

Supporting Information

E/Z Isomerization effects on aggregation-enhanced emission of tetraphenylethene derivatives assisted by host–guest recognition

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Instruments and Materials

¹H and ¹³C NMR spectra were recorded on a JNM-ECS400 or Varian 600MHz spectrometer, using CD₂Cl₂ or CDCl₃ with TMS as an internal standard. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were obtained on a Bruker APEX II FT-MS mass spectrometer. UV-vis absorption spectra were recorded by using a SHIMADZU UV-2550 spectrophotometer. Luminescence measurements were made on a Hitachi-7000 spectrofluorimeter with a xenon lamp as the excitation source. SEM images were obtained with JSM-5600LV. TEM images were recorded on JEM-2100 operating at 200 kV. Elemental analyses were performed with an Elementar VarioELcube. Melting points (M.p.) were determined on a Kofler apparatus. All measurements were carried out at room temperature. All reaction operations were performed under an anhydrous Ar atmosphere. Toluene was distilled over Na.

Synthesis of 4DB24C8-TPE and E/Z-2DBA-TPE

E/Z-2Br-TPE^{s1} was synthesized according to the procedure as described previously and showed an identical ¹H NMR spectrum to the reported one therein.

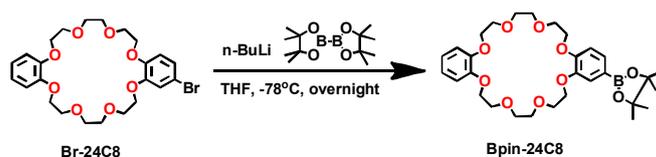
E/Z-2CHO-TPE: E/Z-2Br-TPE (490 mg, 1.00 mmol), 4-Formylphenylboronic acid (450 mg, 3.00 mmol), Na₂CO₃ (848 mg, 8.00 mmol) and Pd (PPh₃)₄ (115.6 mg, 0.10 mmol) were added to a mixture solvent of toluene (15 mL) and H₂O (4 mL) in an oven dried Schlenk flask under an argon atmosphere. The resulting mixture was stirred at 100 °C for 3 days. The crude product was extracted with dichloromethane three times, and then the organic layers were merged and dried over anhydrous MgSO₄. The crude product was further purified by column chromatography (SiO₂) using dichloromethane/petroleum (1:4) as eluent to afford E-2CHO-TPE as a yellow solid (80 mg, 15% yield). ¹H NMR (400 MHz, CDCl₃, ppm), δ: 10.04 (s, 2H, CHO), 7.91 (d, *J* = 8.0 Hz, 4H, Ar), 7.72 (d, *J* = 8.0 Hz, 4H, Ar), 7.41 (d, *J* = 8.0 Hz, 4H, Ar), 7.17-7.10 (m, 14H, Ar). ¹³C NMR (400 MHz, CDCl₃, ppm), δ: 191.87, 146.56, 144.00, 143.32, 140.84, 137.42, 135.05, 131.99, 131.37, 130.21, 127.94, 127.34, 126.83, 126.53, 77.32, 77.00, 76.68. HR-ESI-MS (*m/z*), [C₄₀H₂₈O₂+H]⁺ calculated: 541.2162, found: 541.2153. Elemental analysis calcd. for C₄₀H₂₈O₂·0.4CH₂Cl₂: C 84.44, H 5.05; found: C 84.35, H 4.67. M.p. 265–266 °C.

Z-2CHO-TPE was obtained as a luminous yellow solid (50 mg, 11% yield). ¹H NMR (400 MHz, CDCl₃, ppm), δ: 10.03 (s, 2H, CHO), 7.91 (d, *J* = 8.0 Hz, 4H, Ar), 7.72 (d, *J* = 8.0 Hz, 4H, Ar), 7.44 (d, *J* = 8.0 Hz, 4H, Ar), 7.19 (d, *J* = 8.0 Hz, 4H, Ar), 7.15-7.13 (m, 6H, Ar), 7.09-7.06 (m, 4H, Ar). ¹³C NMR (400 MHz, CDCl₃, ppm), δ: 191.83, 146.49, 143.99, 143.33, 140.84, 137.52, 135.08, 132.03, 131.34, 130.21, 127.,79, 127.34, 126.75, 126.67, 77.32, 77.00, 76.68. HR-ESI-MS (*m/z*), [C₄₀H₂₈O₂+H]⁺ calculated: 541.2162, found: 541.2155. Elemental analysis calcd. for C₄₀H₂₈O₂·0.4CH₂Cl₂: C 84.44, H 5.05; found: C 83.99, H 5.15. M.p. 192–194 °C.

E-2DBA-TPE: E-2CHO-TPE (120 mg, 0.22 mmol) and benzylamine (23.8 mg, 0.22 mmol) were added into an oven dried Schlenk flask and dissolved in anhydrous dichloromethane (12 mL) under an argon atmosphere. The resulting mixture was

allowed to stir at 35 °C for 1 day. The *in-situ* ^1H NMR spectrum revealed that 99% of E-2CHO-TPE was converted into a Schiff-base form. Subsequently sodium borohydride (134.5 mg, 3.56 mmol) was added under the argon atmosphere. The resulting solution was stirred at room temperature for another day. The solvent was removed and then the crude product was purified by recrystallization in a chloroform/methanol mixture solvent (1/3). The final product E-2DBA-TPE was obtained as a natterblue solid (143 mg, 90% yield). ^1H NMR (400 MHz, CDCl_2 , ppm), δ : 7.51 (d, $J = 8.0$ Hz, 4H, Ar), 7.38-7.29 (m, 16H, Ar), 7.25-7.21 (m, 2H, Ar), 7.15-7.08 (m, 14H, Ar), 3.80 (d, $J = 4.0$ Hz, 8H, NCH_2). ^{13}C NMR (400 MHz, CDCl_2 , ppm), δ : 144.35, 144.34, 141.28, 140.45, 139.18, 132.25, 131.84, 129.07, 128.82, 128.65, 128.34, 127.34, 127.15, 126.50, 54.54, 54.27, 54.00, 53.73, 53.46, 30.25. HR-ESI-MS (m/z), $[\text{C}_{54}\text{H}_{48}\text{N}_2+\text{H}]^+$ calculated: 723.3734, found: 723.3718. Elemental analysis calcd. for $\text{C}_{54}\text{H}_{48}\text{N}_2 \cdot 0.3\text{CHCl}_3$: C 85.72, H 6.40, N 3.68; found: C 85.28, H 6.45, N 3.19. M.p. 174–175 °C.

Z-2DBA-TPE was similarly obtained as a gray solid, but using Z-2CHO-TPE as a reactant (116 mg, 73% yield). ^1H NMR (400 MHz, CDCl_2 , ppm), δ : 7.52 (d, $J = 8.0$ Hz, 4H, Ar), 7.41-7.29 (m, 16H, Ar), 7.25-7.21 (m, 2H, Ar), 7.15-7.07 (m, 14H, Ar), 3.79 (d, $J = 8.0$ Hz, 8H, NCH_2). ^{13}C NMR (400 MHz, CDCl_2 , ppm), δ : 144.43, 143.26, 141.27, 141.25, 140.43, 139.48, 139.28, 132.24, 131.85, 129.05, 128.81, 128.64, 128.21, 127.33, 127.18, 126.99, 126.63, 54.54, 54.27, 54.00, 53.73, 53.46, 30.25. HR-ESI-MS (m/z), $[\text{C}_{54}\text{H}_{48}\text{N}_2+\text{H}]^+$ calculated: 723.3734, found: 723.3721. Elemental analysis calcd. For $\text{C}_{54}\text{H}_{48}\text{N}_2 \cdot 0.3\text{CH}_2\text{Cl}_2$: C 87.14, H 6.28, N 3.74; found: C 87.04, H 6.18, N 3.56. M.p. 190–192 °C.



Scheme S1 Synthesis of Bpin-24C8.^{S2}

4I-TPE: 4Br-TPE (1.30 g, 2.0 mmol) was added to 50 mL THF in an oven dried Schlenk flask under an argon atmosphere at room temperature. Then the mixture

solution was cooled to $-78\text{ }^{\circ}\text{C}$. *n*-BuLi (6.0 mL, 9.6 mmol) was added to the solution and stirred for 1 h. Then, I_2 (3.05 g, 12.0 mmol) was added to the mixture solution and stirred at room temperature overnight. Sodium thiosulfate pentahydrate was added to the mixture solution to quench the reaction and then the crude product was extracted by dichloromethane ($3 \times 50\text{ mL}$). The organic layers were merged and dried by anhydrous MgSO_4 . Further purification was achieved by column chromatography (SiO_2) using petroleum ether as eluent. 4I-TPE was isolated as a white solid (1.05 g, 63% yield). ^1H NMR (400 MHz, CDCl_3 , ppm), δ : 7.46 (d, $J = 8.0\text{ Hz}$, 8H, Ar), 6.70 (d, $J = 8.0\text{ Hz}$, 8H, Ar). ^{13}C NMR (400 MHz, CDCl_3 , ppm), δ : 142.03, 139.76, 137.22, 132.94, 132.74, 131.28, 77.32, 77.00, 76.68. HR-ESI-MS (m/z), $[\text{C}_{26}\text{H}_{16}\text{I}_4]^+$ calculated: 835.7425, found: 835.7413. Elemental analysis calcd. for $\text{C}_{26}\text{H}_{16}\text{I}_4 \cdot 0.4\text{C}_6\text{H}_{14}$: C 39.19, H 2.50; found: C 39.47, H 1.82. M.p. 294–296 $^{\circ}\text{C}$.

