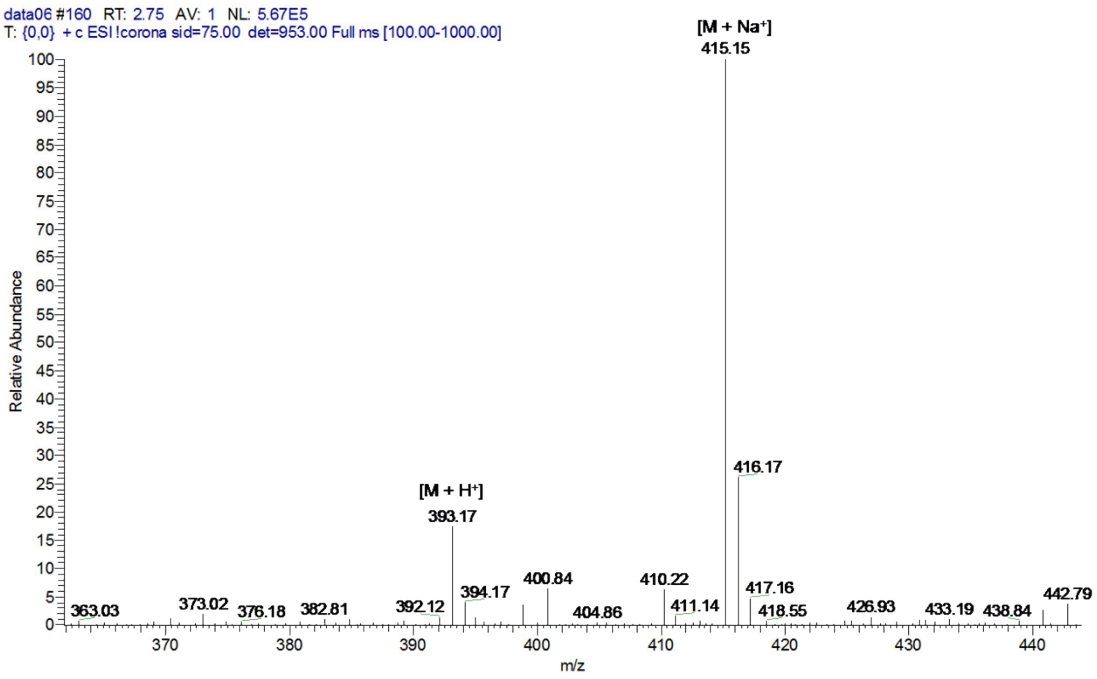


Fig. S6. ESI-MS spectrum of **TPEOMe**.

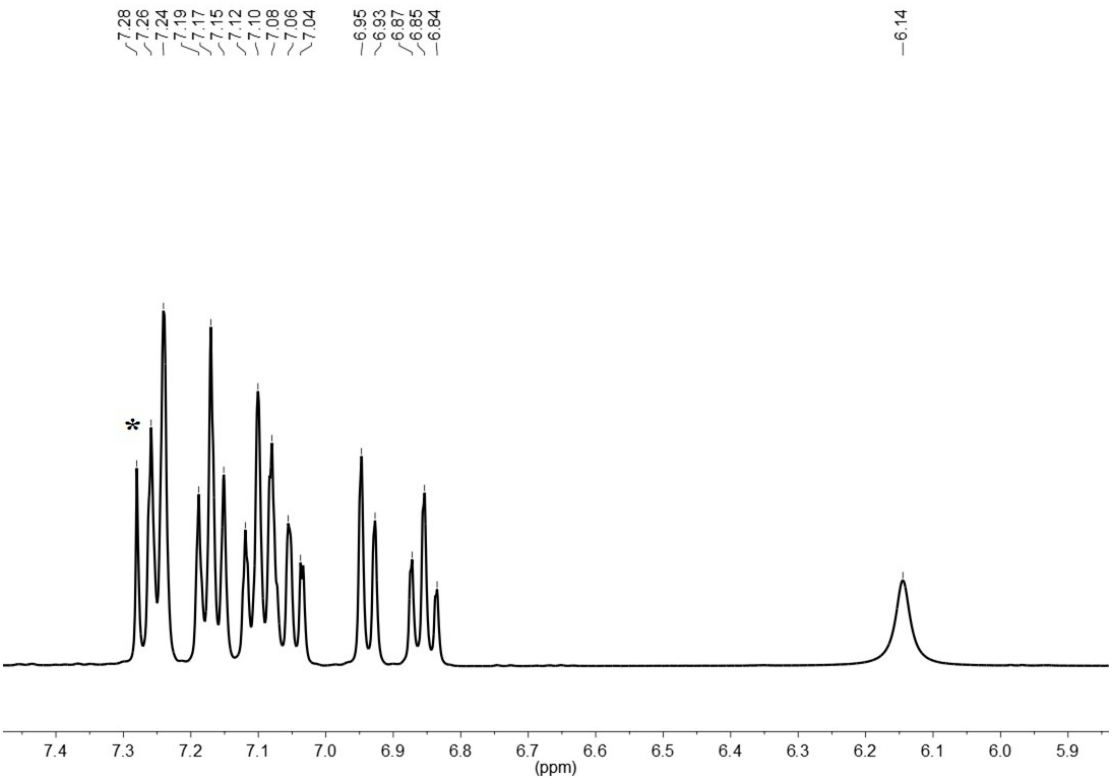


Fig. S7. ^{1}H NMR spectrum of **TPEC1** in $CDCl_3$. The residual solvent signals are marked with asterisks.

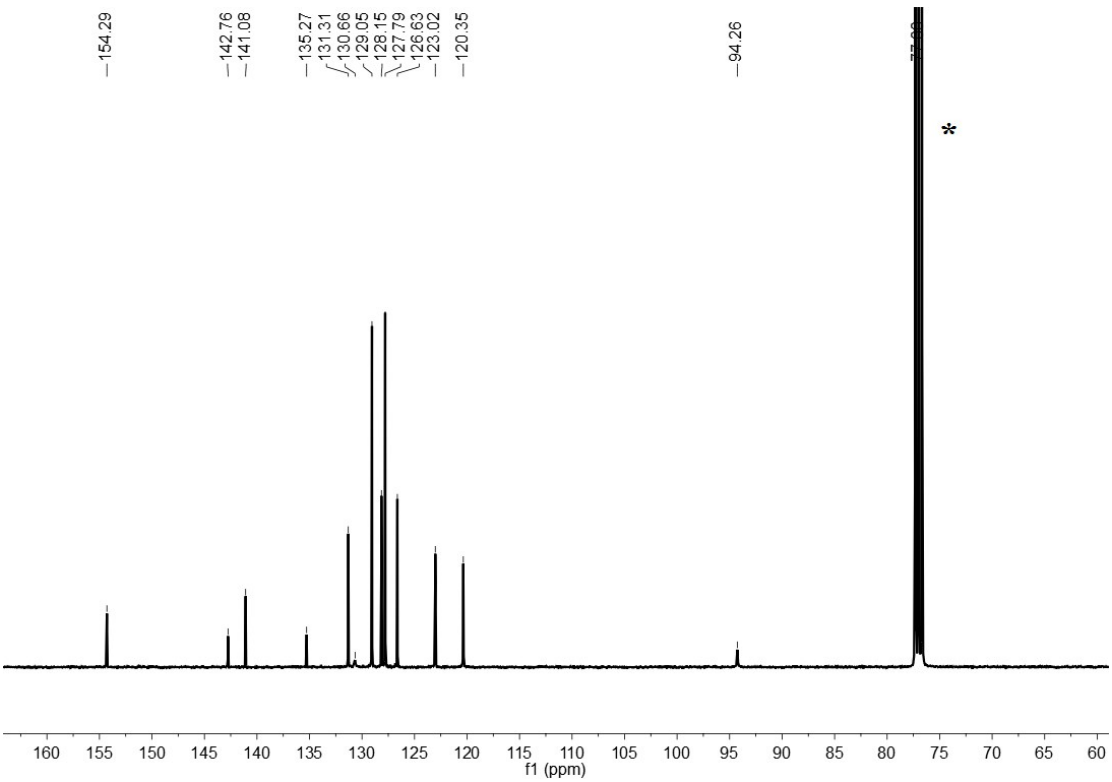


Fig. S8. ^{13}C NMR spectrum of **TPEC1** in $CDCl_3$. The residual solvent signals are marked with asterisks.

