Trans/*Cis*-Stereoisomers of Triterpenoid-Substituted Tetraphenylethene: Aggregation-Induced Emission, Aggregate Morphology and Mechano-chromism

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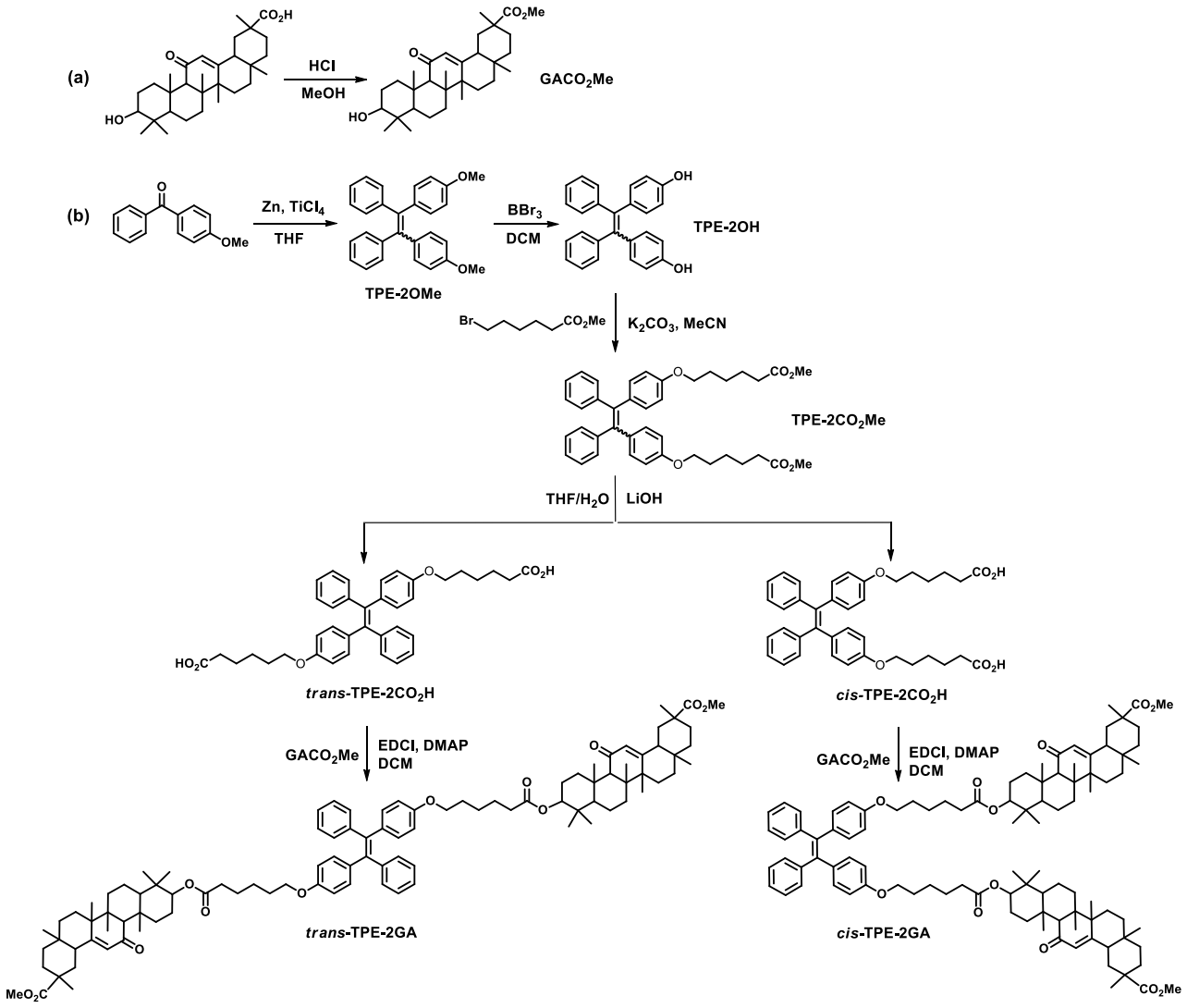
Contents

1. Synthesis and Characterization of *Trans*-/*Cis*-TPE-2GA Isomers



Scheme S1. Synthetic route of *trans*-/*cis*-TPE-2GA.

1.1 Synthesis of $GACO_2Me$.

$GACO_2Me$ was synthesized according to literature.[1] Yield: 90%. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.66 (s, 1H, 12-C*H*=C), 3.68 (s, 3H, OCH_3), 3.24-3.20 (m, 1H, 3-C*H*-O), 1.36, 1.14, 1.13, 1.12, 1.00, 0.80 (s, 7 × 3H, 7 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ =200.4, 177.1, 169.3, 128.7, 78.9, 62.0, 55.1, 51.9, 48.5, 45.5, 44.2, 43.3, 41.3, 39.3, 37.9, 37.2, 32.9, 32.0, 31.3, 28.7, 28.5, 28.2, 27.5, 26.6, 23.5, 18.8, 17.6, 16.5, 15.7.

1.2 Synthesis of TPE-2OMe.

TPE-2OMe was synthesized according to literature.[2] Yield: 59%.^1H NMR (400 MHz, $CDCl_3$): δ = 7.14-7.00 (m, 10H, Ar*H*), 6.96-6.90 (m, 4H, Ar*H*), 6.67-6.61 (m, 4H, Ar*H*), 3.75-3.73 (ss, 6H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ =158.1, 144.4, 139.8, 136.5, 132.7, 131.5, 127.8, 126.3, 113.1, 55.2.

1.3 Synthesis of TPE-2OH.

TPE-2OH was synthesized according to literature.[2,3] Yield: 93%.^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14-6.99 (m, 10H, Ar*H*), 6.91-6.86 (m, 4H, Ar*H*), 6.59-6.54 (m, 4H, Ar*H*), 4.58-4.55 (ss, 2H, O*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.0, 144.3, 144.2, 139.8, 136.8, 136.7, 132.9, 131.5, 127.8, 127.7, 126.4, 114.8, 114.7.

1.4 Synthesis of TPE-2CO_2Me.

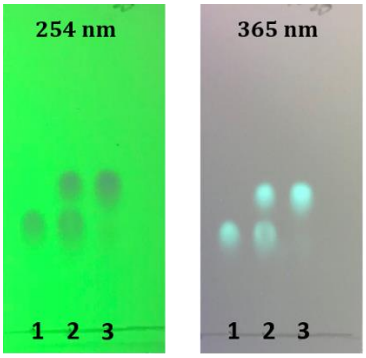
Methyl 6-bromohexanoate (3.0 mL, 19.1 mmol) was added into an acetonitrile solution of TPE-2OH (2g, 5.4 mmol) and K_2CO_3 (2.67 g, 19.1 mmol), and then the mixture was stirred at 80 °C for 24 h. After that, the reaction solution was filtered and the filtrate was evaporated under reduced pressure to remove the organic solvents. The obtained crude product was purified by column chromatography (PE: EA: DCM =20/1/5) to give TPE-2CO_2Me. Yeild: 75%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.16-7.04 (m, 6H, Ar*H*), 6.98-6.92 (m, 4H, Ar*H*), 6.86-6.80 (m, 4H, Ar*H*), 6.69-6.63 (m, 4H, Ar*H*), 3.87-3.82 (m, 4H, OCH_2), 3.57 (s, 6H, COOCH_3), 2.33-2.28 (dt, 4H, CH_2COO), 1.69-1.63 (m, 4H, CH_2), 1.58-1.52 (m, 4H, CH_2), 1.42-1.33 (m, 4H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 173.3, 157.0, 143.8, 139.3, 135.5, 131.9, 130.7, 127.7,126.2, 113.6, 67.1, 51.2, 33.2, 28.4, 25.1, 24.2.

1.5 Synthesis of *Trans*-/*Cis*-TPE-2CO_2H.

TPE-2CO_2Me (500 mg, 0.81 mmol) and LiOH (290 mg, 12.09 mmol) were added into a mixed solvent of THF/H_2O (5:1, v/v) and stirred at room temperature for 12 h. After removing THF under reduced pressure, 1M HCl was added to adjust the pH to 1, and then dichloromethane was used to extract the product three times, followed by drying with anhydrous Na_2SO_4. After that, the Na_2SO_4 was filtered and the organic phase was concentrated. The crude was purified by column chromatography (PE: EA: DCM =2/2/1) to give *cis*-TPE-2CO_2H (R_f = 0.30) and *trans*-TPE-2CO_2H (R_f = 0.42), respectively.

***Trans*-TPE-2CO_2H**: ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.98 (s, 2H, COO*H*), 7.16-7.07 (m, 6H, Ar*H*), 6.97-6.96 (d, 4H, *J* = 4.00 Hz, Ar*H*), 6.82-6.80 (d, 4H, *J* = 8.00 Hz, Ar*H*), 6.66-6.64 (d, 4H, *J* = 8.00 Hz, Ar*H*), 3.86-3.83 (t, 4H, J_1 = 8.00 Hz, J_2 = 4.00 Hz, OCH_2), 2.22-2.19 (t, 4H, J_1 = 4.00 Hz, J_2 = 8.00 Hz, CH_2COOH), 1.68-1.61 (m, 4H, CH_2), 1.56-1.49 (m, 4H, CH_2), 1.41-1.33 (m, 4H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 174.4, 157.0, 143.8, 139.3, 135.5, 131.9, 130.7, 127.8, 126.3, 113.6, 67.1, 33.6, 28.5, 25.2, 24.3.

***Cis*-TPE-2CO_2H**: ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.99 (s, 2H, COO*H*), 7.12-7.04 (m, 6H, Ar*H*), 6.94-6.92 (d, 4H, *J* = 8.00 Hz, Ar*H*), 6.86-6.84 (d, 4H, *J* = 8.00 Hz, Ar*H*), 6.70-6.68 (d, 4H, *J* = 8.00 Hz, Ar*H*), 3.88-3.85 (t, 4H, J_1 = 4.00 Hz, J_2 = 8.00 Hz, OCH_2), 2.23-2.19 (t, 4H, J_1 = 8.00 Hz, J_2 = 8.00 Hz, CH_2COOH), 1.70-1.63 (m, 4H, CH_2), 1.57-1.50 (m, 4H, CH_2), 1.42-1.35 (m, 4H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 174.4, 157.1, 143.8, 139.2, 135.6, 131.9, 130.7, 127.7, 126.2, 113.7, 67.1, 33.6, 28.5, 25.2, 24.3.