4DB24C8-TPE: 4I-TPE (100 mg, 0.12 mmol), Bpin-24C8 (413 mg, 0.72 mmol), Na_2CO_3 (153 mg, 1.44 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (27.73 mg, 0.024 mmol) were dissolved to a mixture solvent of water (5 mL) and toluene (10 mL) in an oven dried Schlenk flask under an argon atmosphere. The resulting mixture was stirred at 100 $^{\circ}\text{C}$ for 3 d. The solvent was removed and then the crude product was extracted by dichloromethane ($3 \times 25\text{ mL}$). The organic layers were merged and dried over anhydrous MgSO_4 . Further purification was achieved by column chromatography (SiO_2) using dichloromethane/methanol (10/1) as eluent. 4DB24C8-TPE was isolated as a dark green solid (43 mg, 17% yield). ^1H NMR (400 MHz, CDCl_3 , ppm), δ : 7.32 (d, $J = 8\text{ Hz}$, 8H, Ar), 7.14–7.08 (m, 16H, Ar), 6.90–6.88 (m, 20H, Ar), 4.19–4.16 (m, 32H, OCH_2), 3.92 (s, 32H, OCH_2), 3.83–3.82 (m, 32H, OCH_2). ^{13}C NMR (600 MHz, CDCl_3 , ppm), δ : 148.96, 148.53, 142.50, 138.54, 134.06, 131.84, 125.91, 121.42, 114.12, 77.21, 77.00, 76.79, 71.28, 69.92, 69.40, 29.69. HR-ESI-MS (m/z), $[\text{C}_{122}\text{H}_{140}\text{O}_{32} + \text{Na}]^+$ calculated: 2140.9253, found: 2140.9229. Elemental analysis calcd. for $\text{C}_{122}\text{H}_{140}\text{O}_{32} \cdot 0.6\text{CHCl}_3$: C 67.24, H 6.47; found: C 67.62, H 5.89. M.p. 147–148 $^{\circ}\text{C}$.

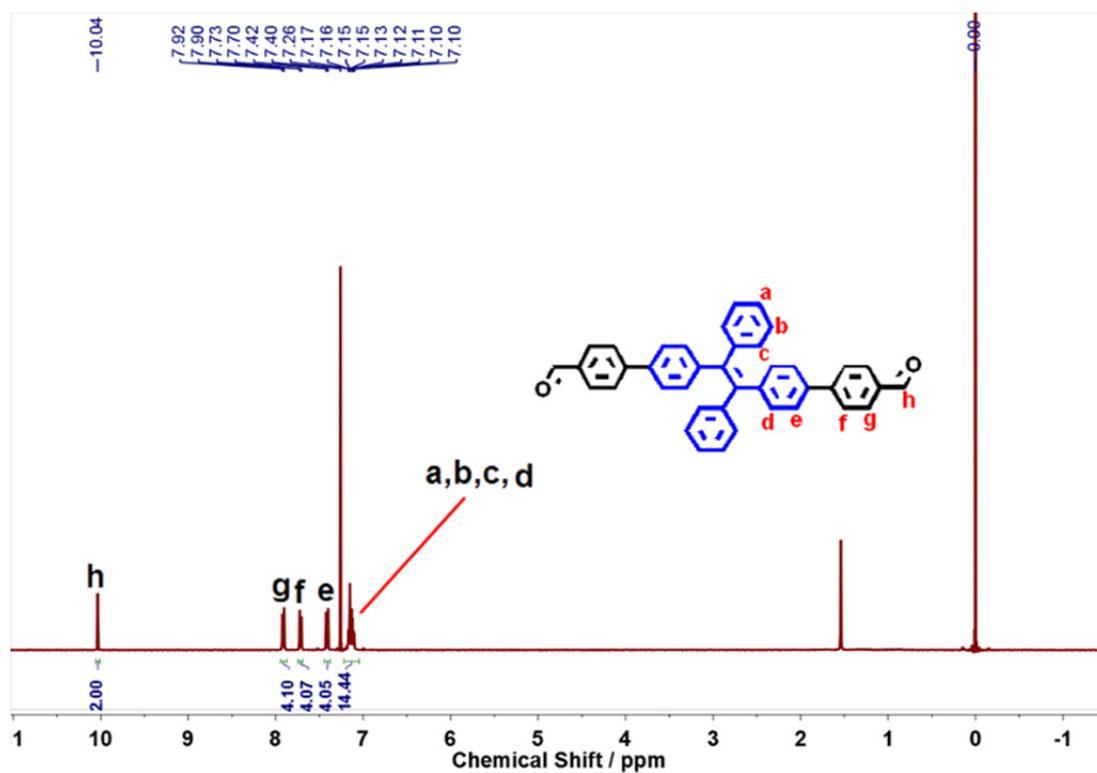


Fig. S1 ^1H NMR spectrum of E-2CHO-TPE.

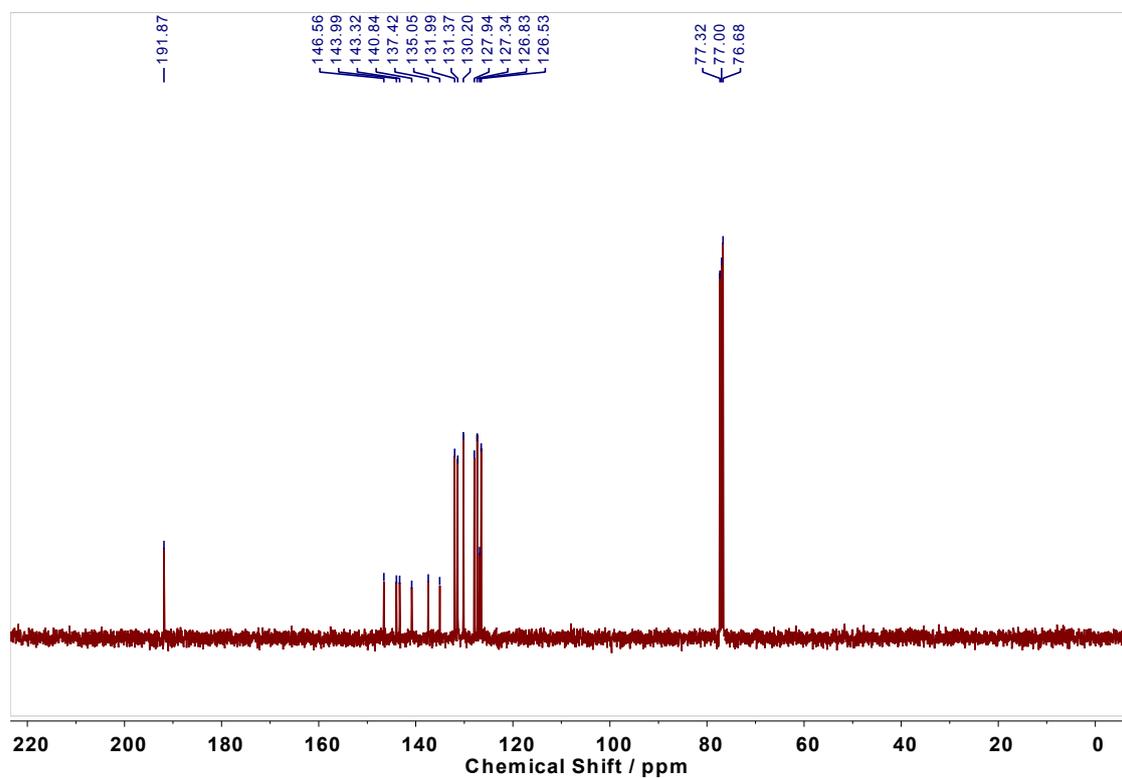


Fig. S2 ^{13}C NMR spectrum of E-2CHO-TPE.

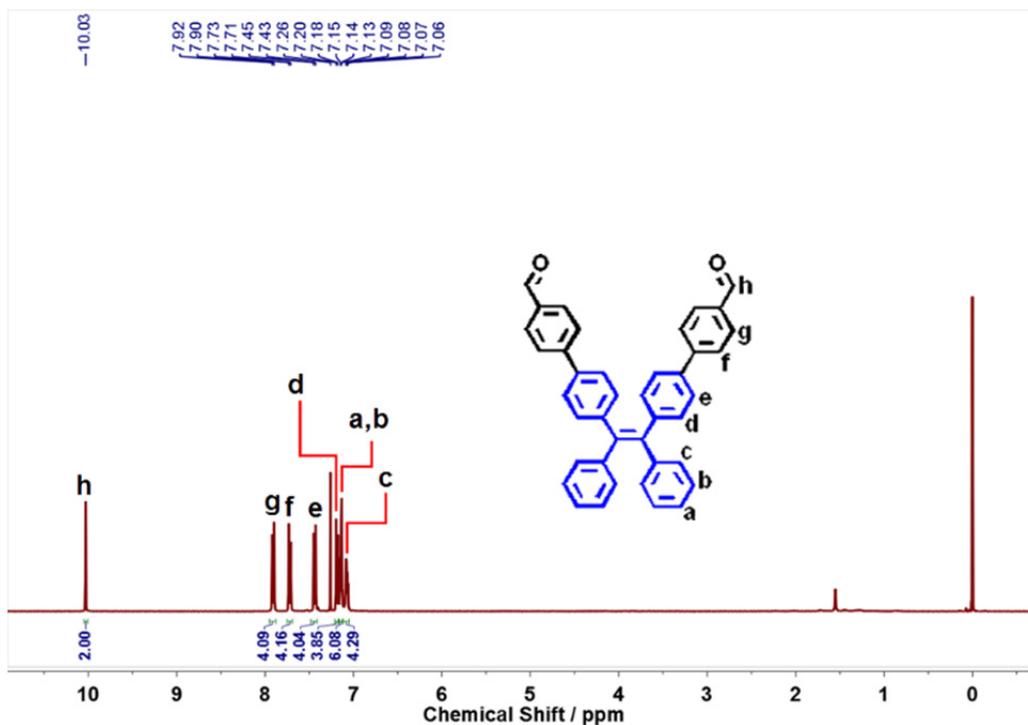


Fig. S3 ^1H NMR spectrum of Z-2CHO-TPE.