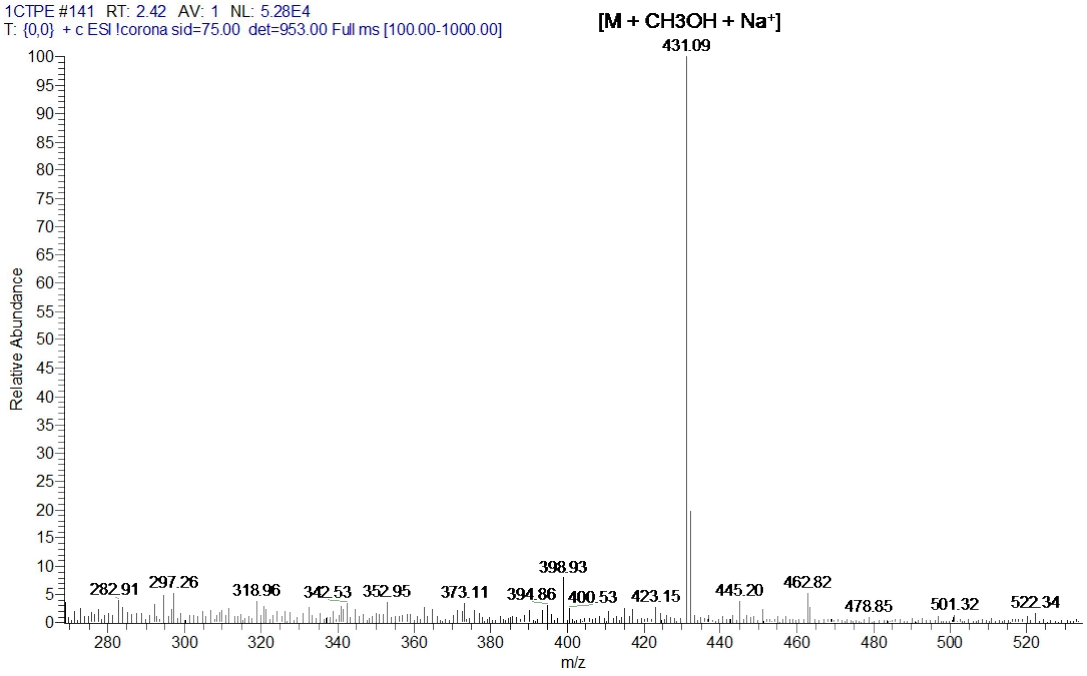


Fig. S9. ESI-MS spectrum of **TPEC1**.

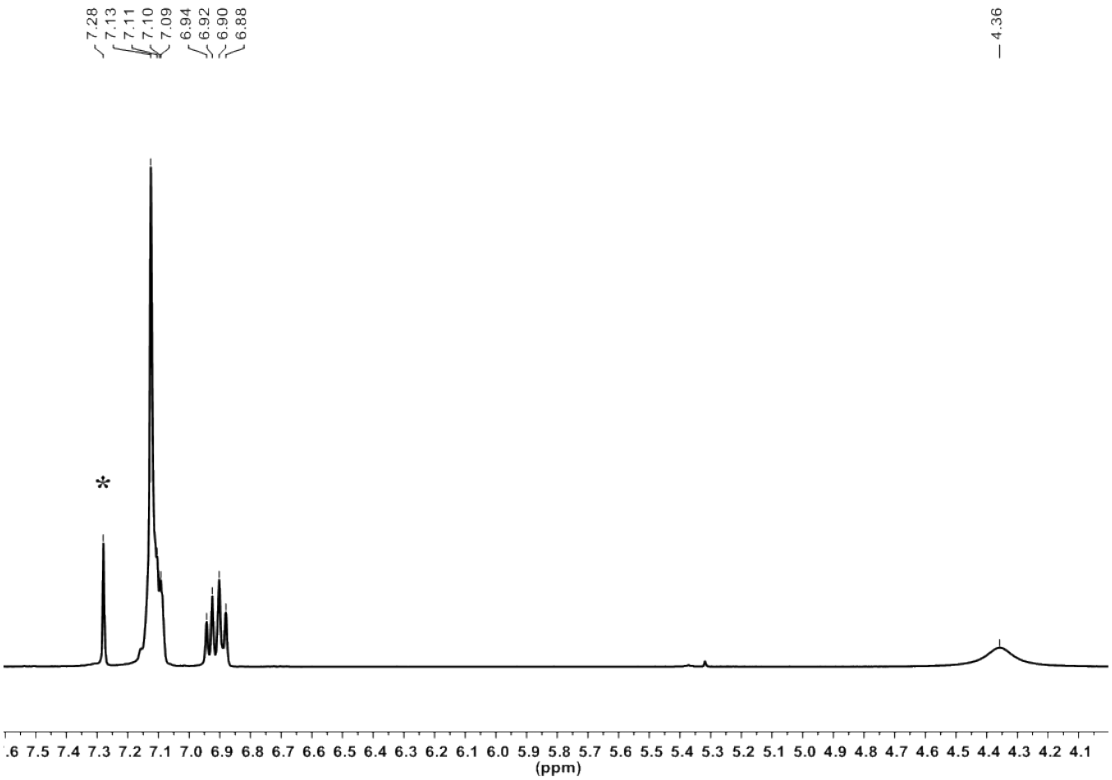


Fig. S10. ^{1}H NMR spectrum of **TPEC2** in $CDCl_3$. The residual solvent signals are marked with asterisks.

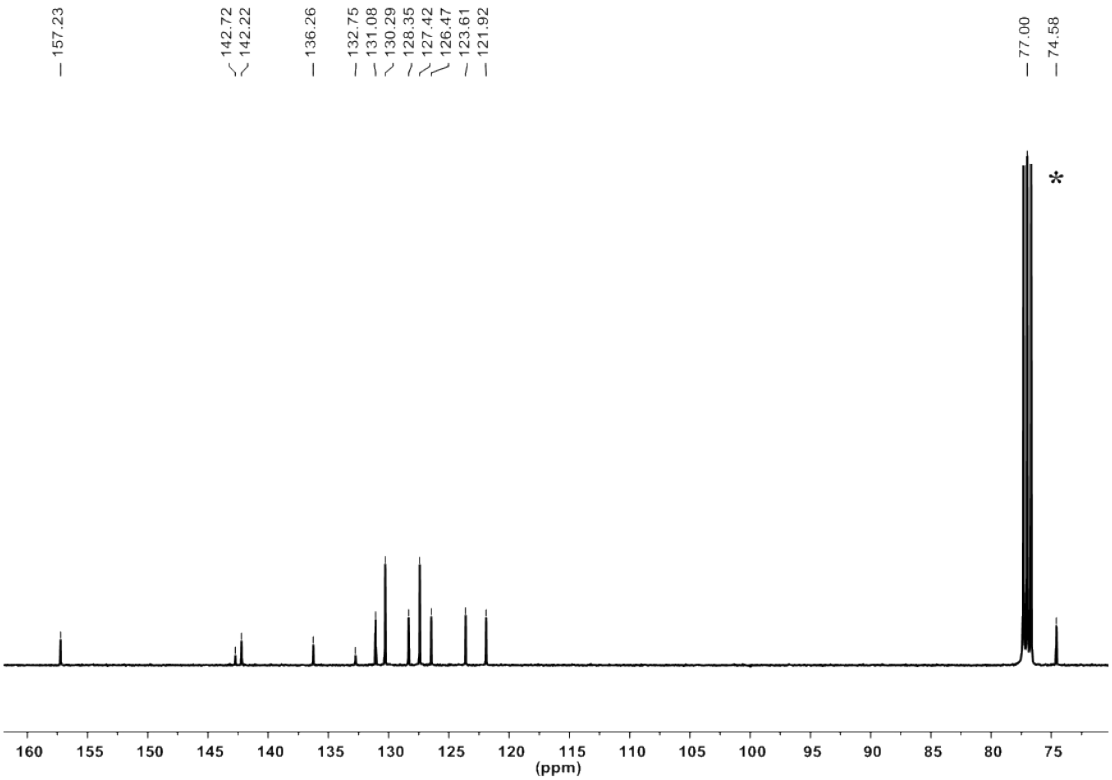


Fig. S11. ^{13}C NMR spectrum of **TPEC2** in $CDCl_3$. The residual solvent signals are marked with asterisks.