1. *cis*-TPE-2CO_2H, R_f = 0.30
2. *cis*/*trans*-TPE-2CO_2H
3. *trans*-TPE-2CO_2H, R_f = 0.42

Figure S1. Digital photos of TLC plates under UV light at 254 and 365 nm, respectively. The eluent was consisted of petroleum ether, ethyl acetate and dichloromethane (2/2/1, volume ratio).

1.6 Spatial Arrangements and Single Crystal Data.

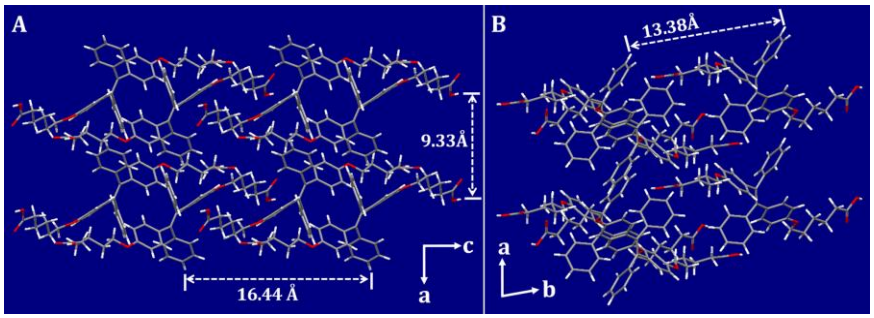


Figure S2. Spatial arrangements of *trans*-TPE-2CO_2H along direction a, b and c in single crystal.

Table S1. Crystal data and structure refinement for *trans*-TPE-2CO_2H

Bond precision	C-C = 0.0024 Å, Wavelength = 1.54184	
Cell	a = 9.3338 (1), b = 13.3779 (2), c = 16.4362 (2) alpha = 79.162 (1), beta = 86.863 (1), gamma = 79.577 (1)	
Temperature	180 K	
	Calculated	Reported
Volume	1982.01 (4)	1982.01 (4)
Space group	$P\bar{1}$	$P\bar{1}$
Hall group	$\bar{P}1$	$\bar{P}1$
Moiety formula	$C_{38}H_{40}O_6$, 2(C2 H6 O S)	
Sum formula	$C_{42}H_{52}O_8S_2$	$C_{42}H_{52}O_8S_2$
Mr	748.96	748.95
Dx, g cm^{-3}	1.255	1.255
Z	2	2
Mu (mm^{-1})	1.633	1.633
F000	800.0	800.0
F000’	803.57	
h, k, lmax	11, 16, 20	11, 16, 20
Nref	8189	7879
Tmin, Tmax	0.855, 0.907	0.730, 1.000
Tmin’	0.698	

Correction method = # Reported T Limits : Tmin =0.730 Tmax =1.000
AbsCorr =MULTI-SCAN		

Data completeness	0.962	
Theta (max)	75.240	
R (reflections)	0.0462 (7047)	
wR2 (reflecions)	0.1335 (7879)	
S	1.057	
Npar	506	

1.7 ^{1}H NMR and ^{13}C NMR of TPE-2GA and Intermediate Compounds

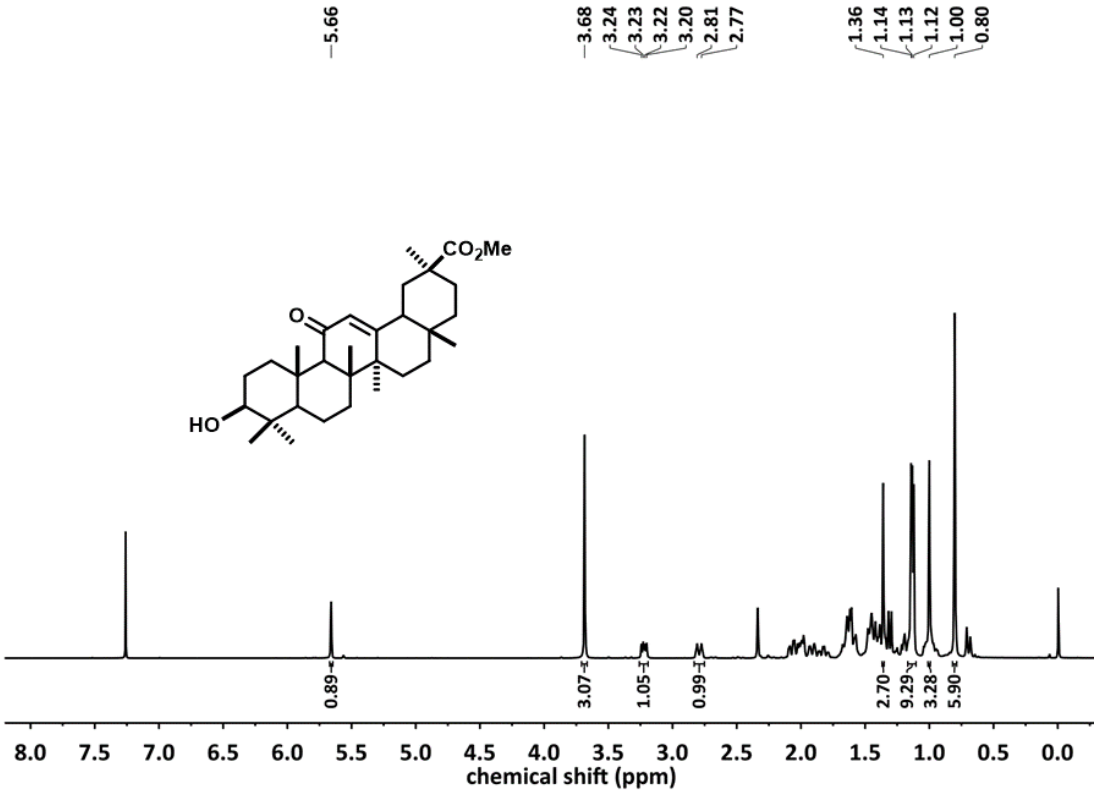


Figure S3. ^{1}H NMR spectrum of $GACO_2Me$ in $CDCl_3$ (400 MHz).

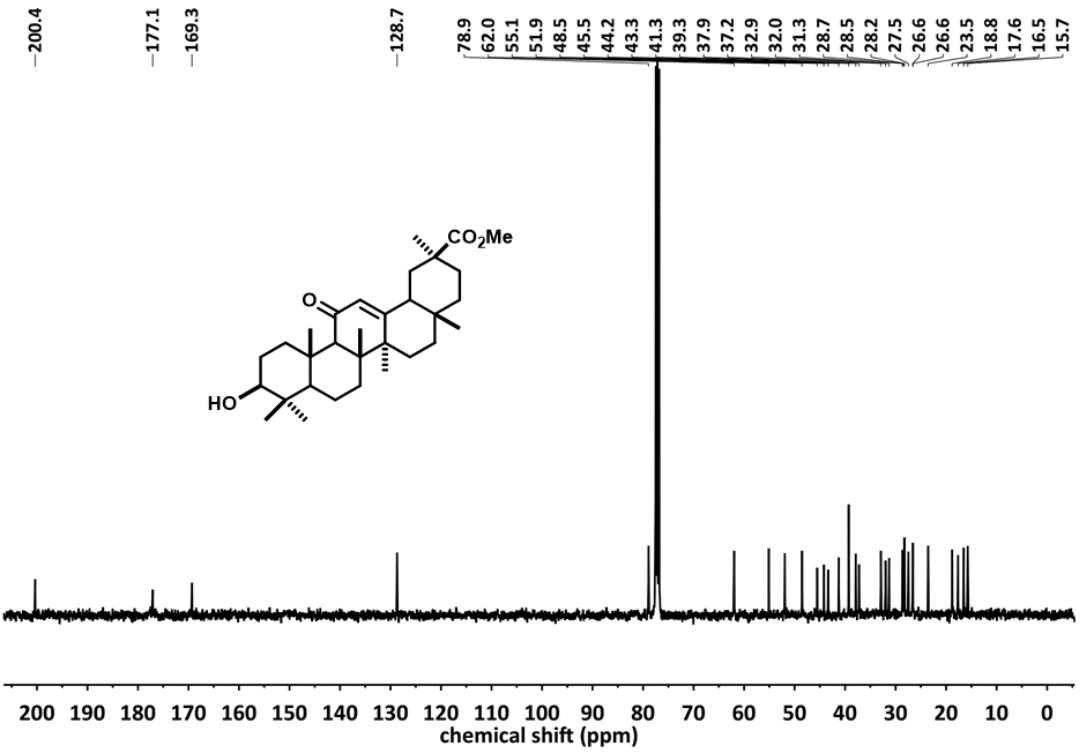


Figure S4. ^{13}C NMR spectrum of $GACO_2Me$ in $CDCl_3$ (100 MHz).

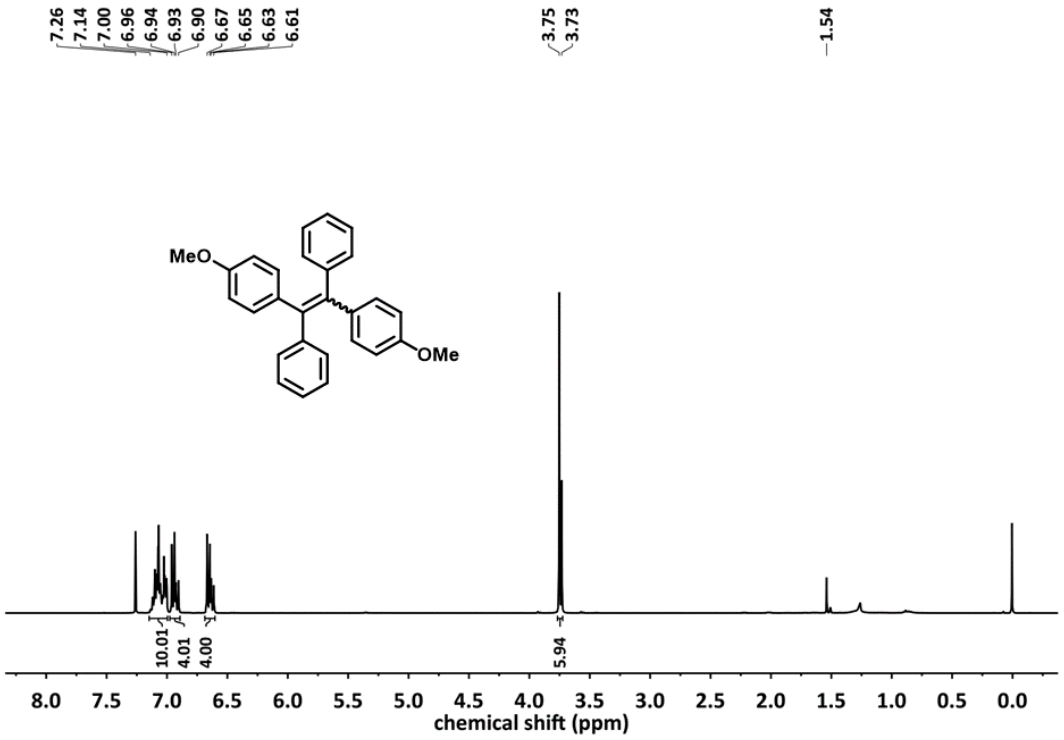


Figure S5. ^{1}H NMR spectrum of *trans*-/*cis*-TPE-2OMe in $CDCl_3$ (400 MHz).