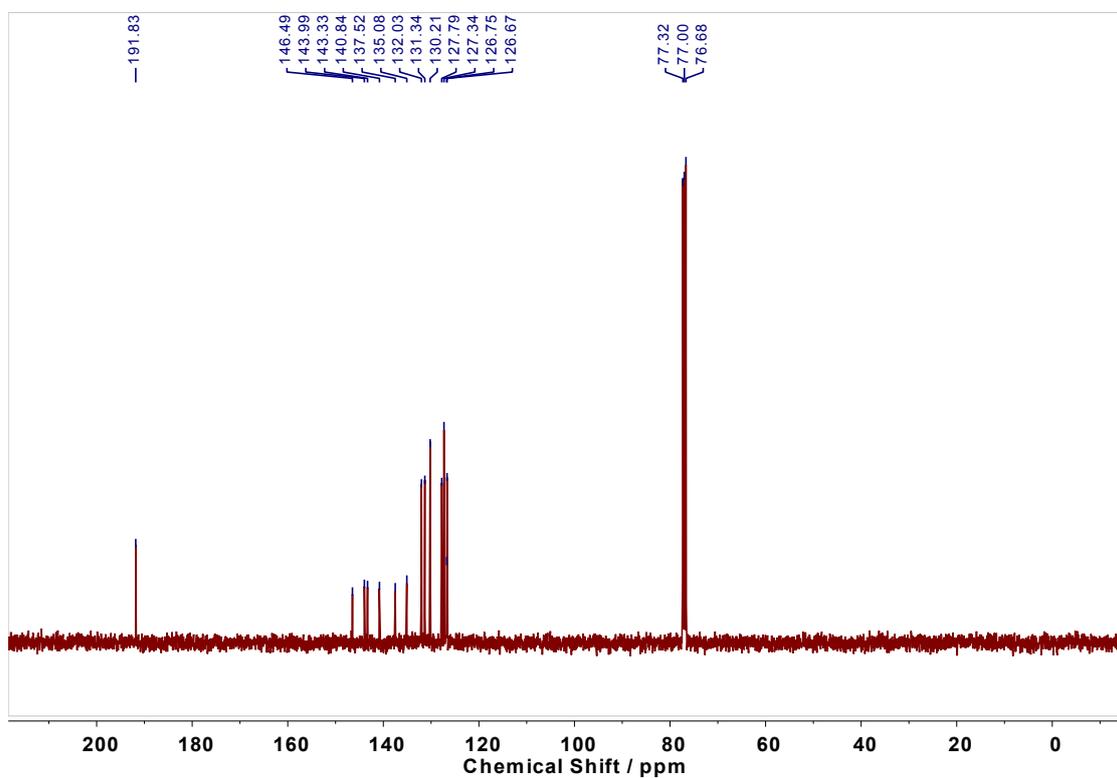


Fig. S4 ^{13}C NMR spectrum of Z-2CHO-TPE.

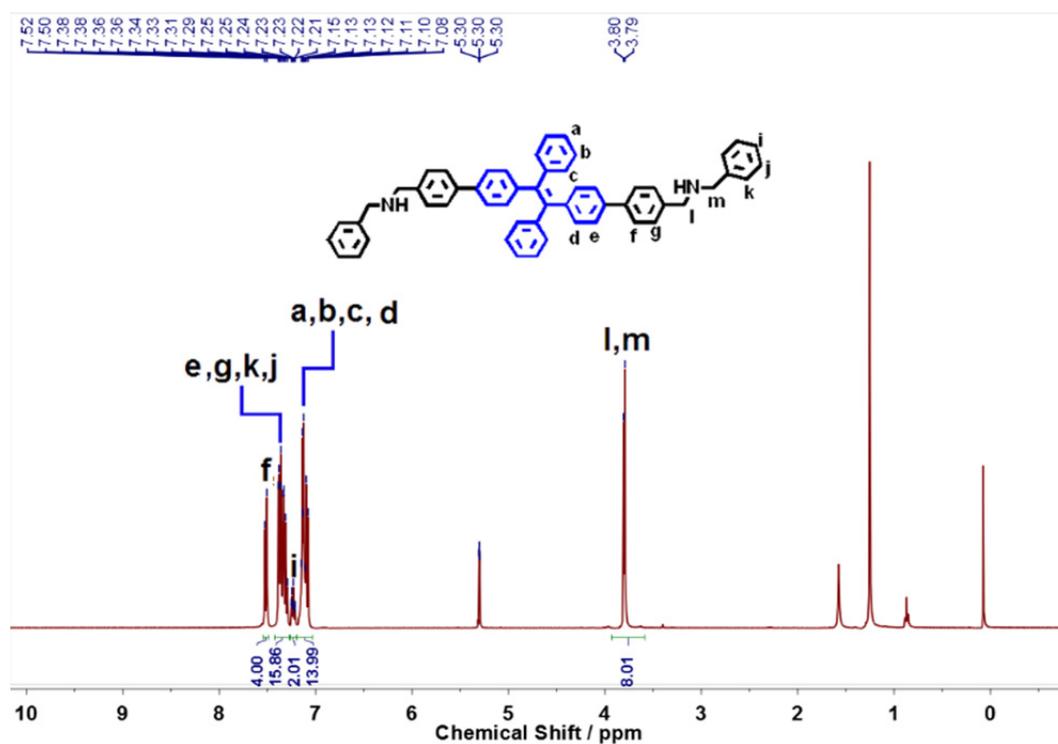


Fig. S5 ^1H NMR spectrum of E-2DBA-TPE.

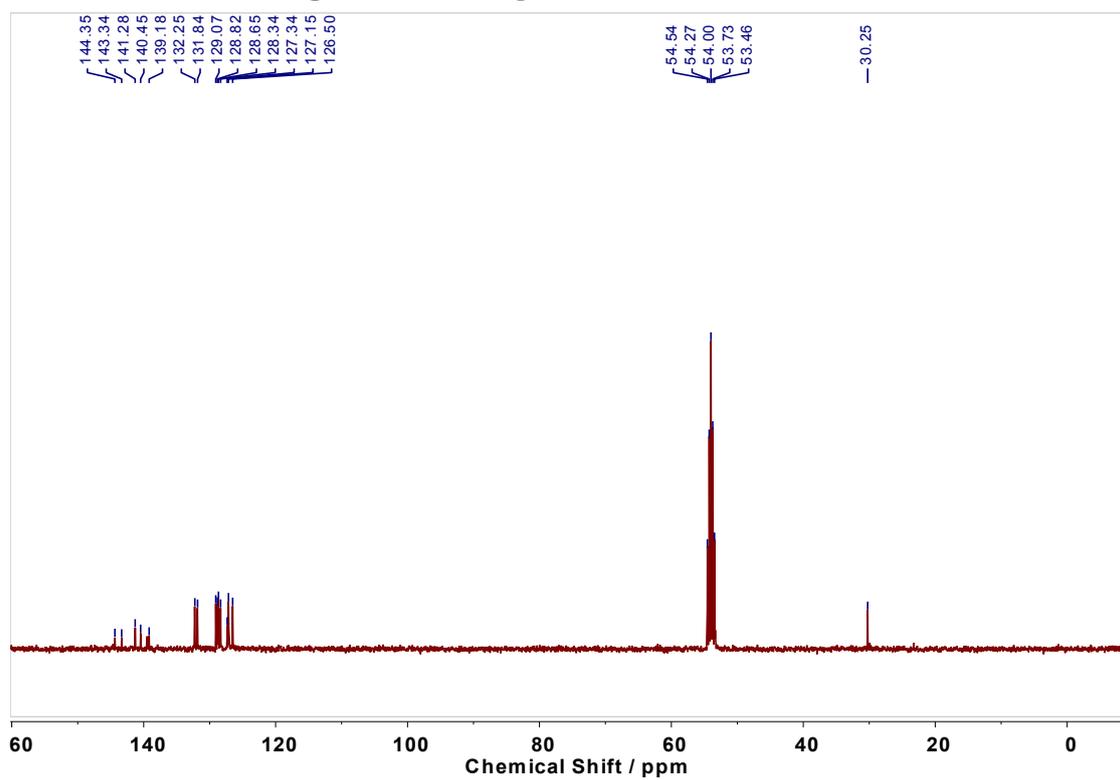


Fig. S6 ^{13}C NMR spectrum of E-2DBA-TPE.

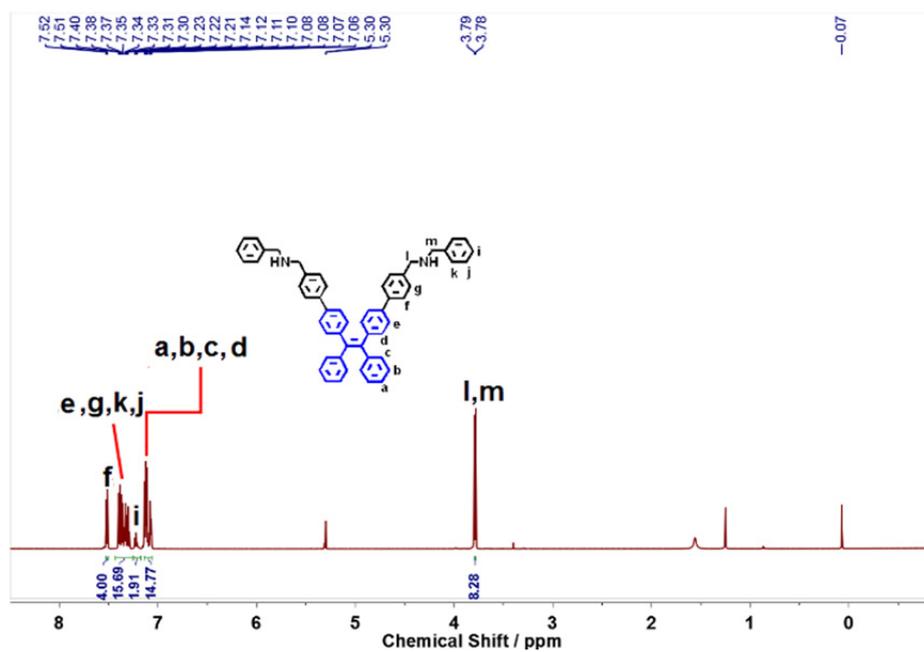


Fig. S7 ^1H NMR spectrum of Z-2DBA-TPE.