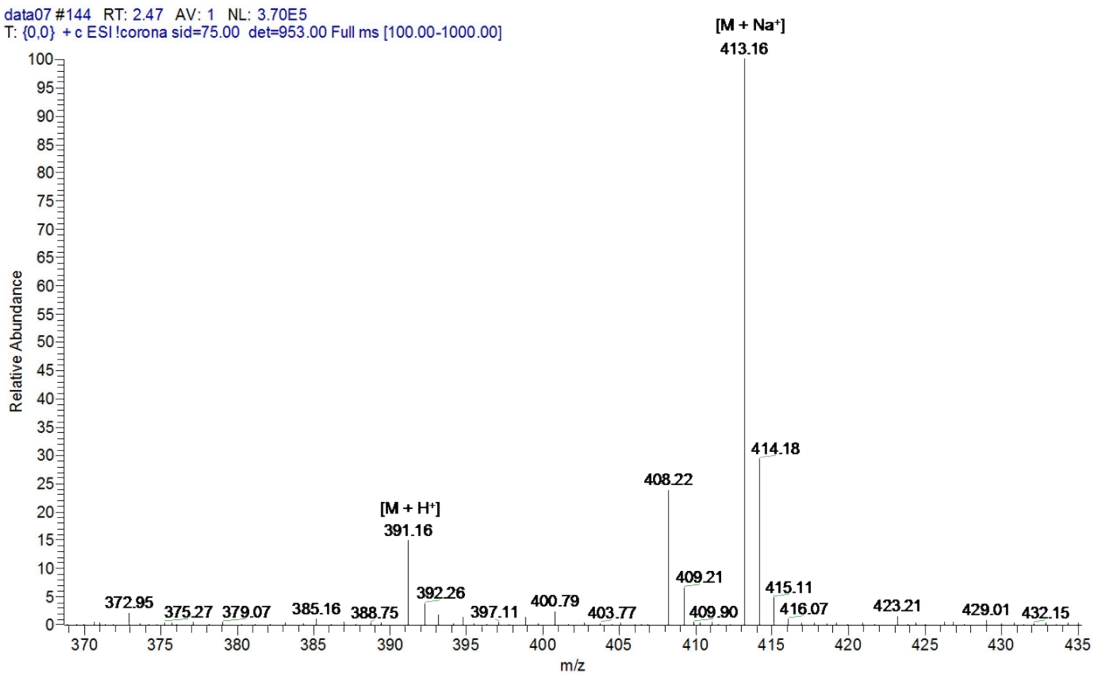


Fig. S12. ESI-MS spectrum of **TPEC2**.

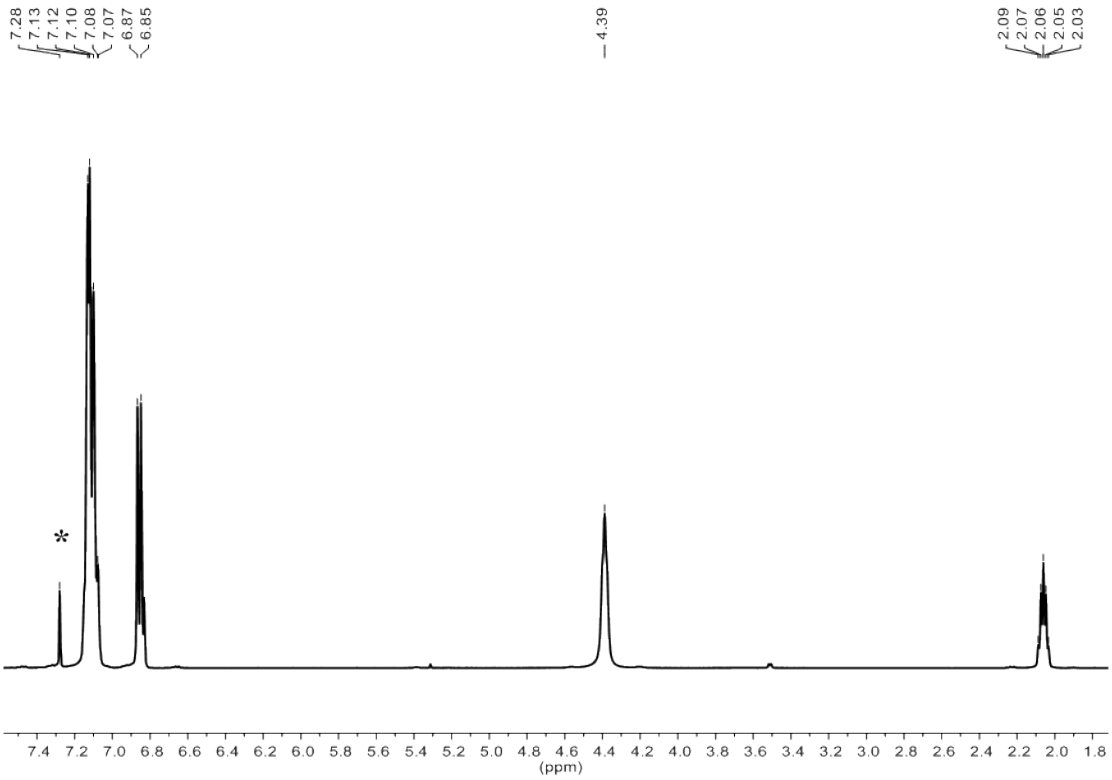


Fig. S13. ^{1}H NMR spectrum of **TPEC3** in $CDCl_3$. The residual solvent signals are marked with asterisks.

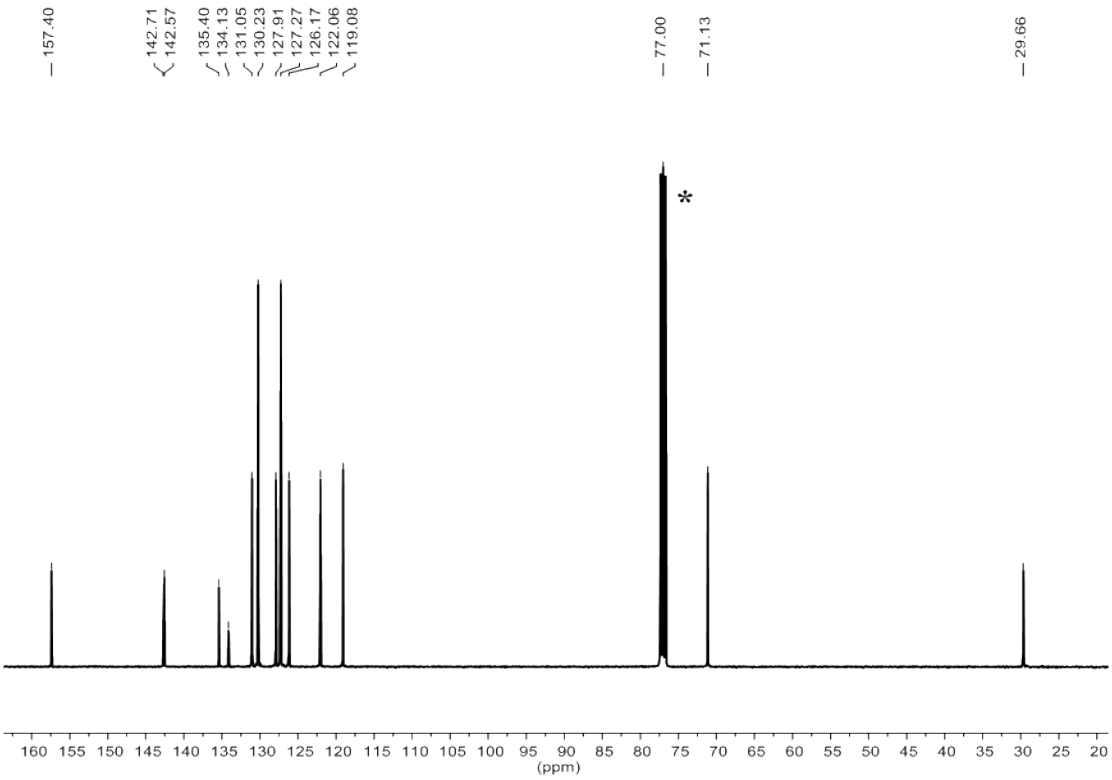


Fig. S14. ^{13}C NMR spectrum of **TPEC3** in $CDCl_3$. The residual solvent signals are marked with asterisks.