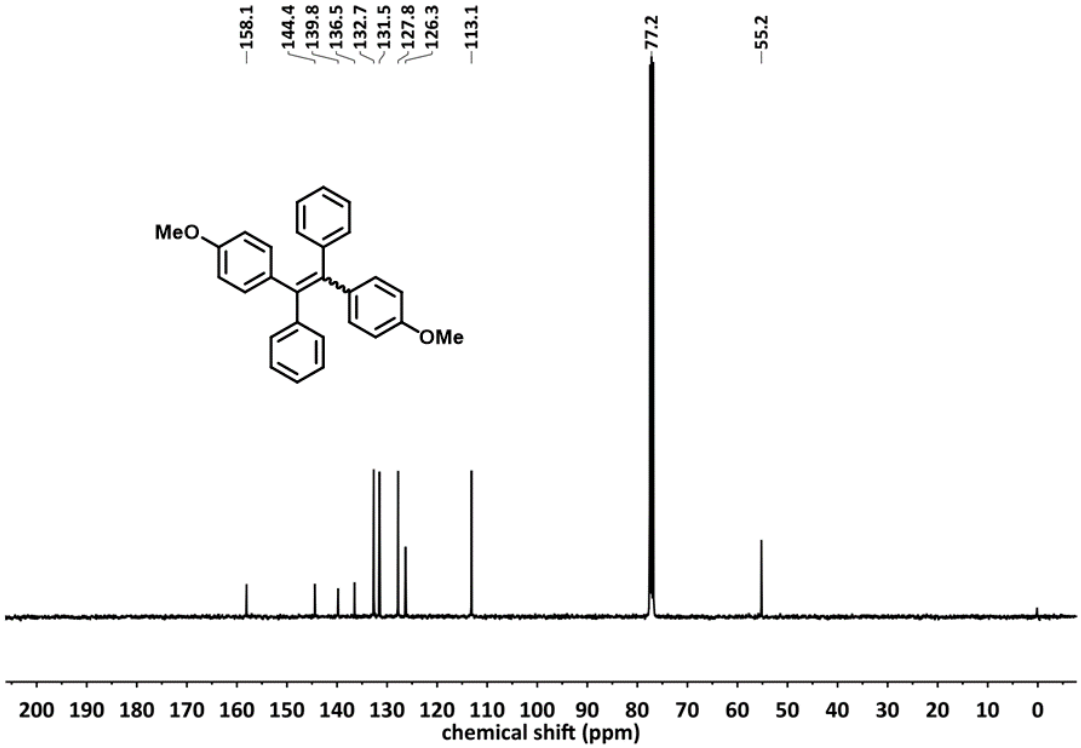


Figure S6. ^{13}C NMR spectrum of *trans*-/*cis*-TPE-2OMe in $CDCl_3$ (100 MHz).

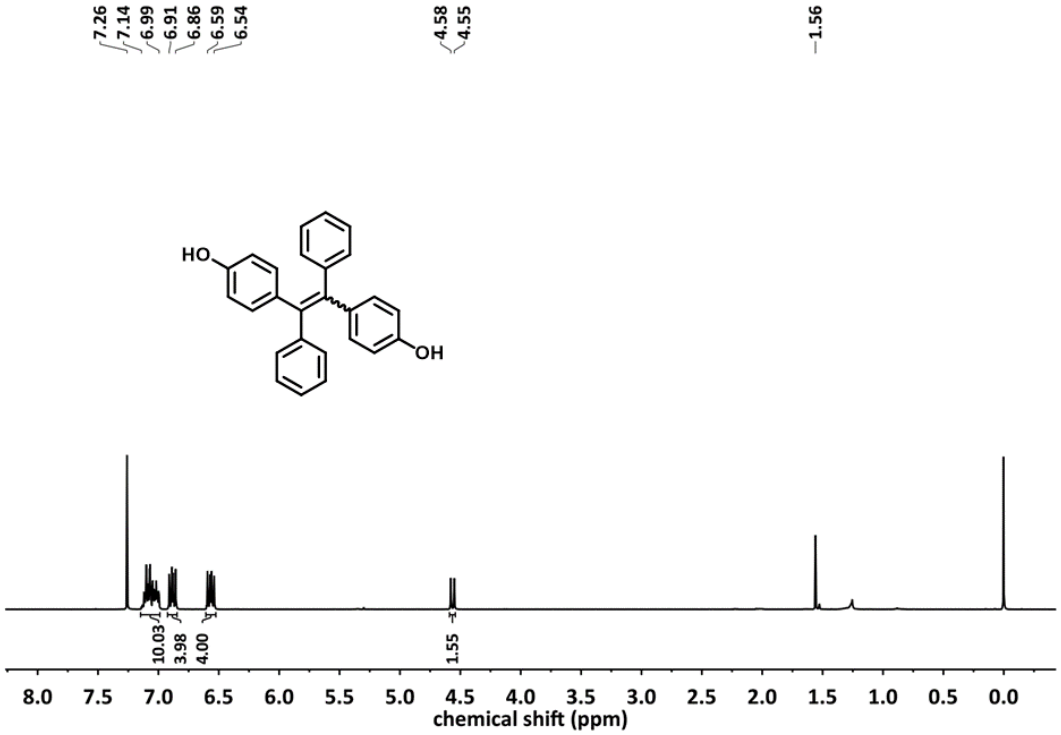


Figure S7. ^{1}H NMR spectrum of *trans*-/*cis*-TPE-2OH in $CDCl_3$ (400 MHz).

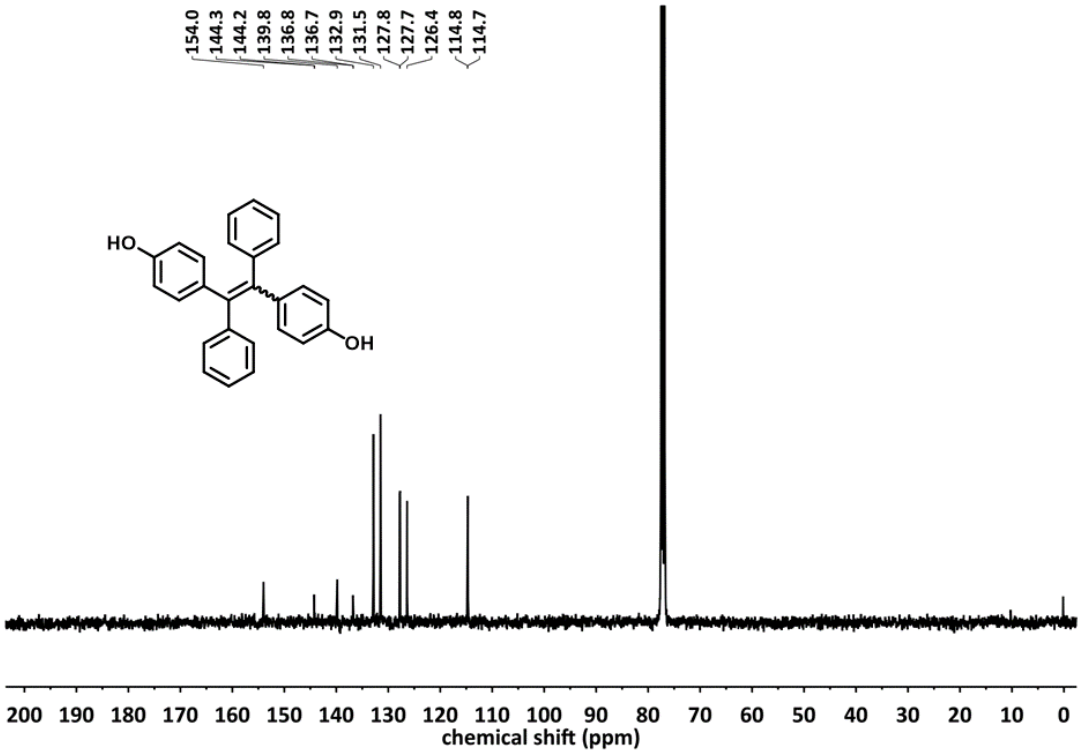


Figure S8. ^{13}C NMR spectrum of *trans*-/*cis*-TPE-2OH in $CDCl_3$ (100 MHz).