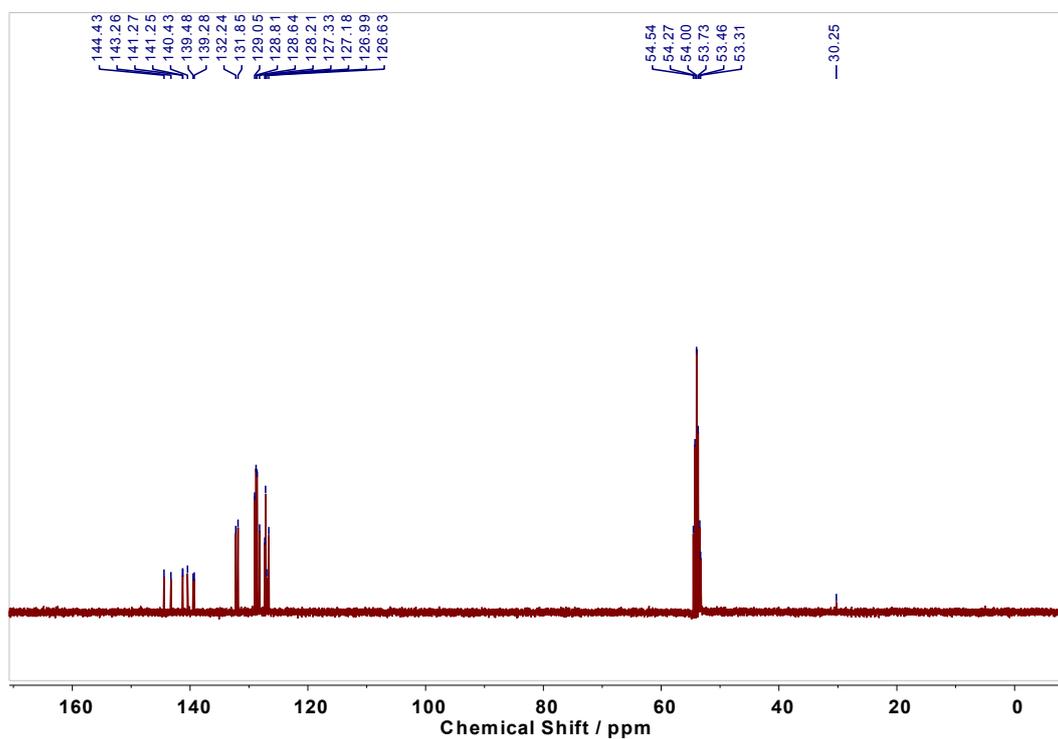


Fig. S8 ^{13}C NMR spectrum of Z-2DBA-TPE.

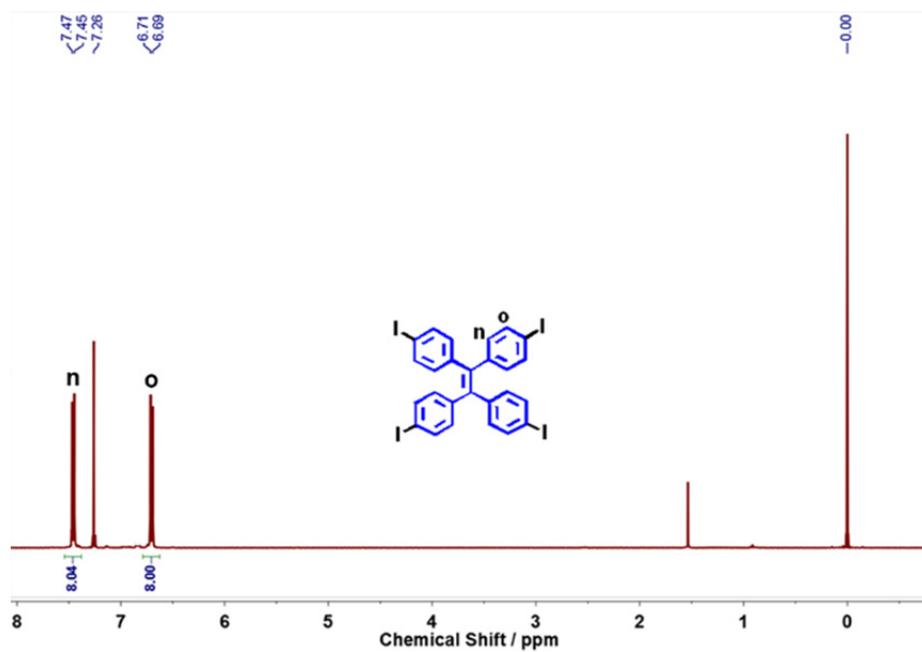


Fig. S9 ^1H NMR spectrum of 4I-TPE.

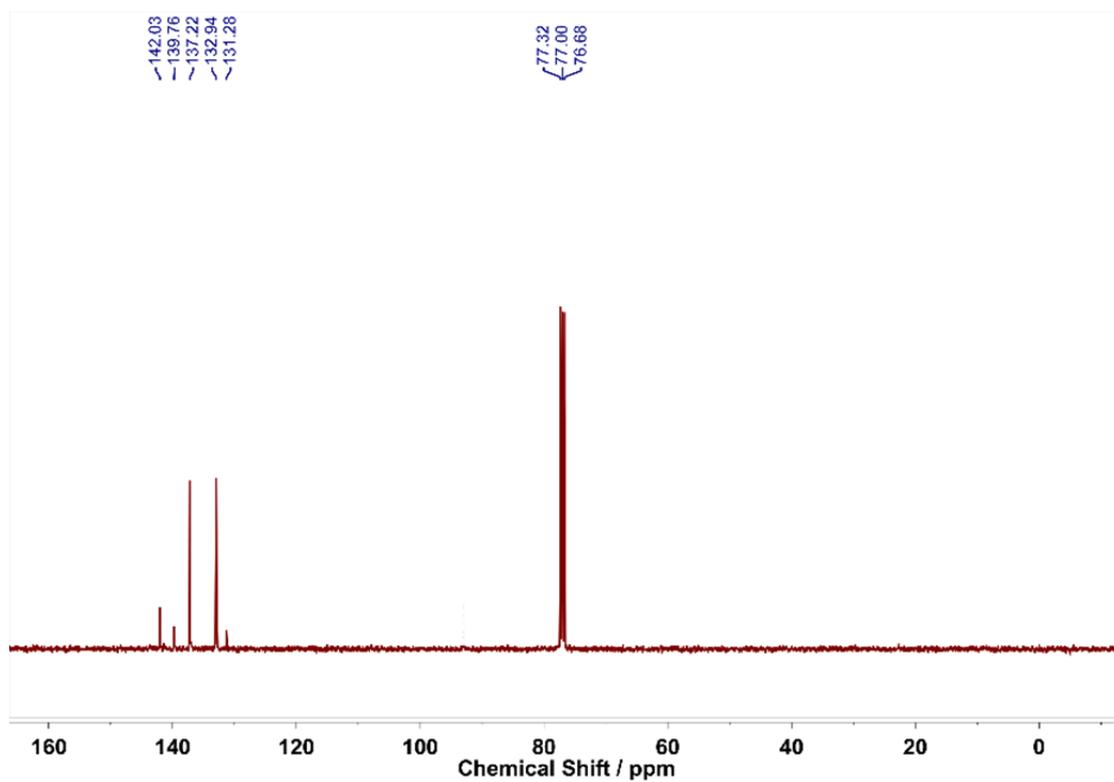


Fig. S10 ^{13}C NMR spectrum of 4I-TPE.

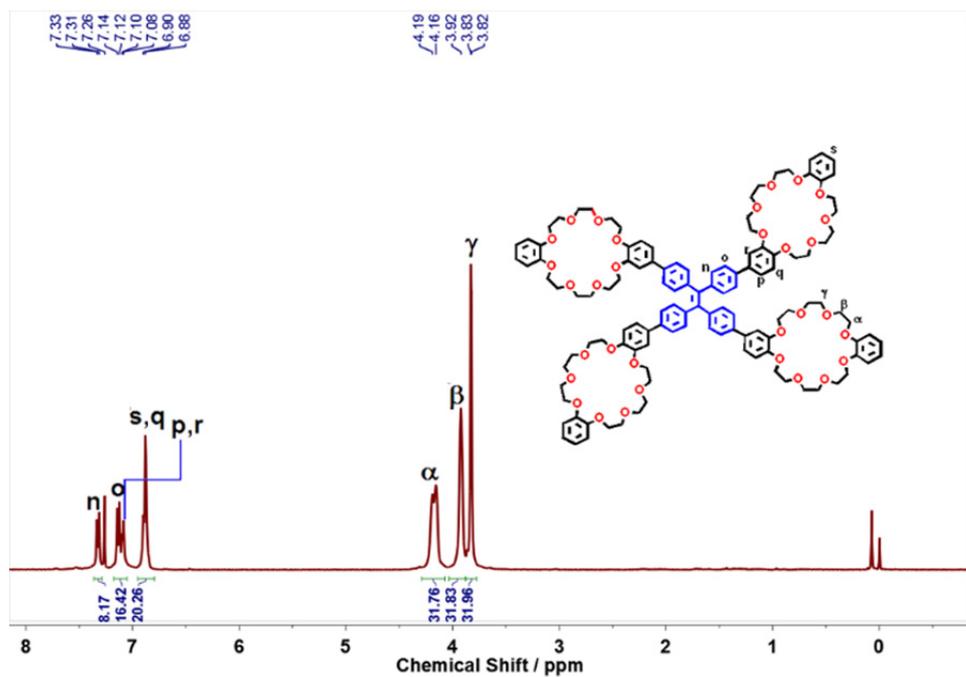


Fig. S11 ^1H NMR spectrum of 4DB24C8-TPE.