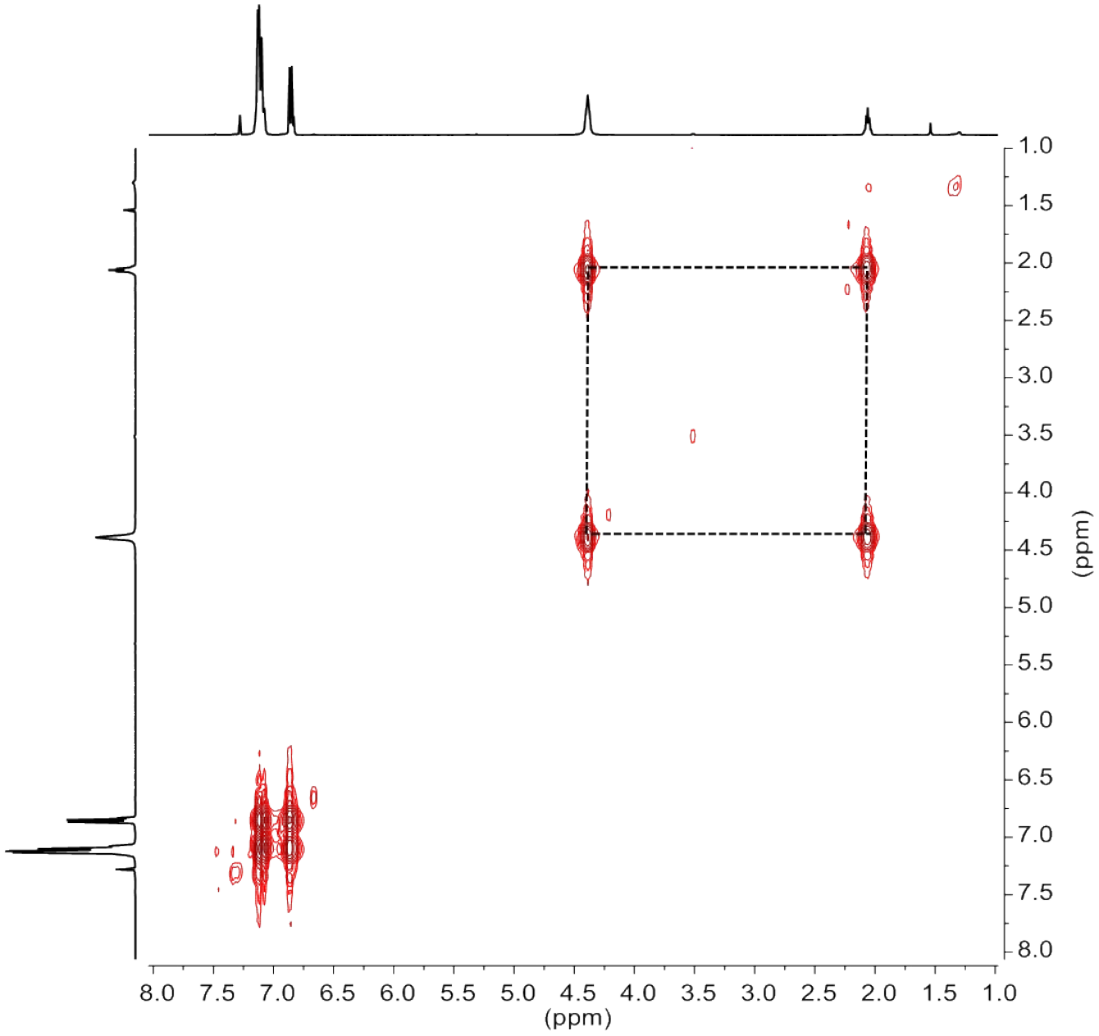


Fig. S15. 2D COSY spectrum of **TPEC3.**

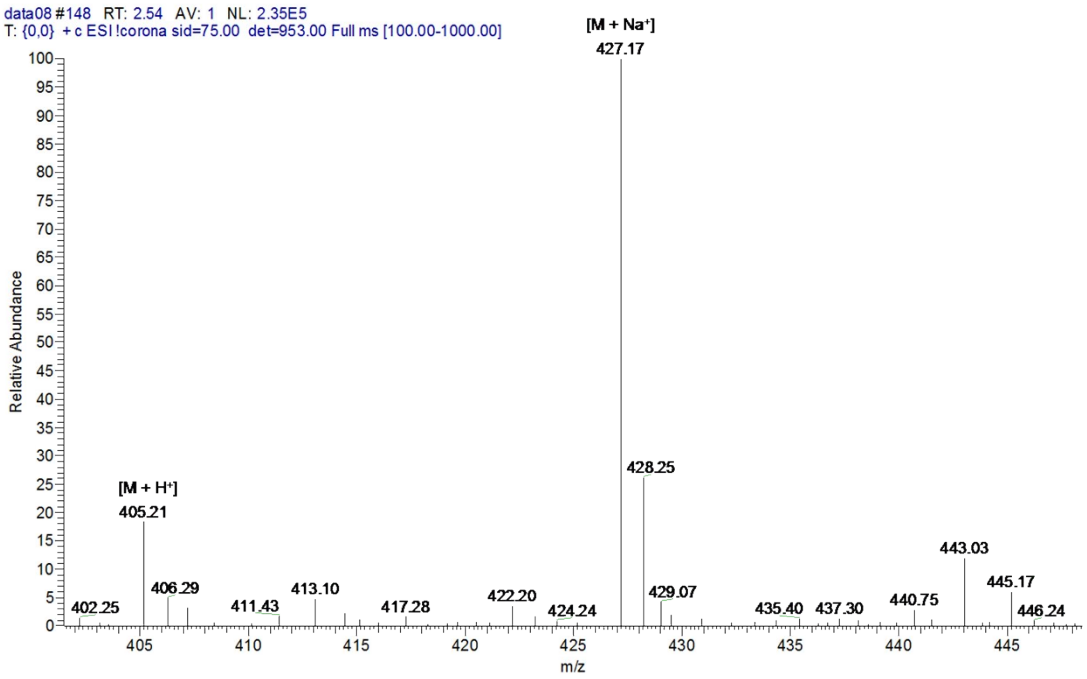


Fig. S16. ESI-MS spectrum of **TPEC3**.

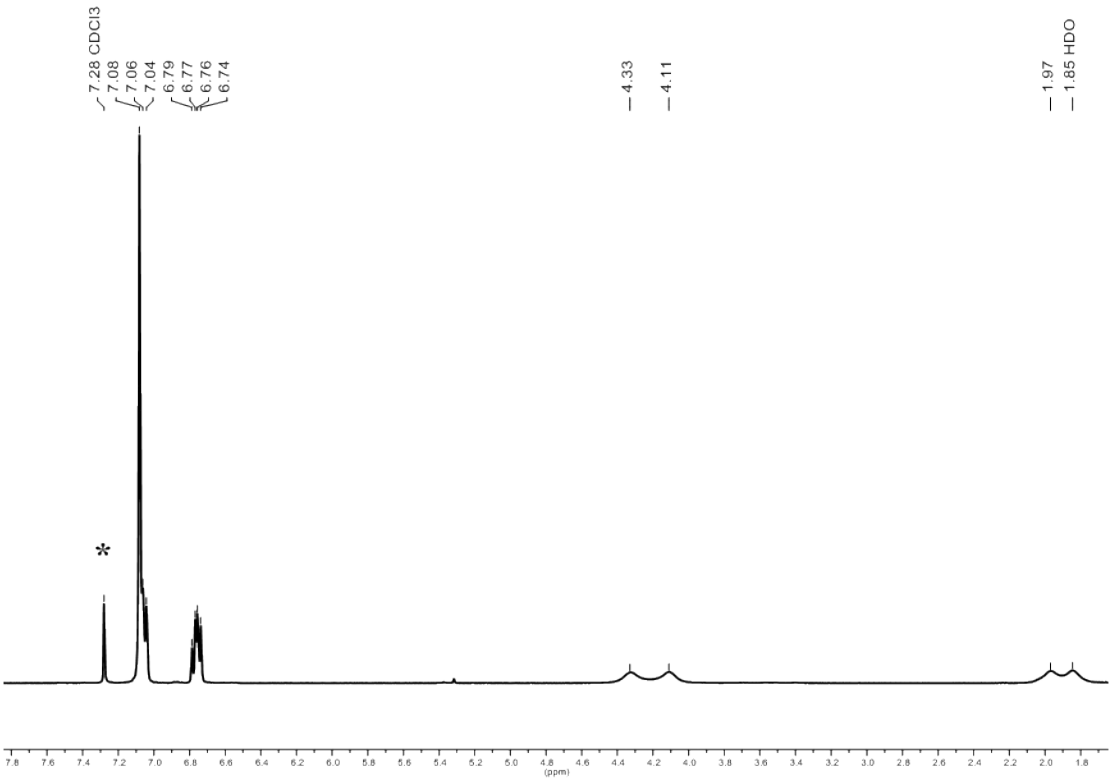


Fig. S17. ^{1}H NMR spectrum of **TPEC4** in $CDCl_3$. The residual solvent signals are marked with asterisks.