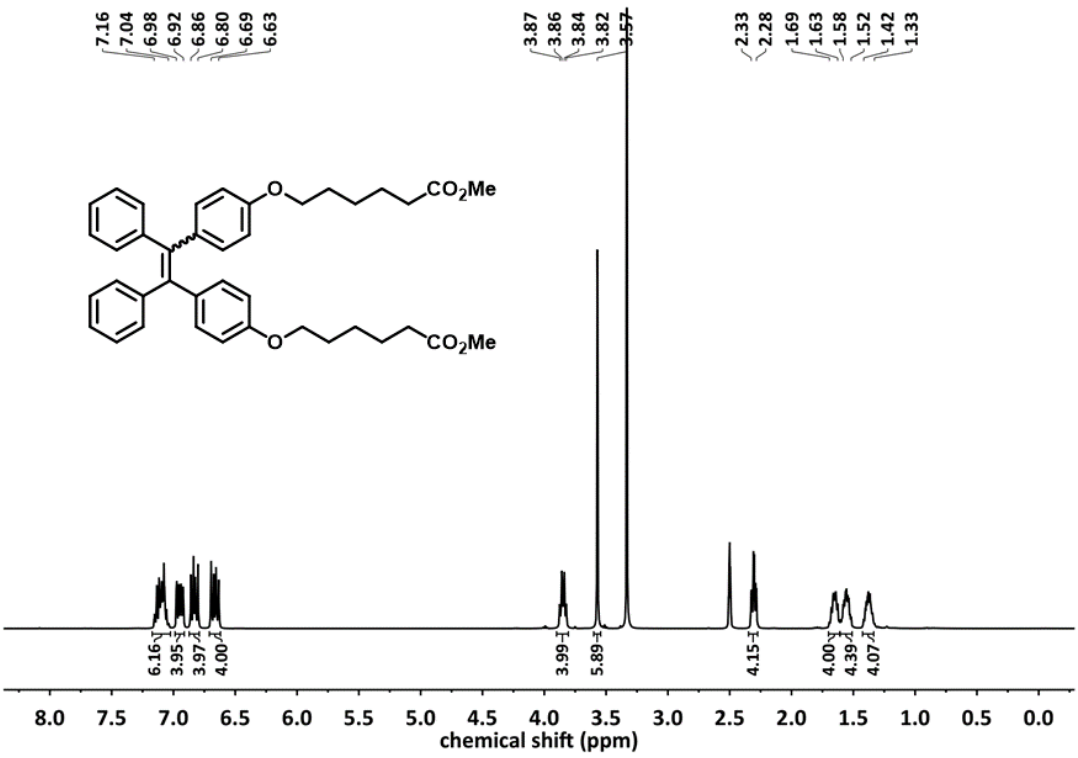


Figure S9. ^{1}H NMR spectrum of *trans*-/*cis*-TPE-2CO_2Me in DMSO-d_6 (400 MHz).

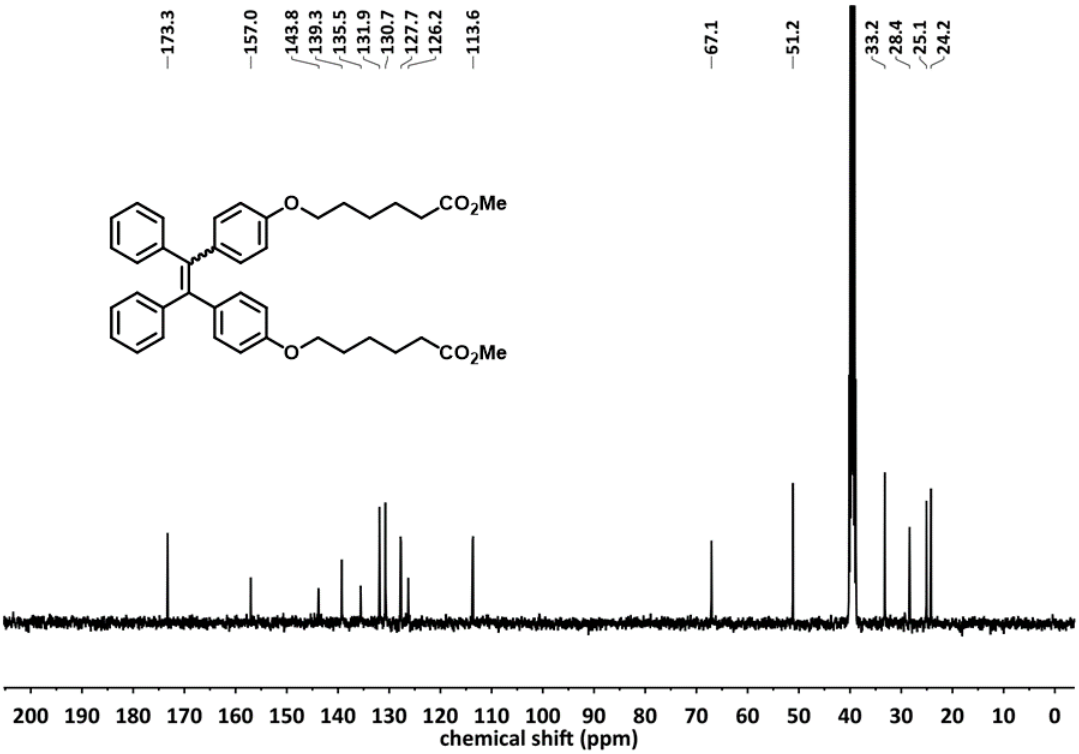


Figure S10. ^{13}C NMR spectrum of *trans*-/*cis*-TPE-2CO_2Me in DMSO-d_6 (100 MHz).

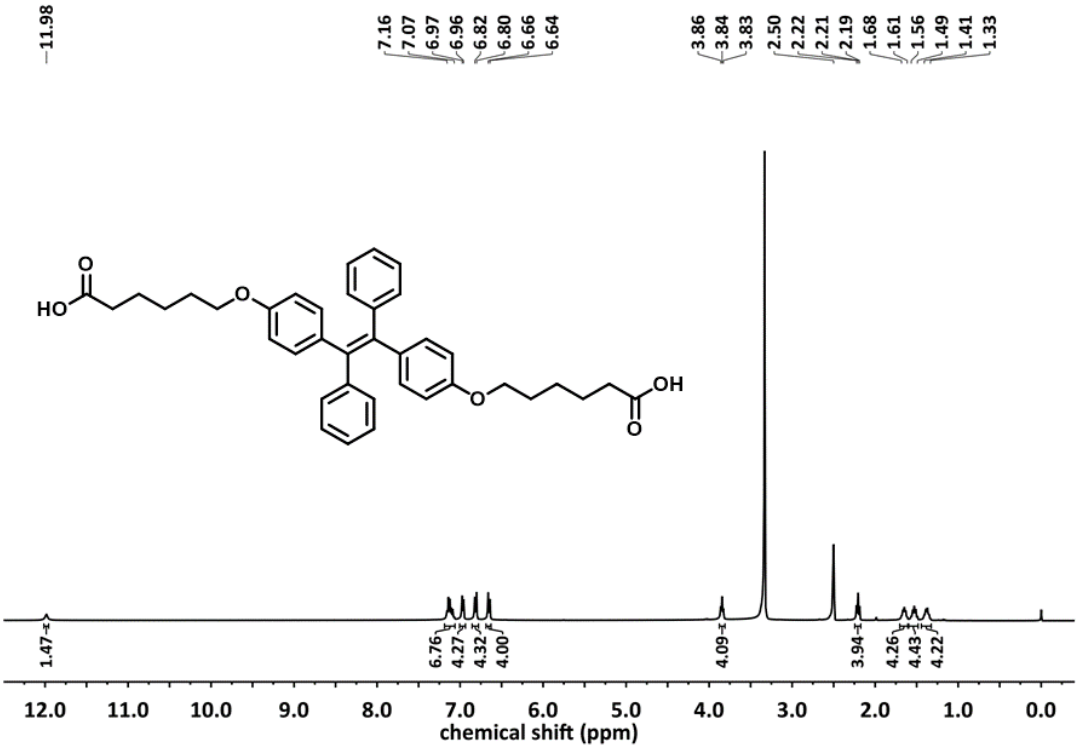


Figure S11. ^{1}H NMR spectrum of *trans*-TPE-2CO_2H in DMSO-d_6 (400 MHz).

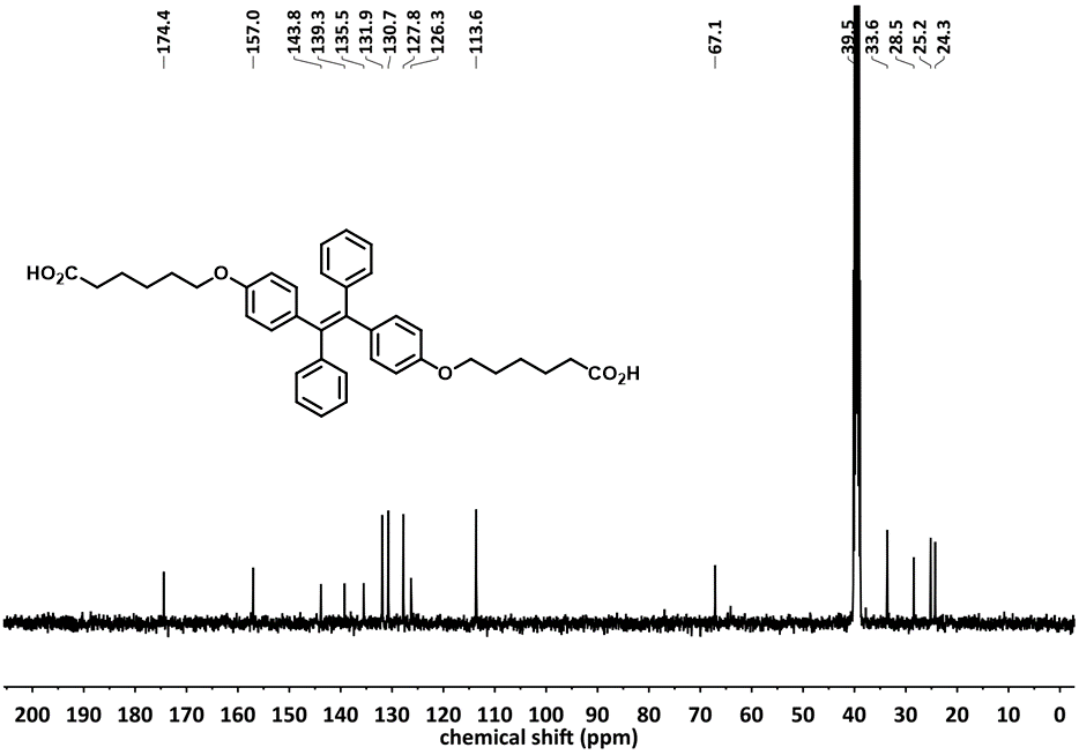


Figure S12. ^{13}C NMR spectrum of *trans*-TPE-2CO_2H in DMSO-d_6 (100 MHz).