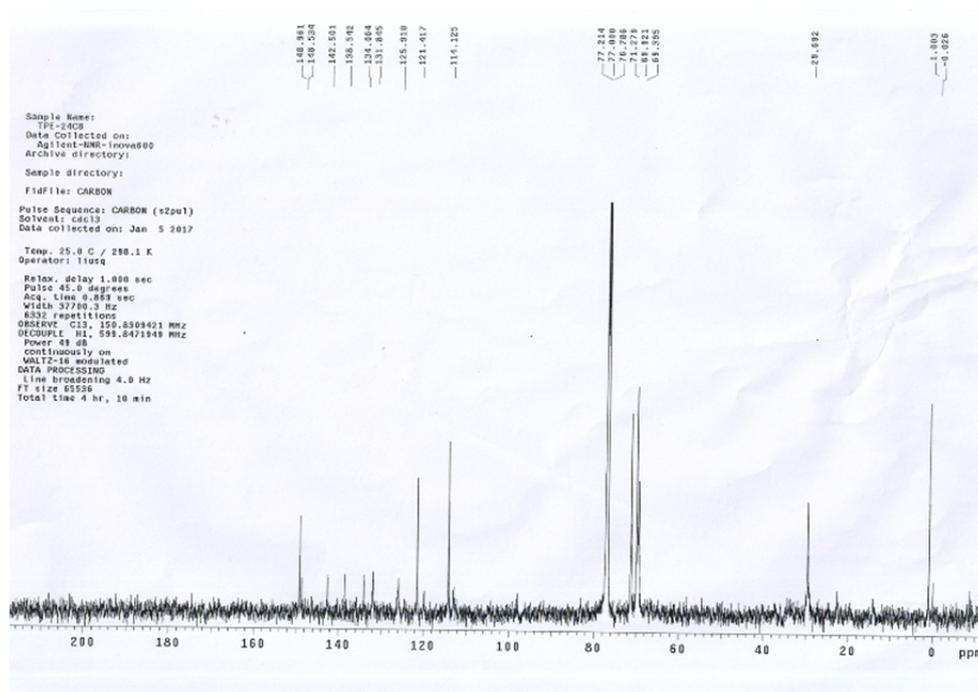


Fig. S12 ^{13}C NMR spectrum of 4DB24C8-TPE.

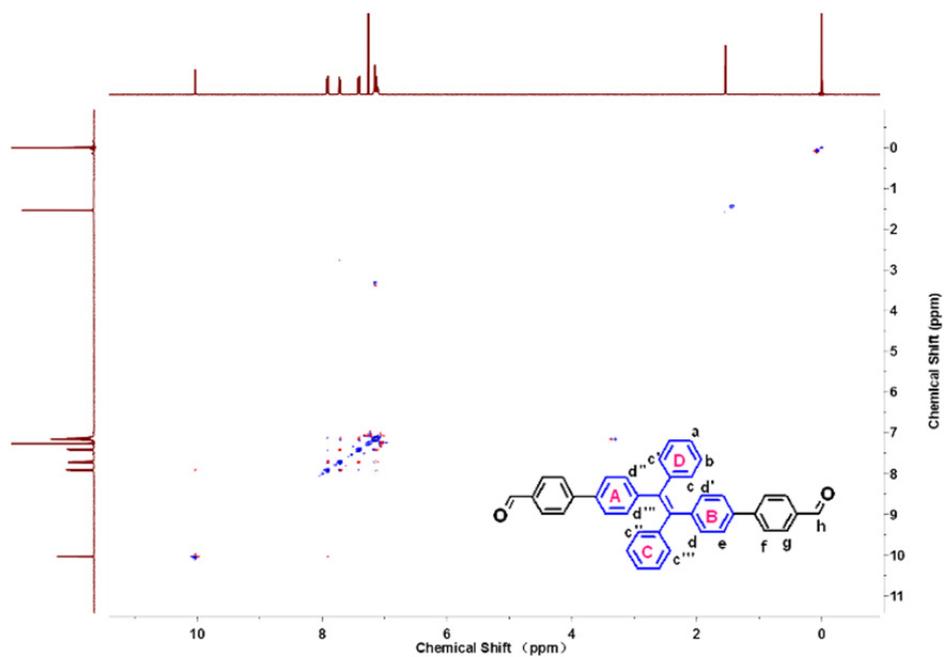


Fig. S13 Full NOESY-NMR of E-2CHO-TPE.

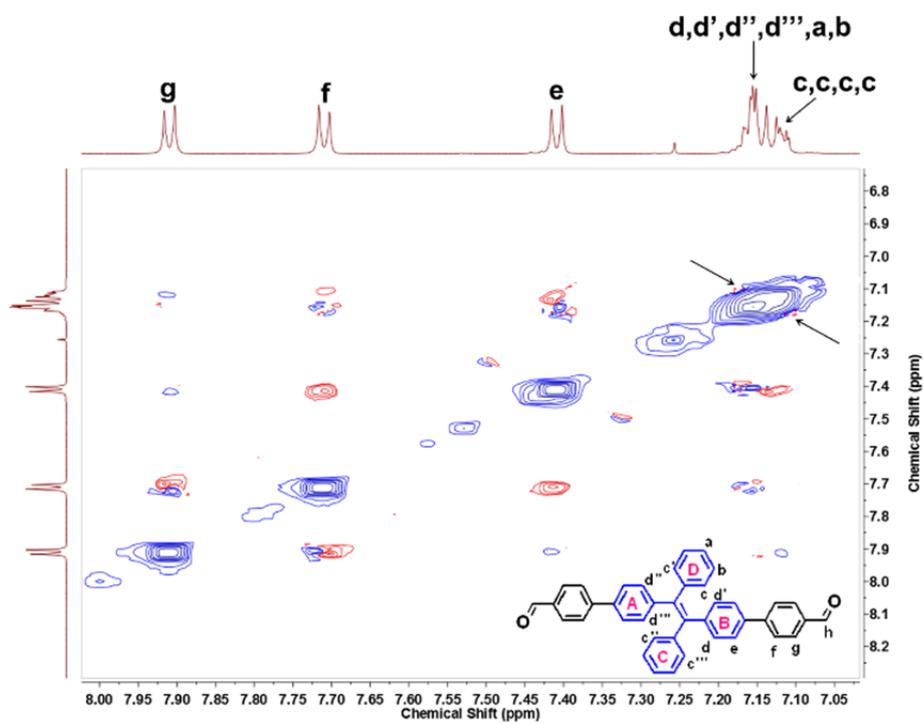


Fig. S14 Partial NOESY-NMR of E-2CHO-TPE.

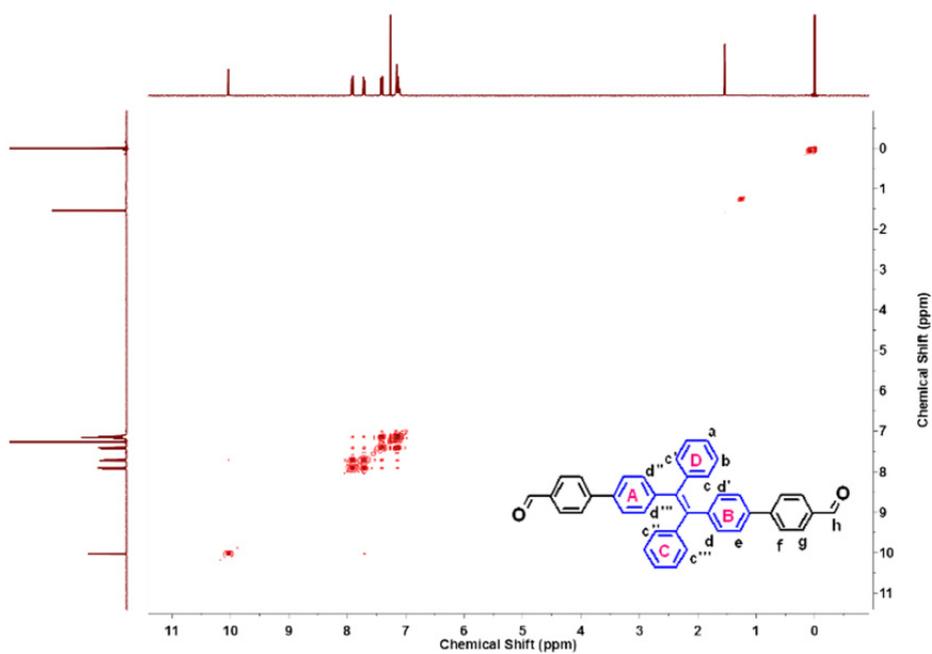


Fig. S15 Full COSY-NMR of E-2CHO-TPE.

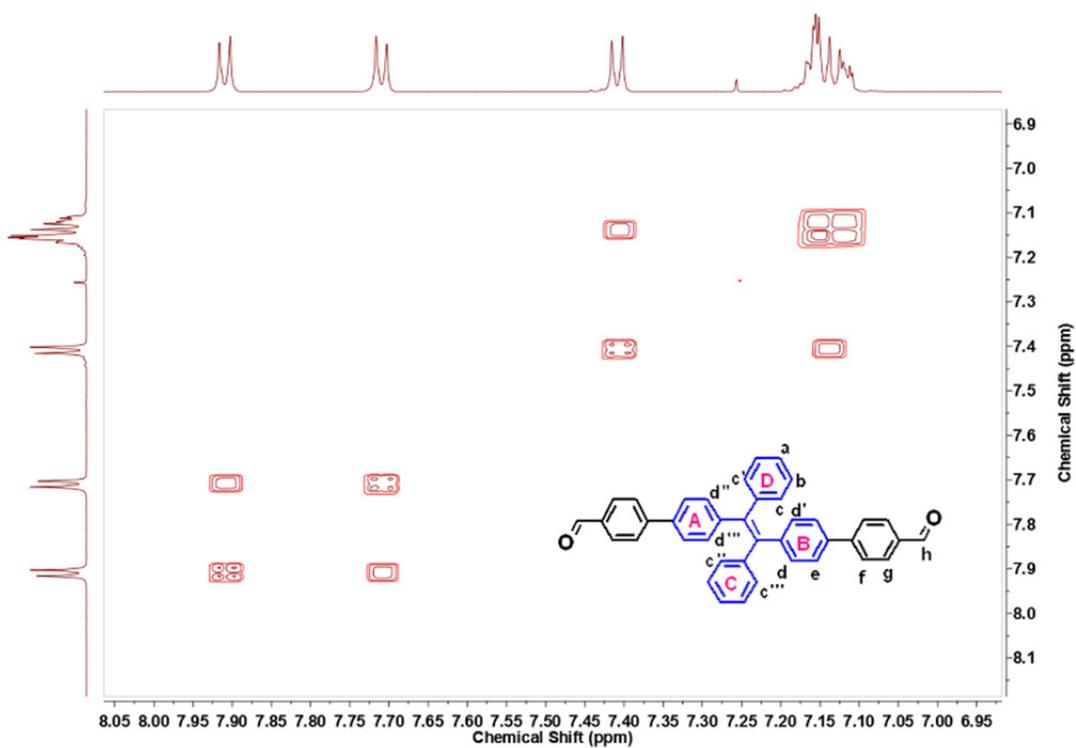


Fig. S16 Partial COSY-NMR of E-2CHO-TPE.