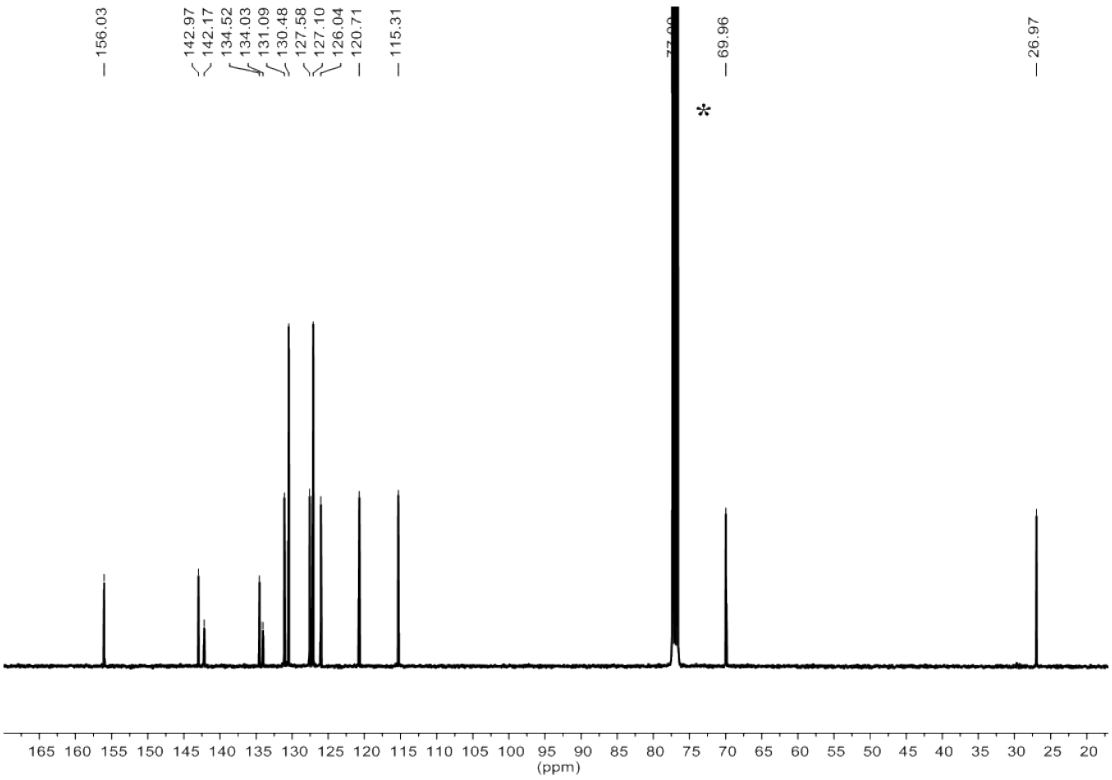


Fig. S18. ^{13}C NMR spectrum of **TPEC4** in $CDCl_3$. The residual solvent signals are marked with asterisks.