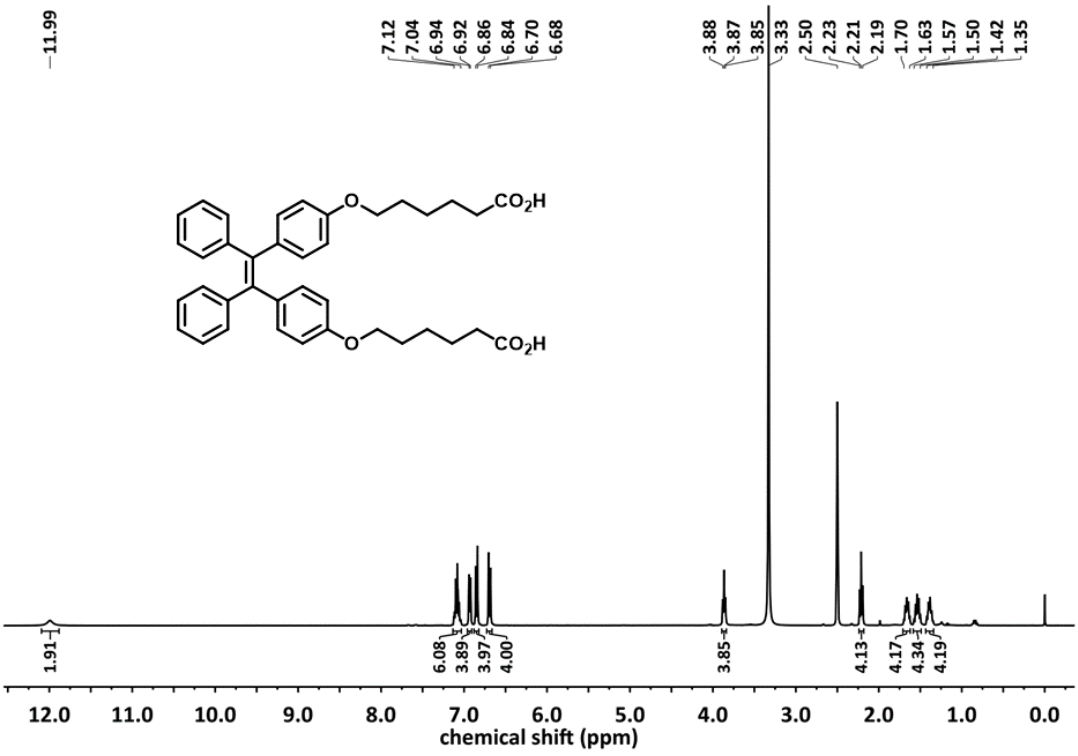


Figure S13. ^{1}H NMR spectrum of *cis*-TPE-2CO_2H in DMSO-d_6 (400 MHz).

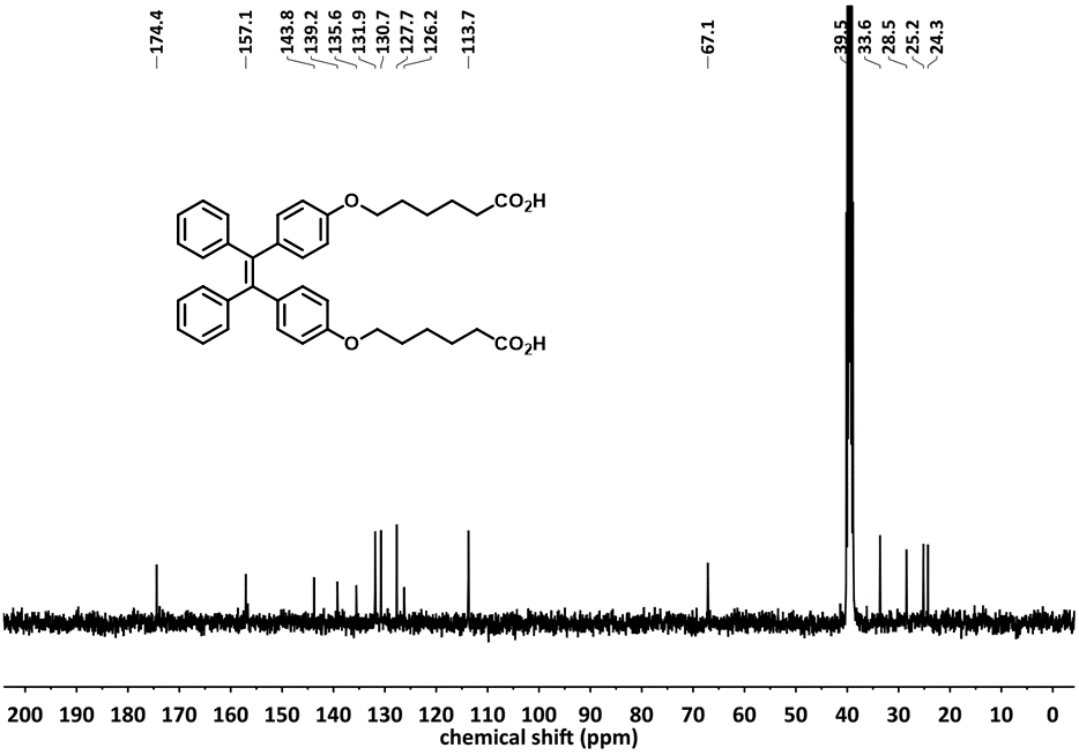


Figure S14. ^{13}C NMR spectrum of *cis*-TPE-2CO_2H in DMSO-d_6 (100 MHz).

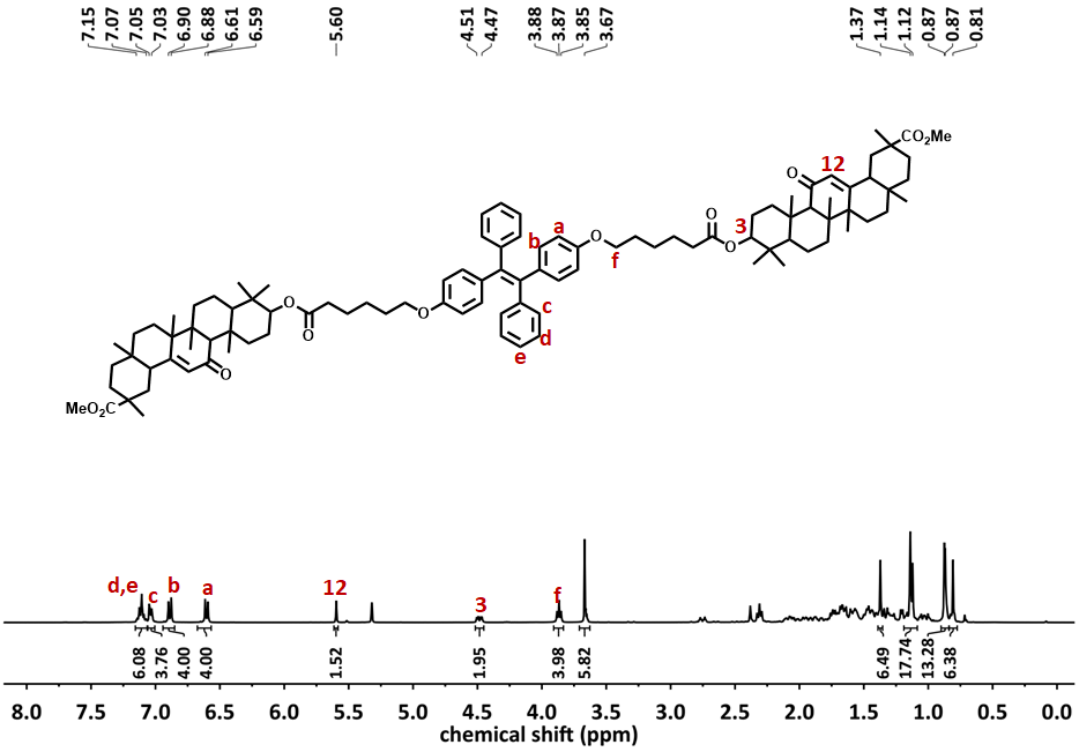


Figure S15. ^{1}H NMR spectrum of *trans*-TPE-2GA in CD_2Cl_2 (400 MHz).

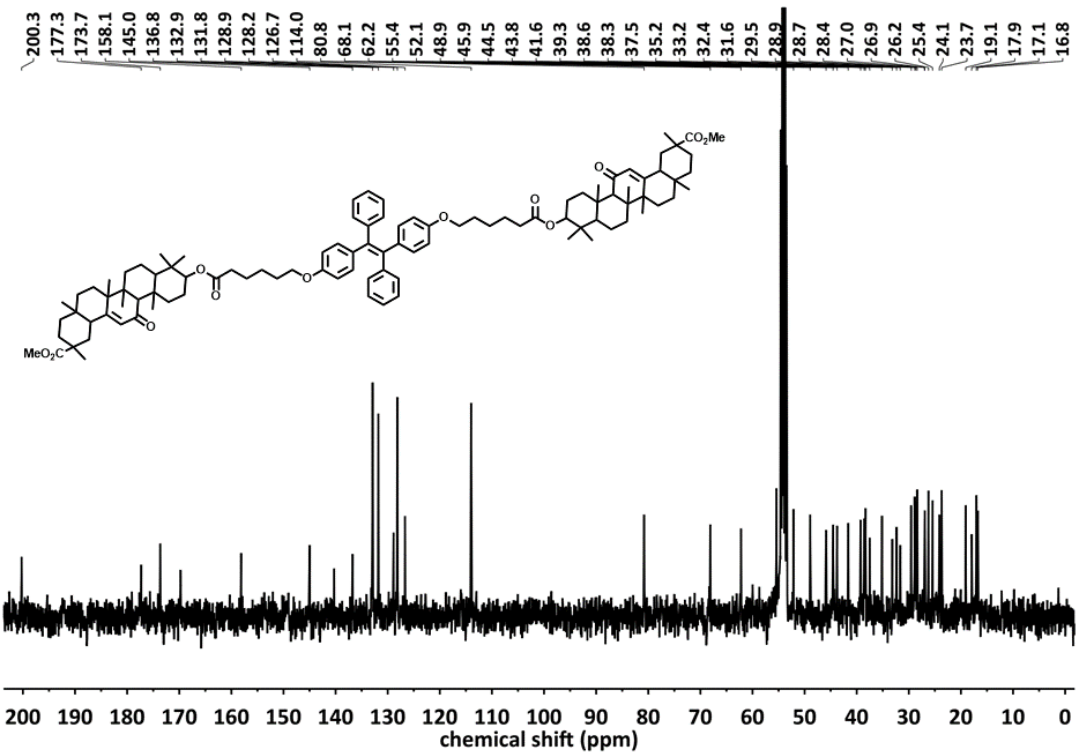


Figure S16. ^{13}C NMR spectrum of *trans*-TPE-2GA in CD_2Cl_2 (100 MHz).