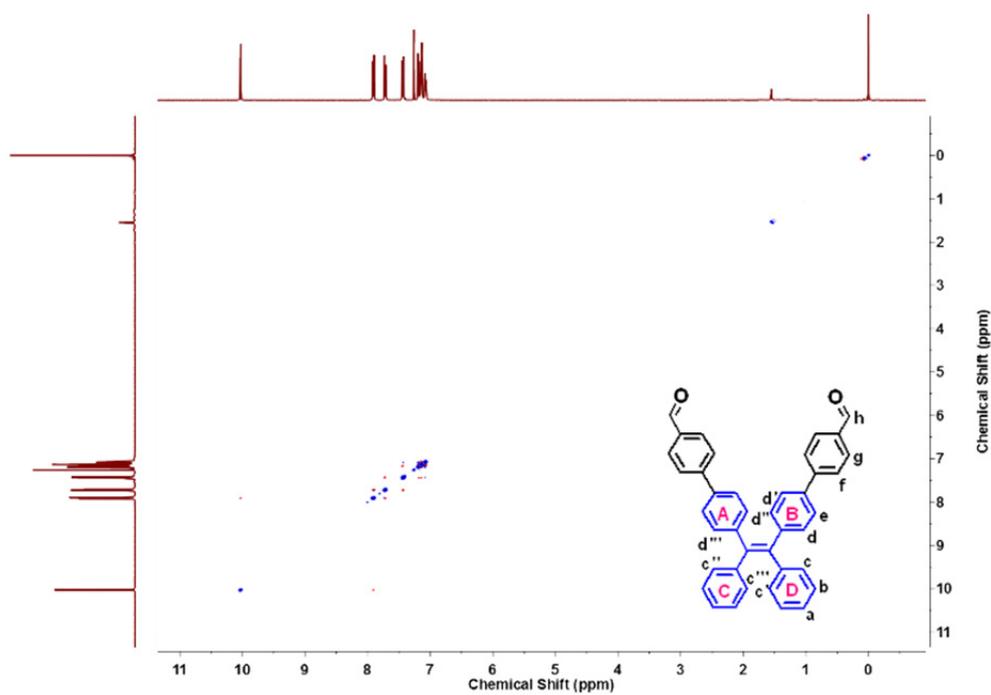


Fig. S17 Full NOESY-NMR of Z-2CHO-TPE.

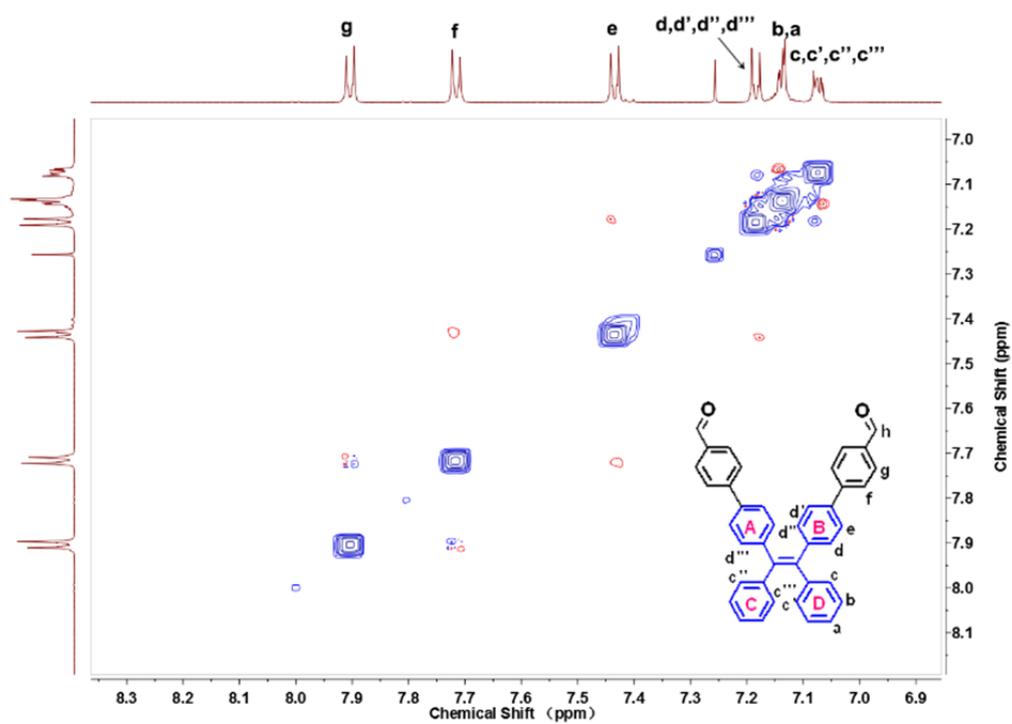


Fig. S18 Partial NOESY-NMR of Z-2CHO-TPE.

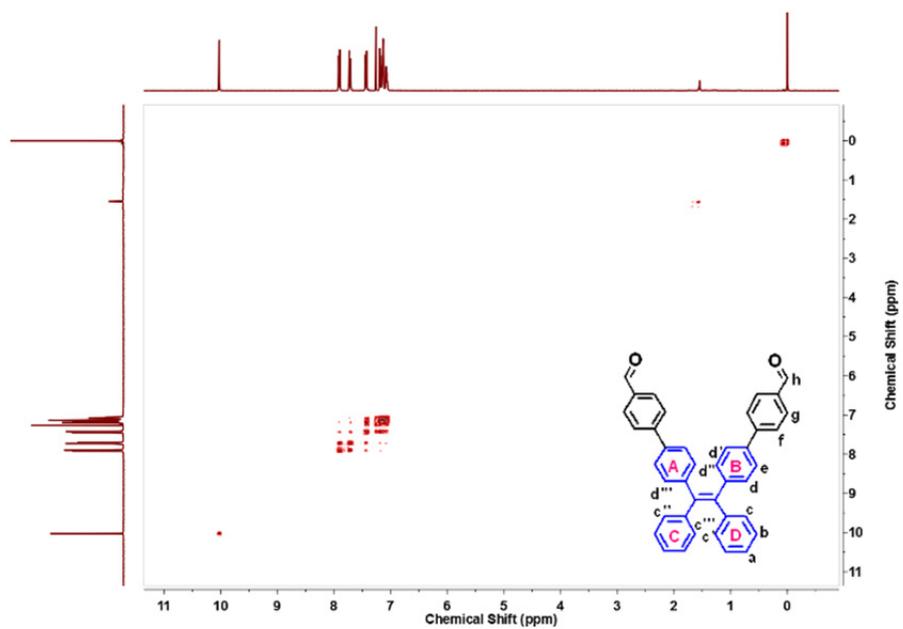


Fig. S19 Full COSY-NMR of Z-2CHO-TPE.

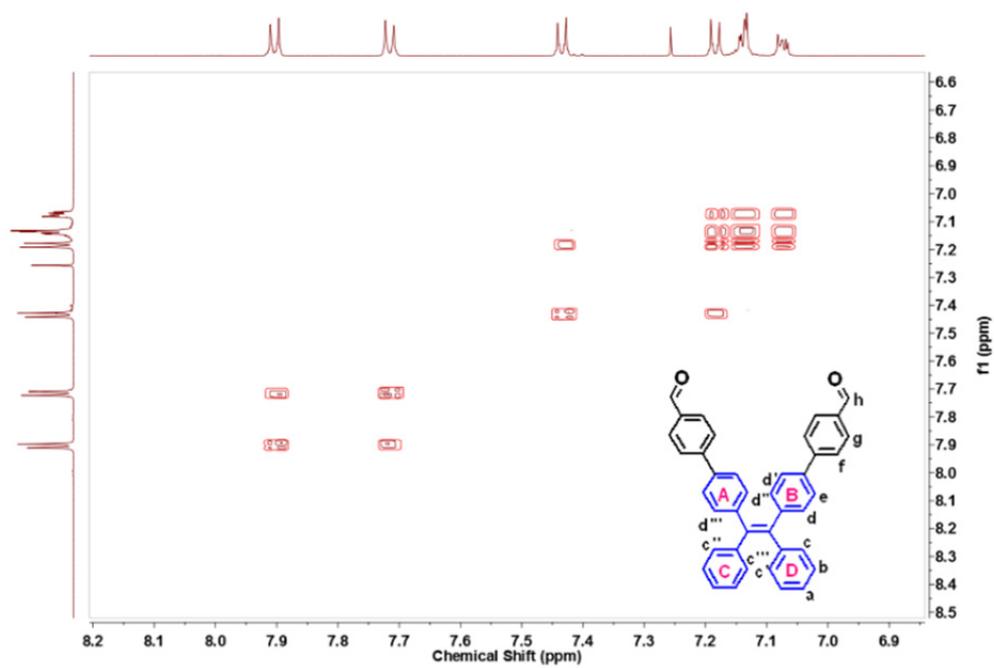


Fig. S20 Partial COSY-NMR of Z-2CHO-TPE.