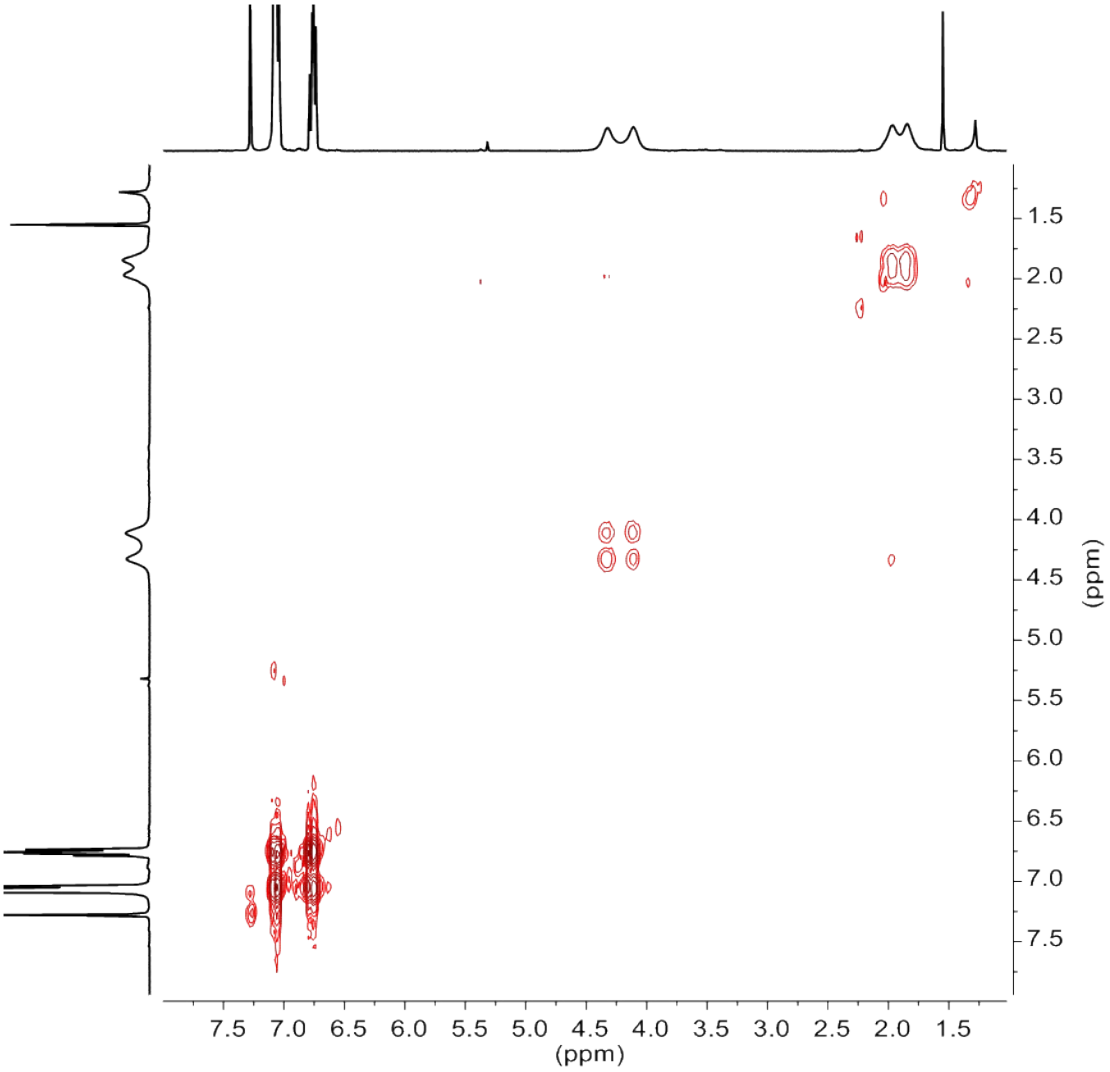


Fig. S19. 2D COSY spectrum of **TPEC4.**

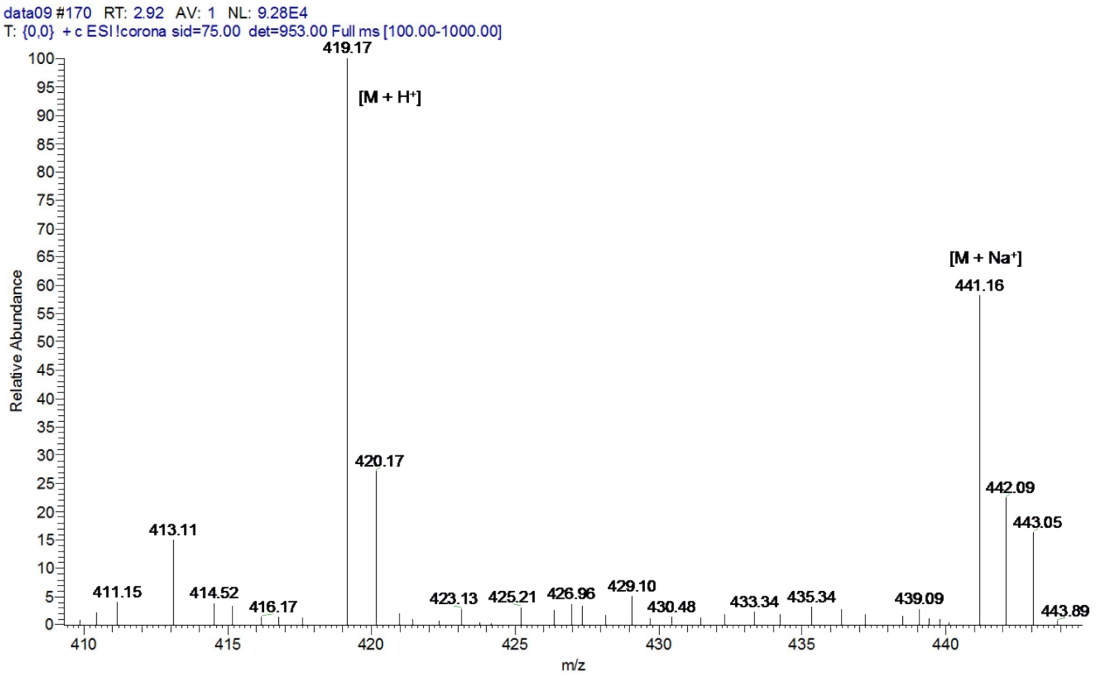
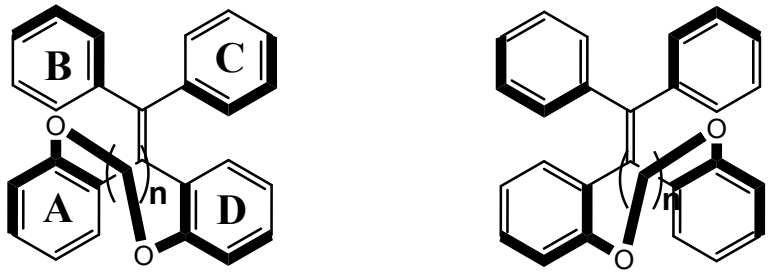


Fig. S20. ESI-MS spectrum of **TPEC4**.



M-TPE **P-TPE**

Fig. S21. The rule for nomination of the two conformational enantiomers of all compounds. The compounds possess propeller-shaped chirality (*P* and *M*) for achiral TPE twisting in one direction.

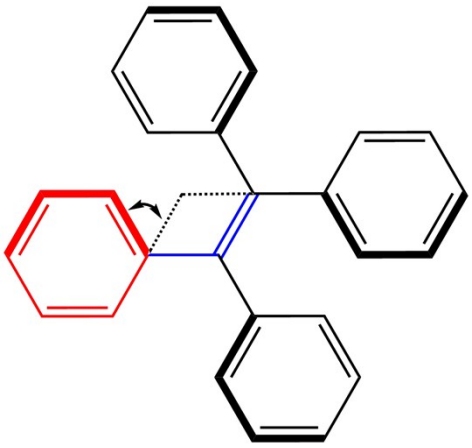


Fig. S22. The definition of the dihedral angles formed between the phenyl rings and the C = C bond.

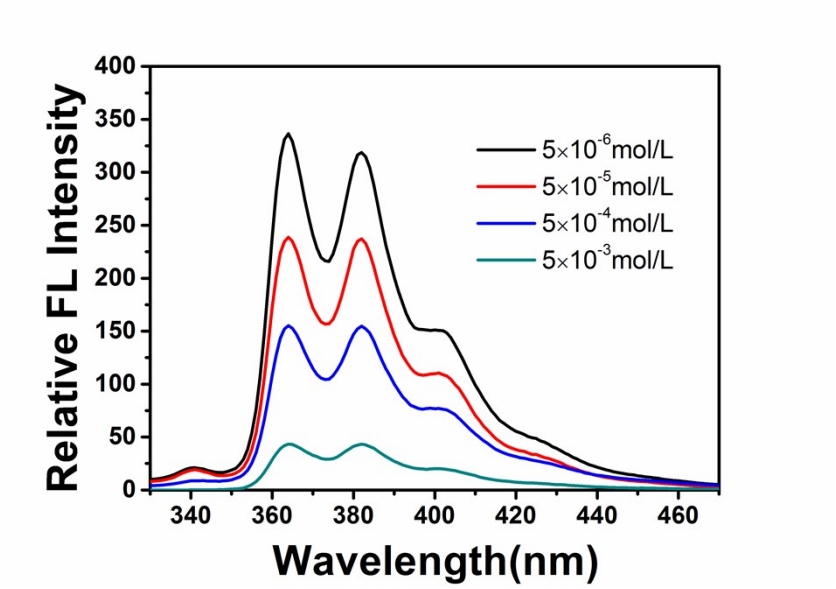


Fig. S23. Fluorescence spectra of **TPEC1** in different concentrations. λ_{ex}: 310 nm (5 nm, 5 nm); 293K. In high concentration, the short-wavelength emission band are selectively attenuated which attributed to the self-absorption.[1]

[1] J.R. Lakowicz, *Principles of Fluorescence Spectroscopy*. Springer US, 1999,57.

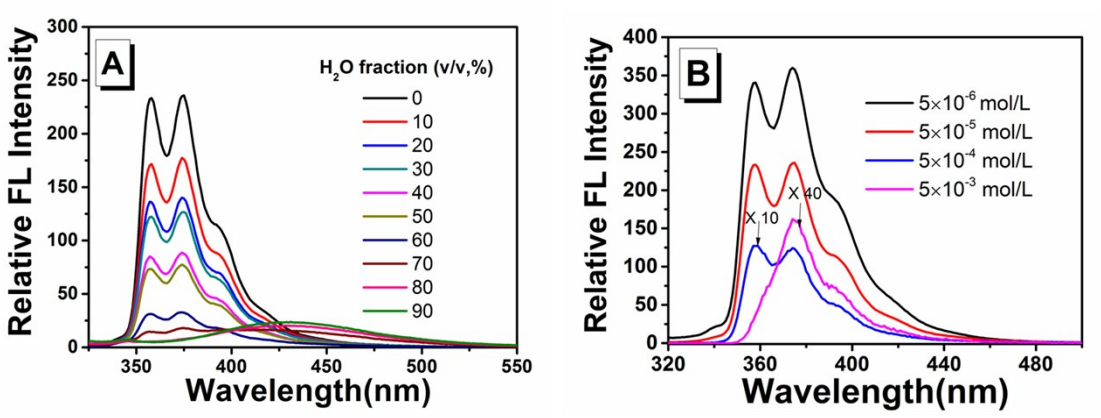


Fig. S24. Fluorescence spectra of triphenylethene in DMSO-water mixtures with different water fractions and in different concentrations. λ_{ex}: 310 nm (5 nm, 5 nm); 293K. In high concentration, the short-wavelength emission band are selectively attenuated which attributed to the self-absorption.[1]

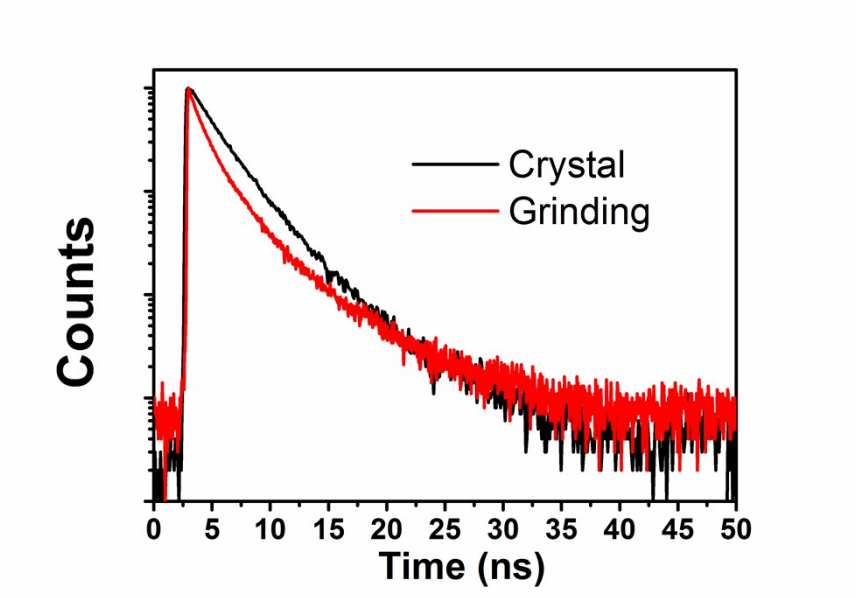


Fig. S25. The time-resolved emission decay curves (λ_{ex}: 375 nm) of **TPEC3** in crystal state and after grinding.