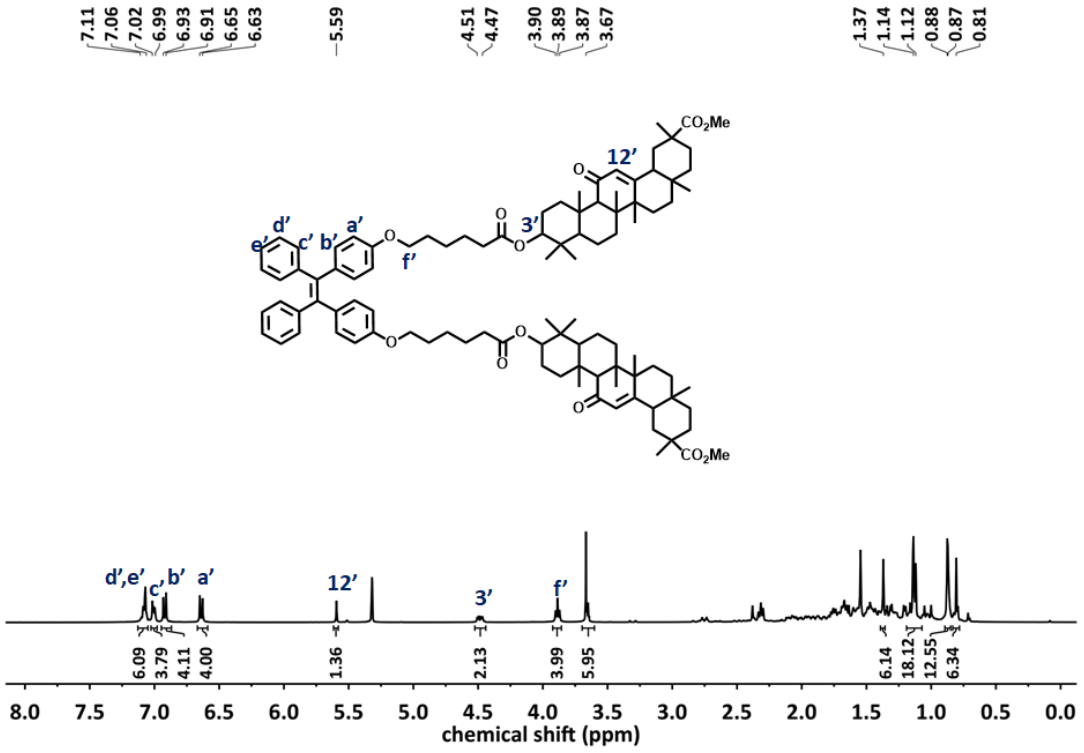


Figure S17. ^{1}H NMR spectrum of *cis*-TPE-2GA in CD_2Cl_2 (400 MHz).

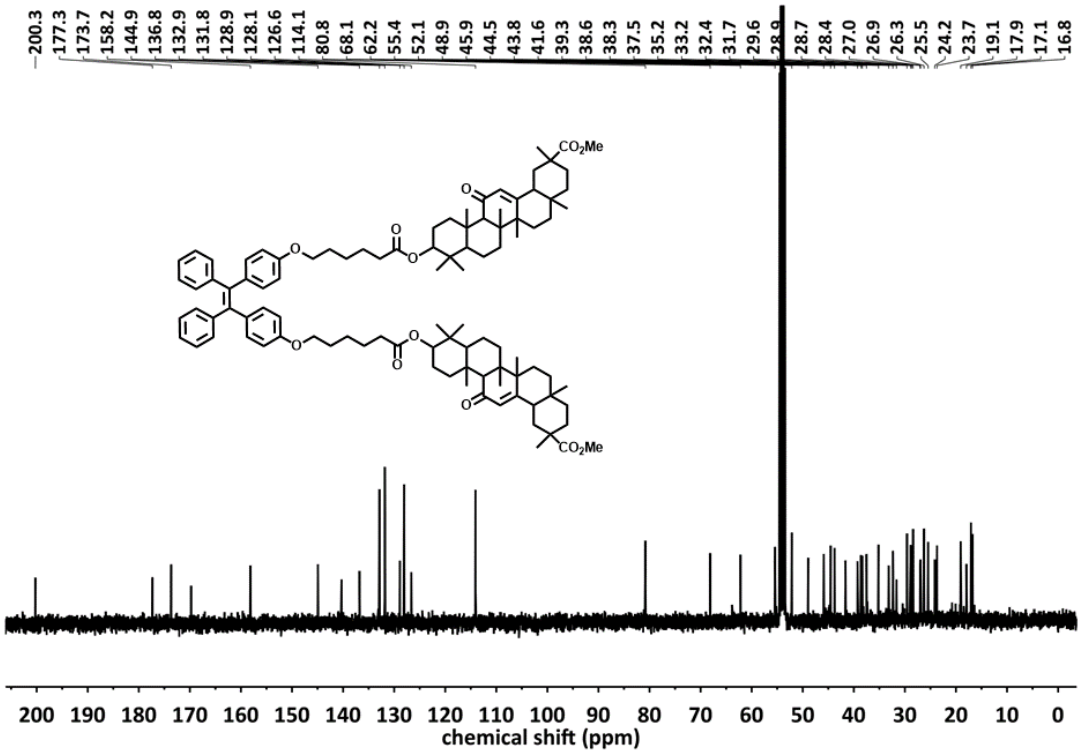


Figure S18. ^{13}C NMR spectrum of *cis*-TPE-2GA in CD_2Cl_2 (100 MHz).

1.8 HRMS of TPE-2GA Isomers

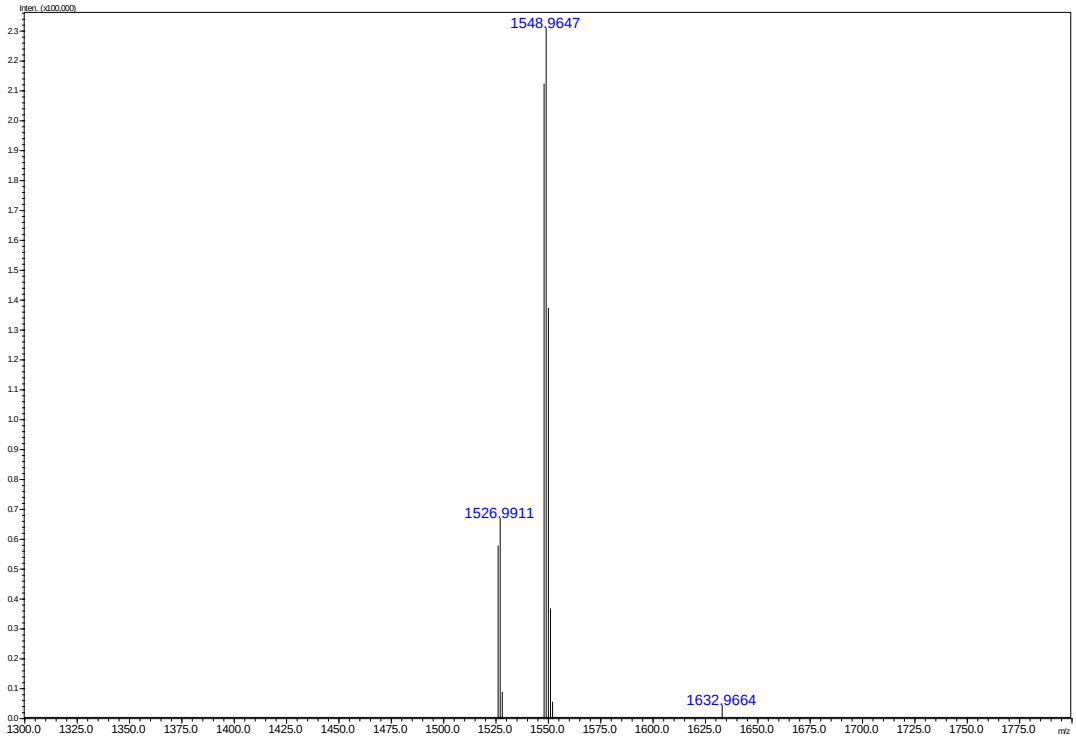


Figure S19. ESI-HRMS (+) spectrum of *trans*-TPE-2GA.

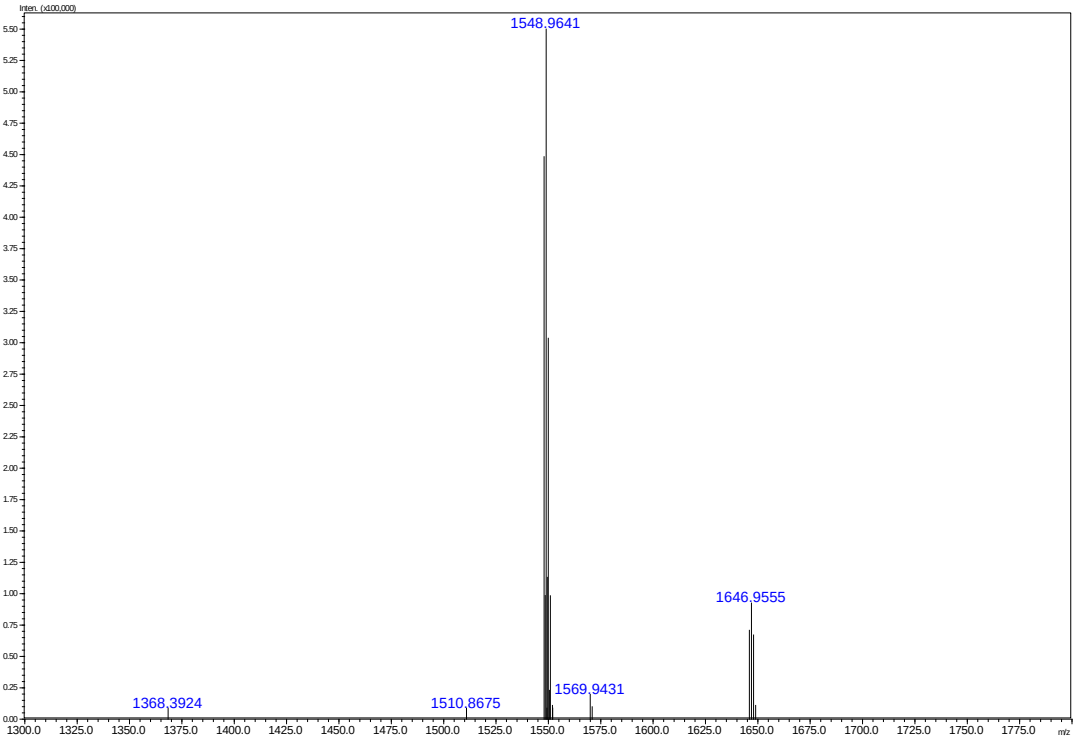


Figure S20. ESI-HRMS (+) spectrum of *cis*-TPE-2GA.