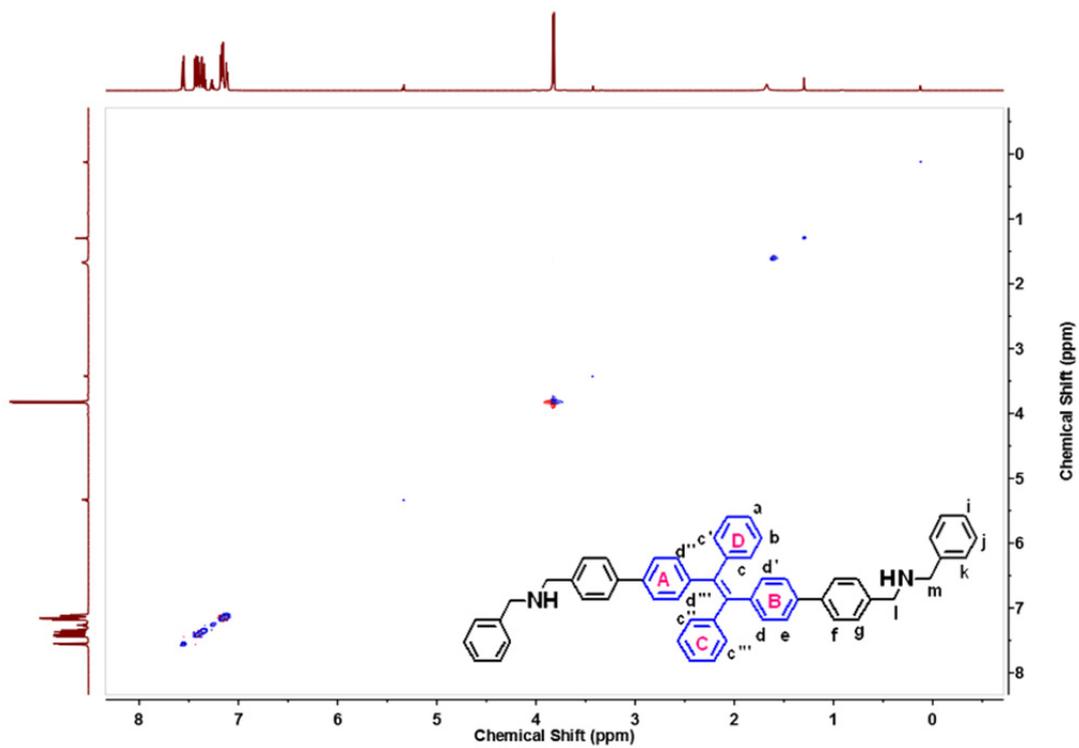


Fig. S21 Full NOESY-NMR of E-2DBA-TPE.

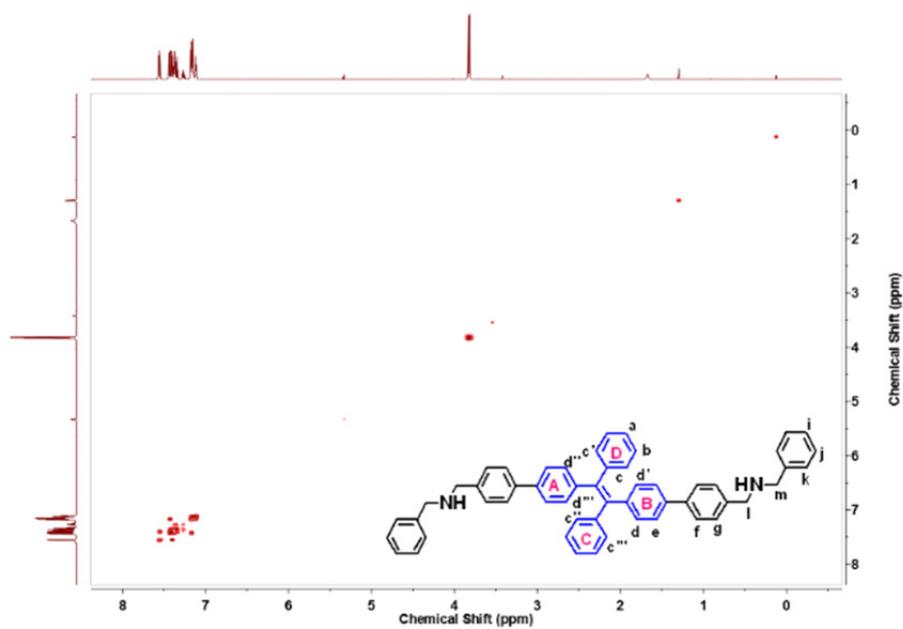


Fig. S22 Full COSY-NMR of E-2DBA-TPE.

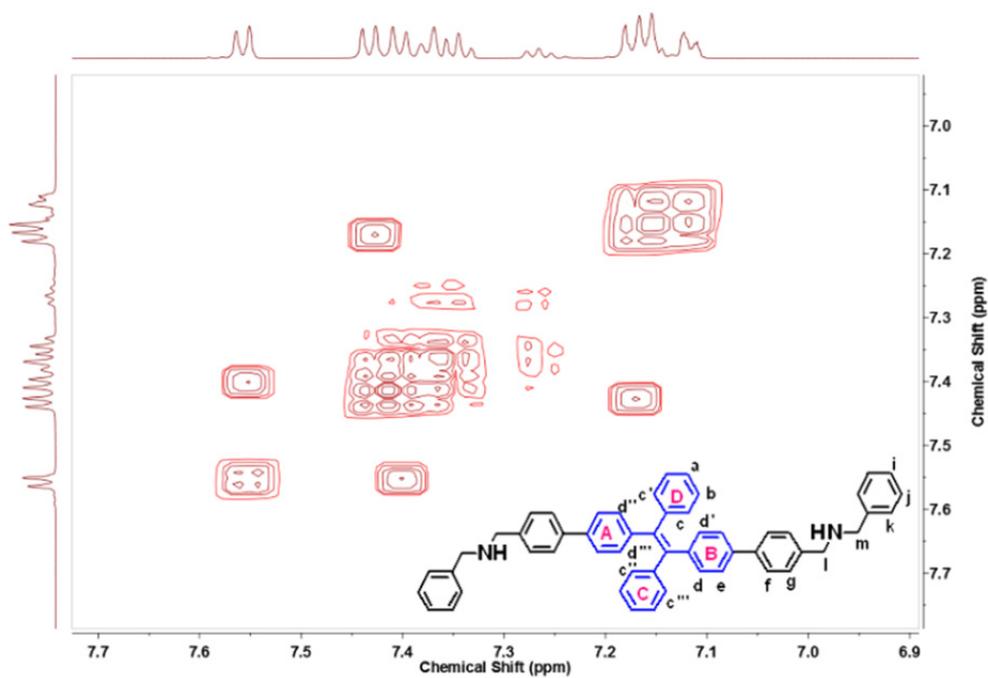


Fig. S23 Partial COSY-NMR of E-2DBA-TPE.

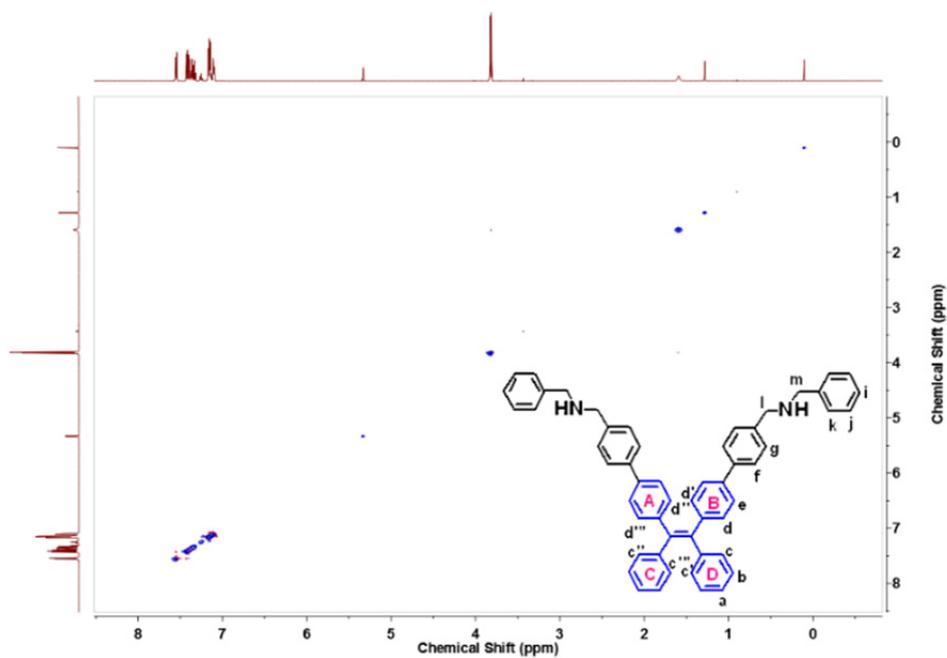


Fig. S24 Full NOESY-NMR of Z-2DBA-TPE.