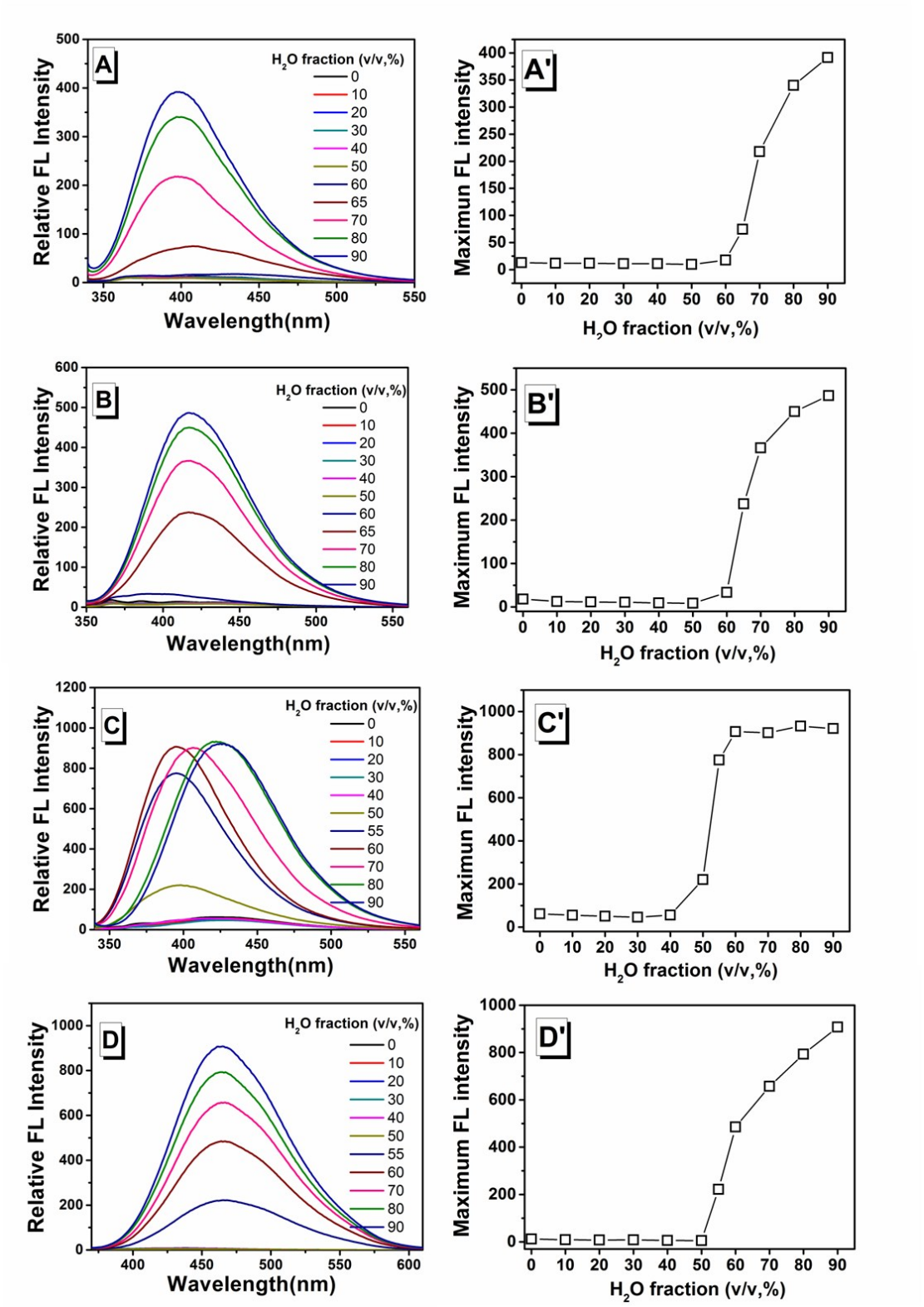


Fig. S26. Fluorescence spectra and plots of the fluorescence intensity at maximum emission of **TPEC2** (A, A'), **TPEC3** (B, B'), **TPEC4** (C, C'), and **TPEOMe** (D, D') in DMSO-water mixtures with different water fractions. Concentration: 50 μM; λ_{ex}: 330 nm (5 nm, 5 nm); 293K.

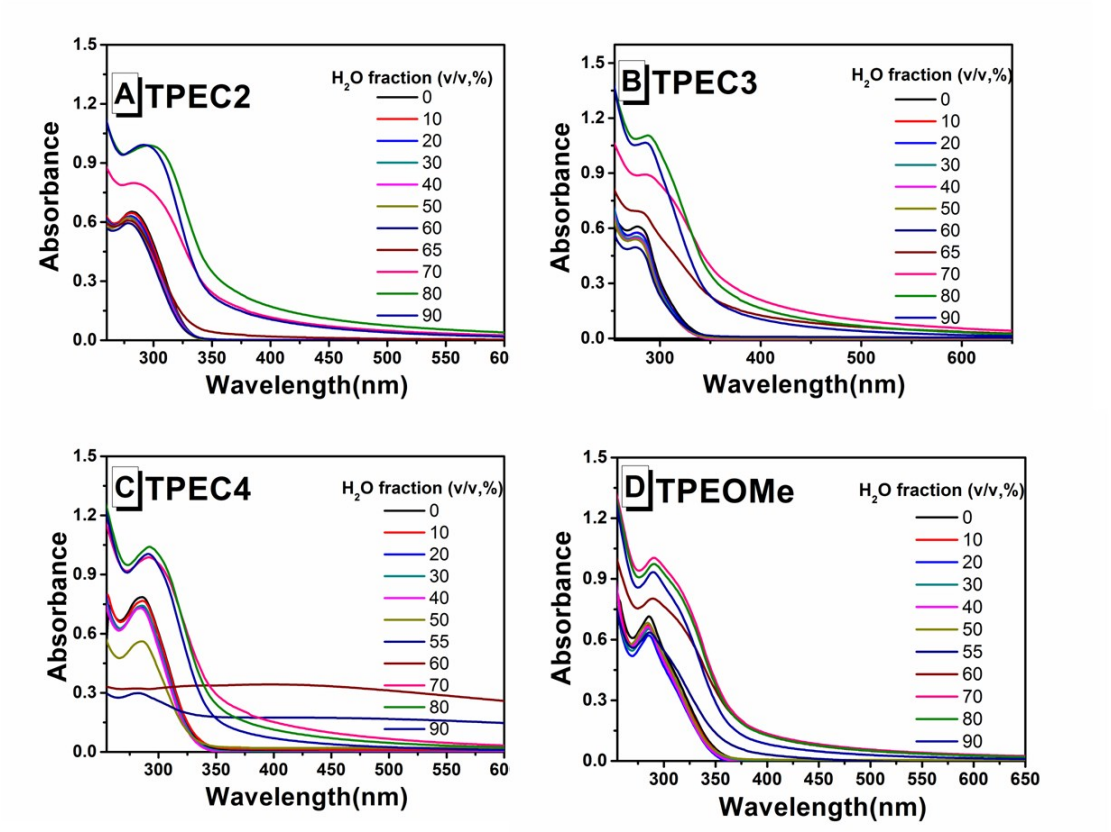


Fig. S27. (A) Uv-vis spectra of **TPEC2** (A), **TPEC3** (B), **TPEC4** (C), and **TPEOMe** (D) in DMSO-water mixtures with different water fractions. Concentration: 50 μM. The absorbance spectra of **TPEC4** at f_w = 55, 60% are not normal which may attribute to the particles formed in these situations make the scattering greater than the absorption.