1.9 FT-IR of TPE-2GA Isomers

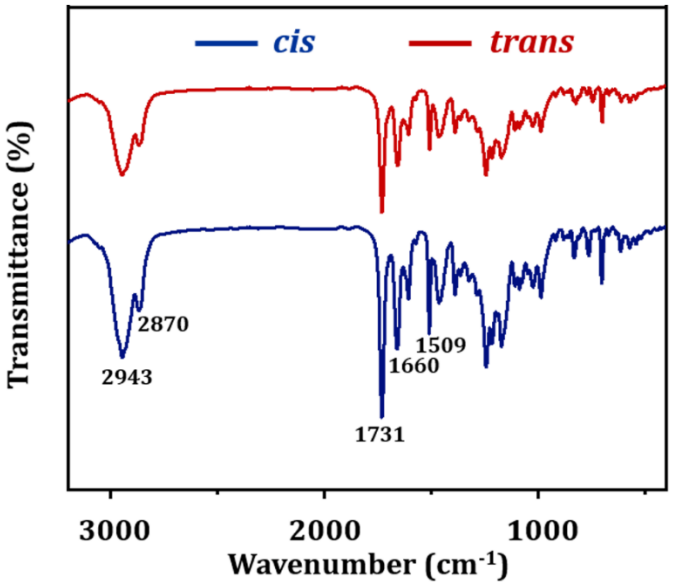


Figure S21. FT-IR spectra of *trans*- and *cis*-TPE-2GA.

1.10 ^{1}H NMR of TPE-2GA Isomers after Heating

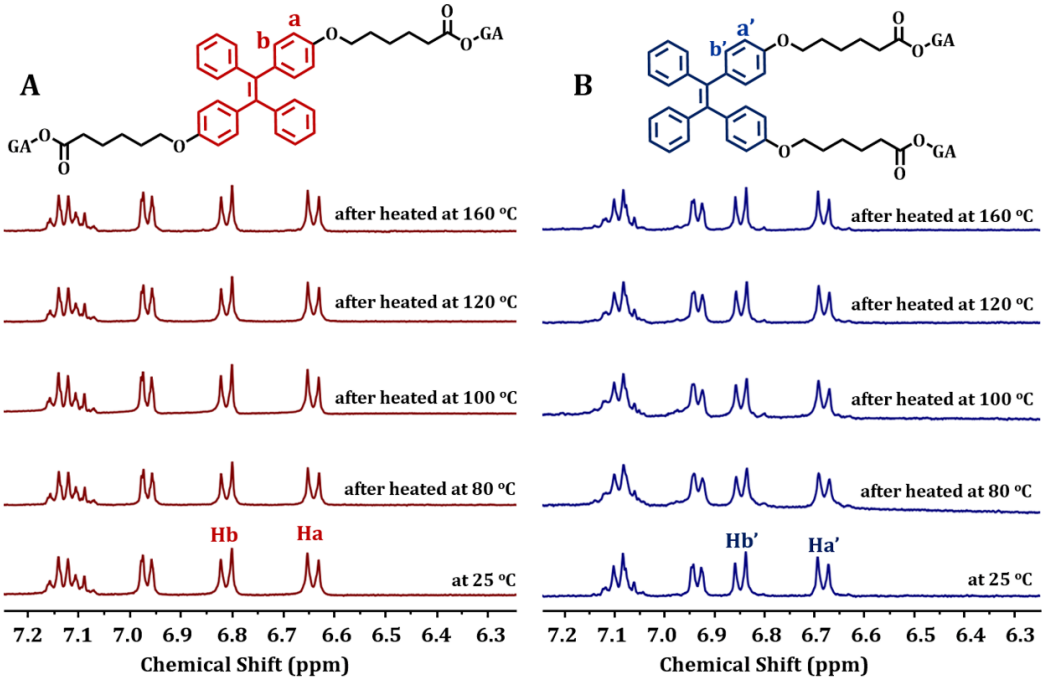


Figure S22. Partial ^{1}H NMR spectra of (A) *trans*-TPE-2GA and (B) *cis*-TPE-2GA in DMSO-d_6 (400 MHz) after heating at different temperatures for 30 min. The abscissas of all NMR spectra are scaled from 6.3 to 7.2 ppm for clarity.

1.11 ^{1}H NMR of TPE-2GA Isomers after Photoisomerization in Solid State

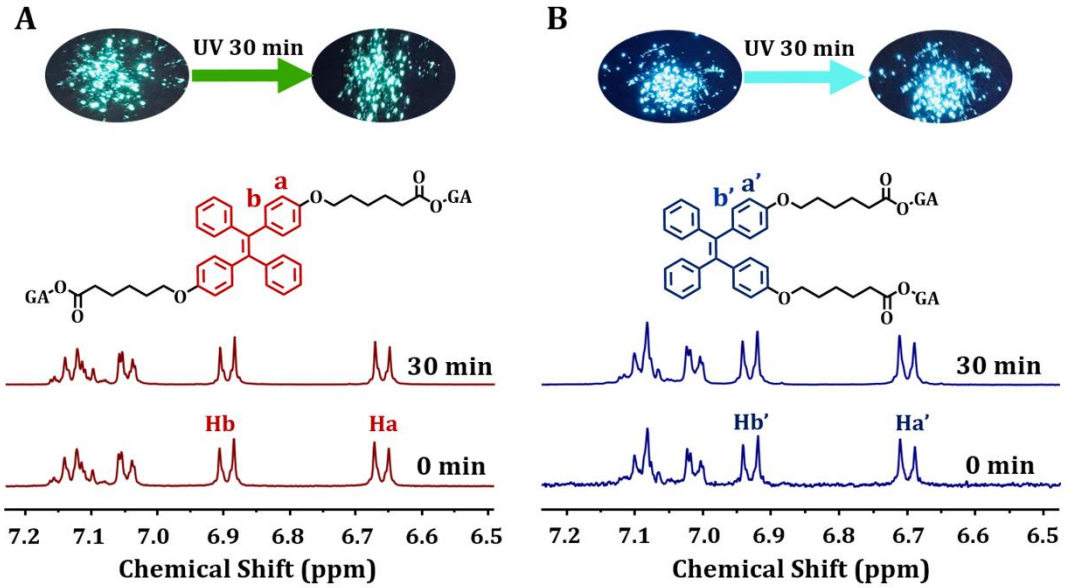


Figure S23. Partial ^{1}H NMR spectra (400 MHz) of (A) *trans*-TPE-2GA and (B) *cis*-TPE-2GA in solid state upon UV irradiation at 365 nm (1.6 mW/cm^2) for 30 min at room temperature. The abscissas of all NMR spectra are scaled from 6.5 to 7.2 ppm for clarity. Insert in (A, B) corresponded to photographs of samples before and after UV irradiation. The solvent is acetone-d_6

2. AIE Properties and Aggregates Morphologies

2.1 UV-vis Spectra of TPE-2GA Isomer

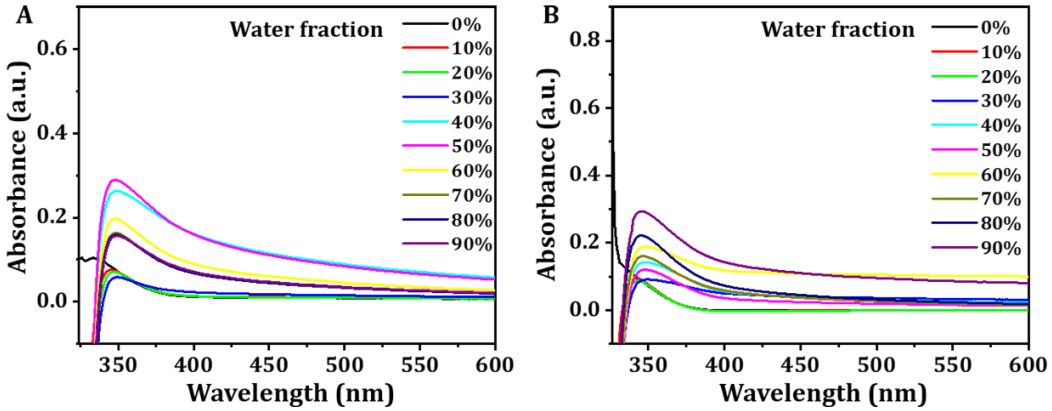


Figure S24. UV-vis spectra of (A) *trans*-TPE-2GA and (B) *cis*-TPE-2GA in water/acetone mixtures with different water fractions, concentration = 10^{-5} M.