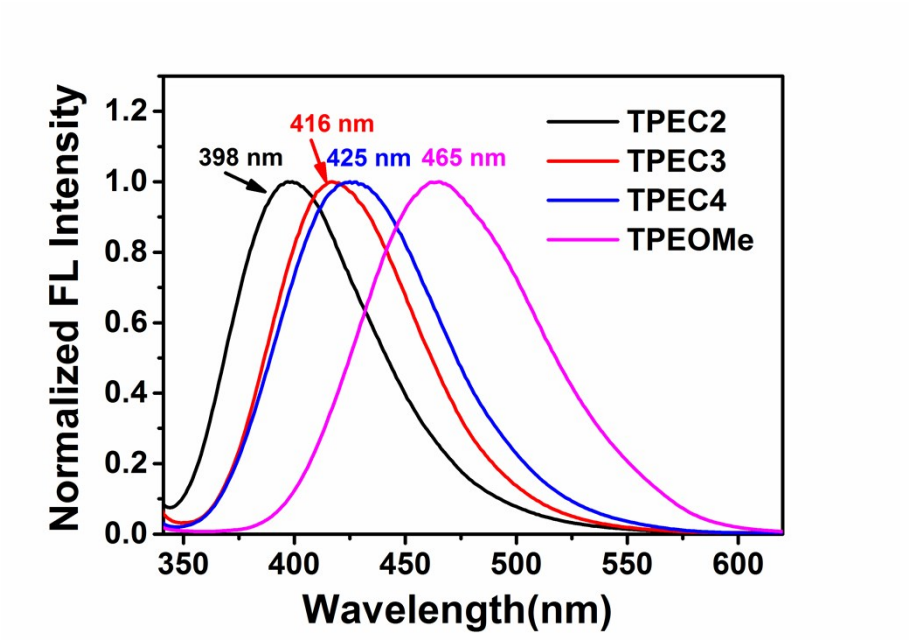


Fig. S28. (A) Normalized fluorescence spectra of **TPEC2**, **TPEC3**, **TPEC4**, and **TPEOMe** in DMSO-water mixtures with f_w = 90%. λ_{ex}: 330 nm (5 nm, 5 nm); 293K.

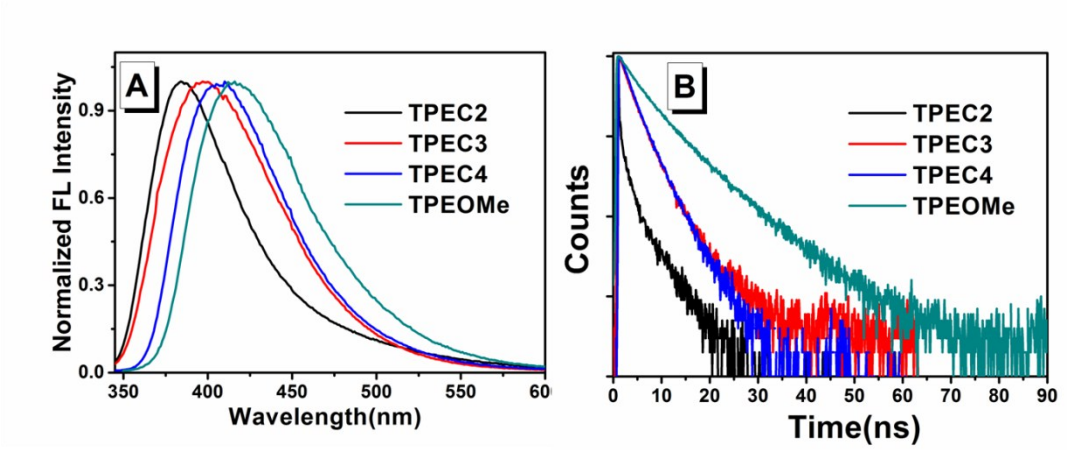


Fig. S29. (A) Fluorescence spectra (λ_{ex}: 330 nm) and (B) time-resolved emission decay curves (λ_{ex}: 375 nm) of **TPEC2**, **TPEC3**, **TPEC4**, and **TPEOMe** in crystal state.

Table S1 Crystallographic data of **TPEOMe**, **TPEC1**, **TPEC2**, **TPEC3**, and **TPEC4**.

Structure	**TPEOMe**	**TPEC1**	**TPEC2**	**TPEC3**	**TPEC4**
Temperature (K)	293(2)	293(2)	293(2)	293(2)	296(2)
chemical formula	$C_{28}H_{24}O_2$	$C_{27}H_{20}O_2$	$C_{28}H_{22}O_2$	$C_{29}H_{24}O_2$	$C_{30}H_{26}O_2$
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*C2/c*	*P21/n*	*P21/n*	*P21/c*	*P21/c*
formula weight	392.50	376.43	390.48	404.51	418.54
a(Å)	14.5500(2)	9.2661(2)	9.1319(3)	14.1335(4)	9.3824(12)
b(Å)	12.0209(2)	8.4682(2)	19.4605(5)	9.1220(2)	9.3181(12)
c(Å)	25.0181(3)	25.0320(5)	12.3122(4)	17.8477(5)	25.644(3)
α(°)	90.00	90.00	90.00	90.00	90.00
β(°)	99.8280(10)	90.00	97.242(3)	109.798(3)	97.845(4)
γ(°)	90.00	90.00	90.00	90.00	90.00
V(Å^3)	4311.55(11)	1946.56(7)	2170.56(11)	2165.02(10)	2221.0(5)
D_c(gcm^{-3})	1.408	1.284	1.195	1.424	1.252
F(000)	1890	792	824	960	888
Z	126	4	8	64	4
μ(mm^{-1})	1.153	0.626	0.579	1.166	0.077
R1,[I > 2σ(I)]	0.1135	0.0379	0.0568	0.0485	0.0731
R1,(all data)	0.1190	0.0402	0.0629	0.0560	0.1177
ωR2, [I > 2σ(I)]	0.2694	0.0959	0.2440	0.1249	0.1638
ωR2, (all data)	0.2734	0.0975	0.2326	0.1329	0.1806
GOF	1.088	1.062	1.009	1.049	1.030

Table S2. The dihedral angles between the phenyl moieties and the C=C bond of **TPEC1**, **TPEC2**, **TPEC3**, **TPEC4**, and **TPEOMe** with *P* conformation.

Compound	A	B	C	D
TPEC1	47.102(89)°	54.667(79)°	**89.276(84)°**	**82.696(66)°**
TPEC2	51.840(157)°	49.929(163)°	64.350(137)°	70.759(152)°
TPEC3	**85.089(105)°**	62.141(90)°	46.324(101)°	**79.061(99)°**
TPEC4	65.745(246)°	34.278(204)°	59.172(237)°	69.776(227)°
TPEOMe	68.978(72)°	38.071(106)°	52.733(79)°	62.796(101)°

Table S3. The maximum emission wavelength, fluorescence quantum efficiency and fluorescence lifetime data of **TPEC1, TPEC2**, **TPEC3**, **TPEC4**, and **TPEOMe** in DMSO, DMSO-water mixtures with f_w = 90%, crystal state and **TPEC3** after grinding.

Compound	In Solution			In Single Crystal State							
	Φ_F (f_w=0)	λ_{em}(nm) (f_w=90%)	Φ_F (f_w=90%)	λ_{em}(nm)	Φ_F	Fluorescence Lifetime					
						τ_1(ns)	A_1	τ_2(ns)	A_2	τ_3(ns)	A_3
TPEC1	90.31	380	28.76	-	4.52	0.06	11%	0.65	82%	5.43	6%
TPEC2	49.22	398	83.70	384	31.57	1.52	50%	4.65	50%		
TPEC3	1.05	417	86.74	398	38.91	2.34	84%	5.10	16%		
TPEC3 Grinding	-	-	-	416	65.14	0.78	36%	2.45	51%	6.86	14%
TPEC4	69.27	425	109.04	407	63.31	0.93	38%	2.40	62%		
TPEOMe	2.34	465	83.31	416	67.76	1.14	20%	2.97	59%	5.26	21%