2.2 Statistics of Emission Peak and CIE Spectra of TPE-2GA Isomer

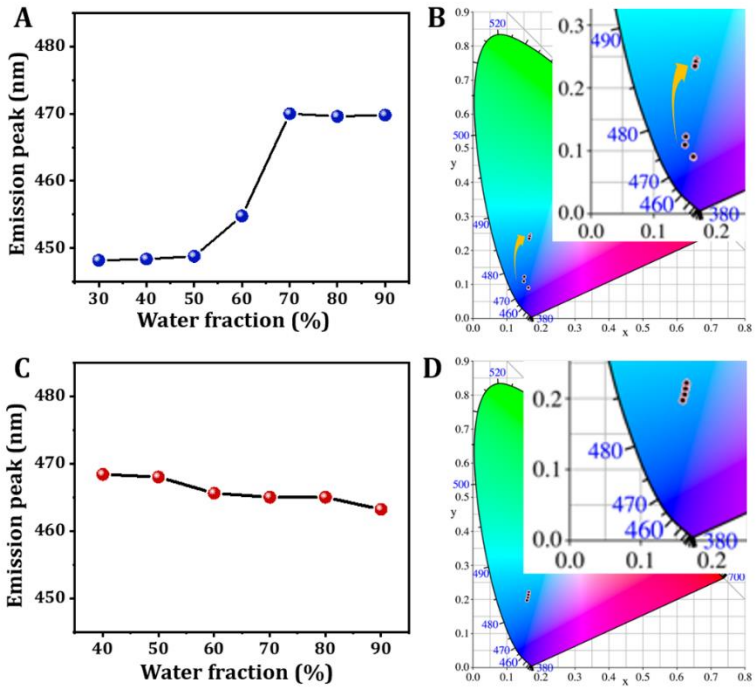


Figure S25. (A) The maximum emission wavelength of *cis*-TPE-2GA with different water fractions, and (B) its corresponding CIE spectrum. (C) The maximum emission wavelength of *trans*-TPE-2GA with different water fractions, and (D) its corresponding CIE spectrum. Inset: partial enlarged view, concentration = 10^{-5} M.

2.3 TEM Images of *Trans*- and *Cis*-TPE-2GA

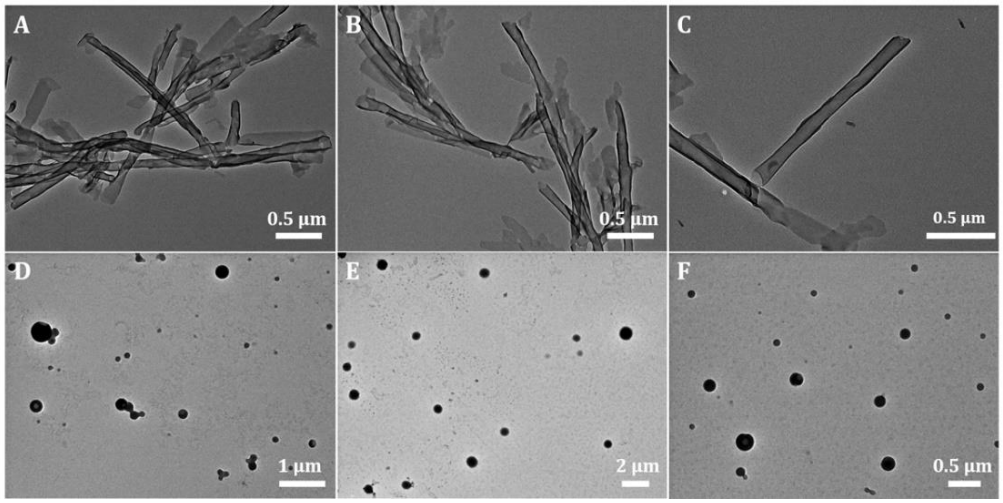


Figure S26. TEM images of *cis*-TPE-2GA in water/acetone at (A, B, C) f_w = 60% and (D) f_w = 80%. TEM images of *trans*-TPE-2GA in water/acetone at (E) f_w = 60% and (F) f_w = 80%.

2.4 Statistical Results the Aggregates of *Trans*- and *Cis*-TPE-2GA

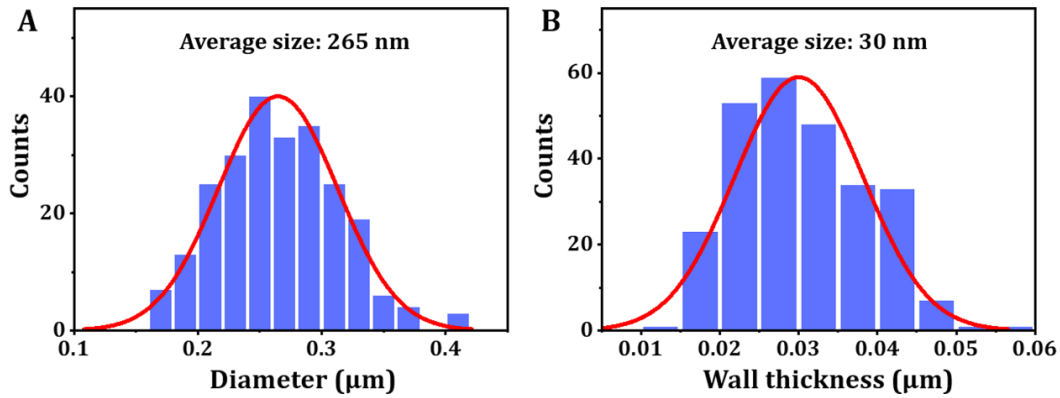


Figure S27. Statistical results (A) of the diameters of nanospheres of *trans*-TPE-2GA and (B) of wall thickness of nanotubes of *cis*-TPE-2GA in the water/acetone mixture with f_w = 60%. Analyses were made for SEM images.

2.5 Schematic of *Cis*-TPE-2GA Molecular Organization in Ribbon-like Aggregate

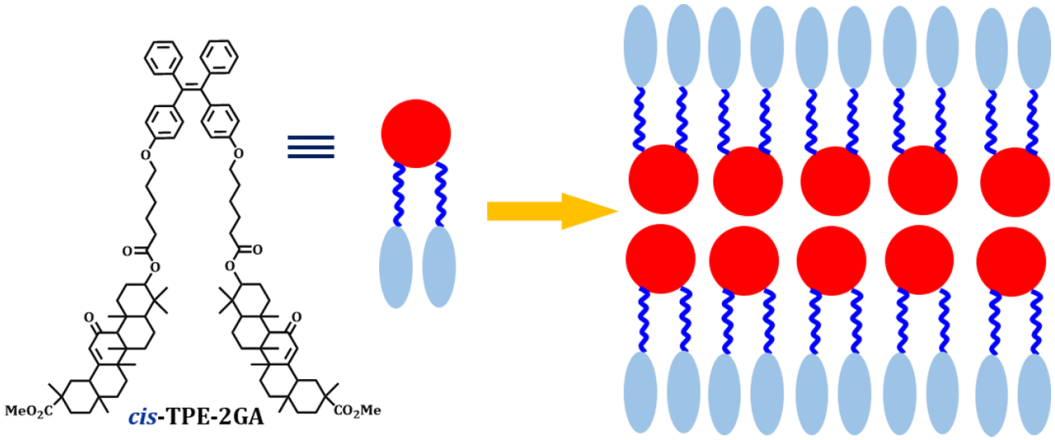


Figure S28. Packing models of ribbons formed by *cis*-TPE-2GA. The red disk represents the TPE moiety, the blue line represents the aliphatic spacer, and the ellipsoid represents the GA skeleton

3. Mechano-chromic Properties of *Trans*- and *Cis*-TPE-2GA in Solid States

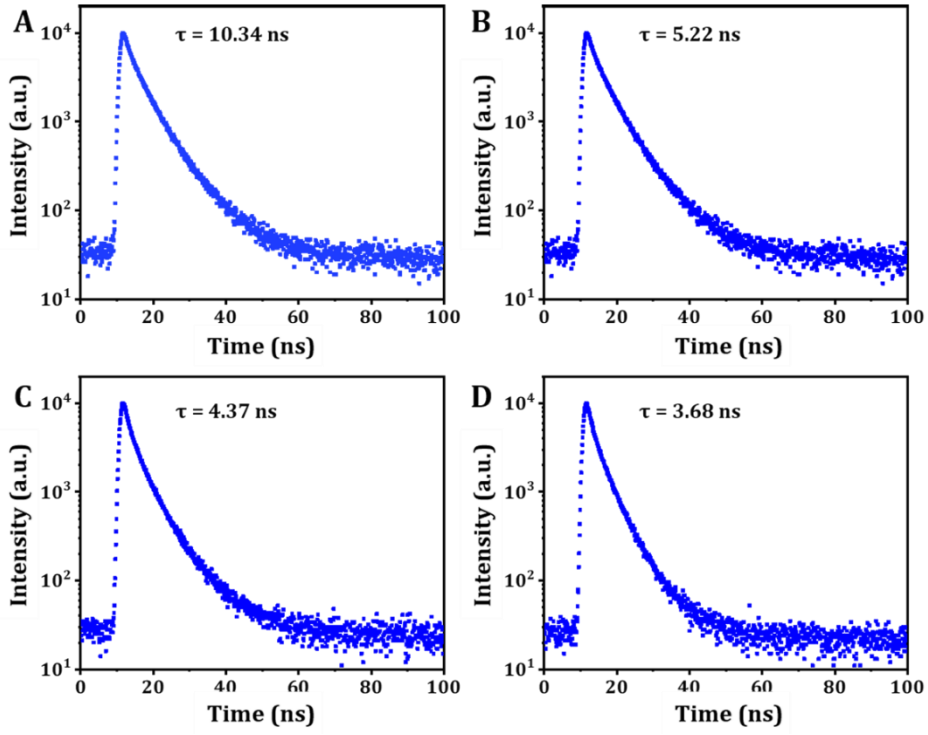


Figure S29. Time-resolved emission decay curves of *cis*-TPE-2GA in (A) pristine and (B) ground states; and *trans*-TPE-2GA in (C) pristine and (D) ground states.

References

1. Gao, Y.; Hao, J.; Wu, J.; Zhang, X.; Hu, J.; Ju, Y. Supramolecular Helical Nanofibers Assembled from a Pyridinium-Functionalized Methyl Glycyrrhetate Amphiphile. *Nanoscale* **2015**, *7*, 13568-13575.
2. Xu, L.; Jiang, L.; Drechsler, M.; Sun, Y.; Liu, Z.; Huang, J.; Tang, B. Z.; Li, Z.; Stuart, M. A. C.; Yan, Y. Self-Assembly of Ultralong Polyion Nanoladders Facilitated by Ionic Recognition and Molecular Stiffness. *J. Am. Chem. Soc.* **2014**, *136*, 1942-1947.
3. Yu, X.; Chen, H.; Shi, X.; Albouy, P.-A.; Guo, J.; Hu, J.; Li, M.-H. Liquid Crystal Gelators with Photo-Responsive and AIE Properties. *Mater. Chem. Front.* **2018**, *2*, 2245-2253.