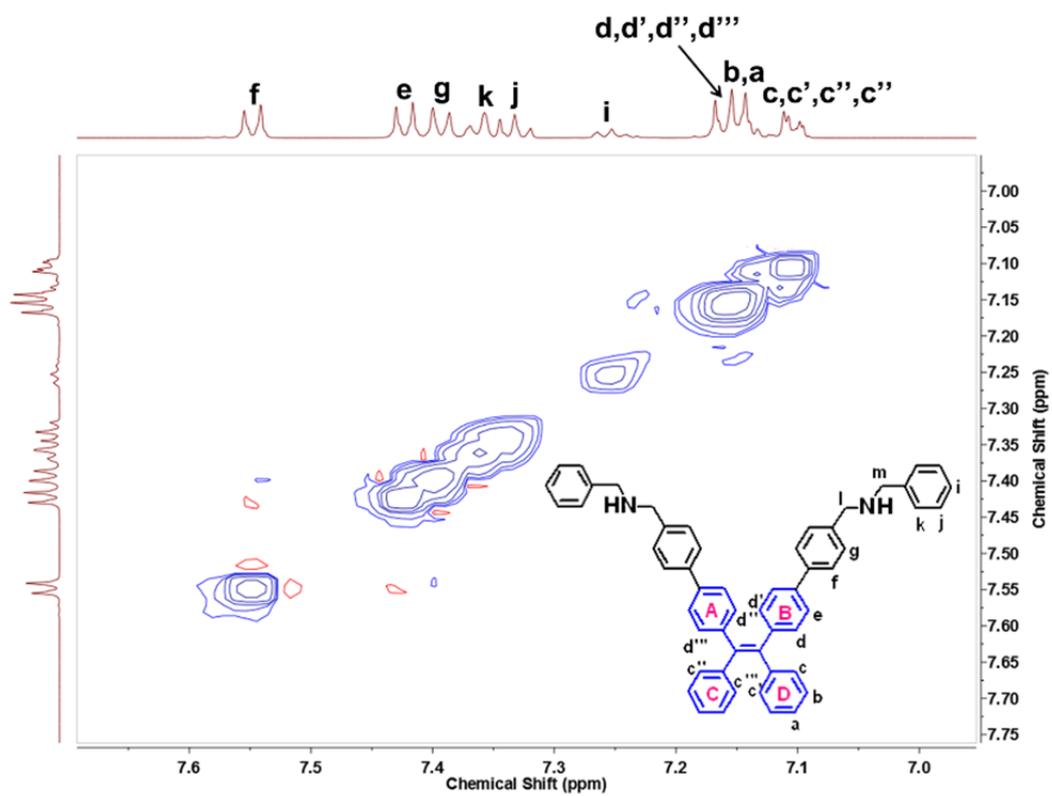


Fig. S25 Partial NOESY-NMR of Z-2DBA-TPE.

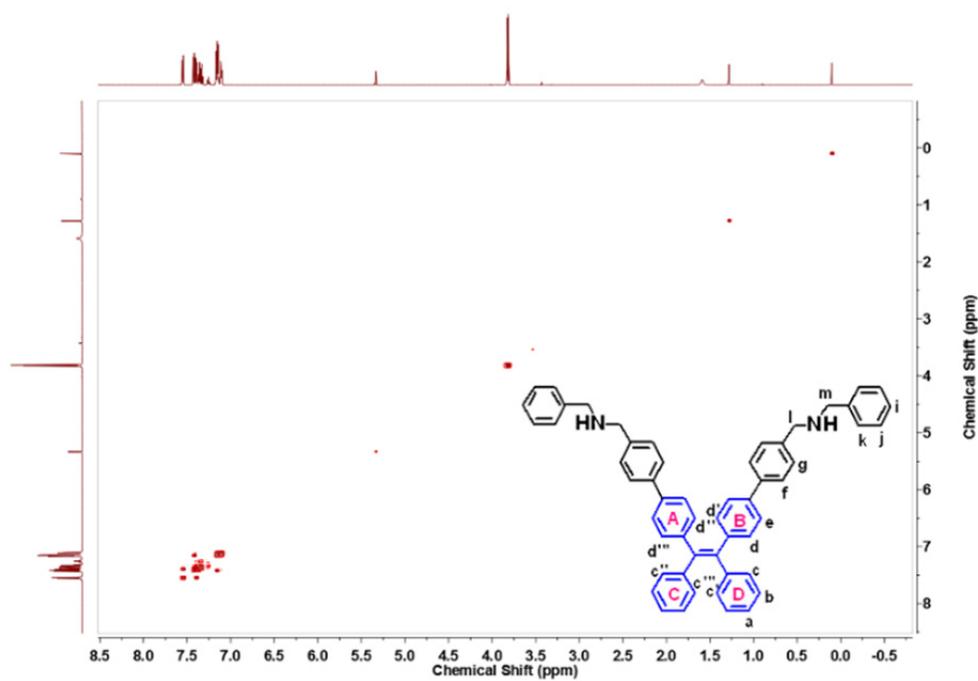


Fig. S26 Full COSY-NMR of Z-2DBA-TPE.

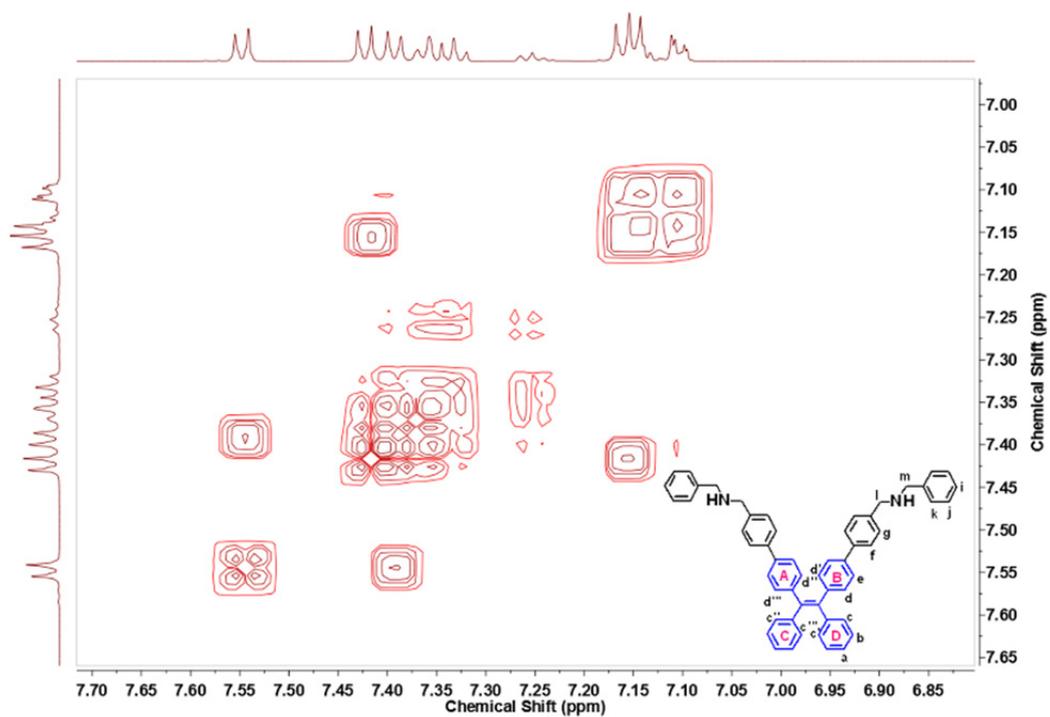


Fig. S27 Partial COSY-NMR of Z-2DBA-TPE.

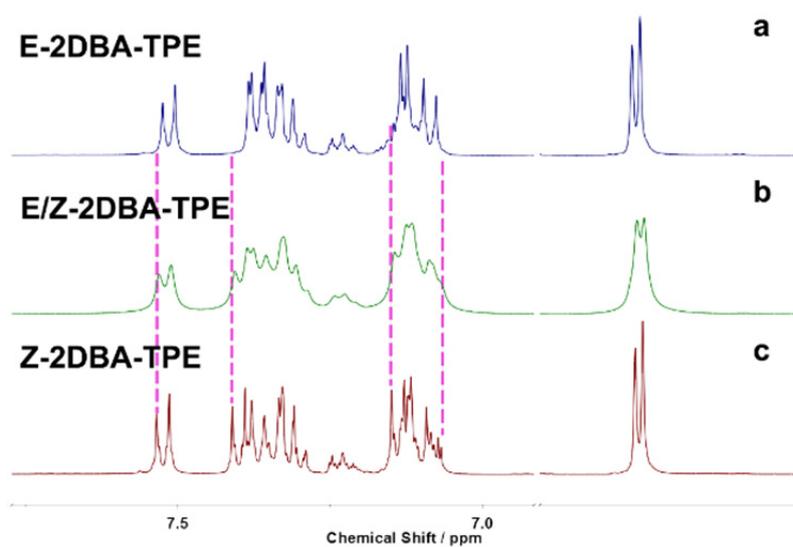


Fig. S28 ^1H NMR spectra of (a) E-2DBA-TPE, (b) E/Z-2DBA-TPE, (c), Z-2DBA-TPE.

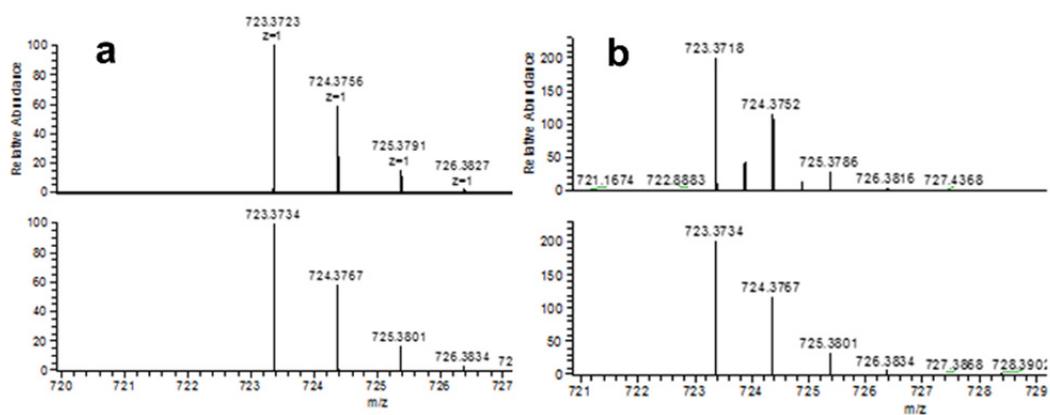


Fig. S29 Measured (top) and calculated (bottom) HR-ESI-MS of (a) E-2DBA-TPE, (b) Z-2DBA-TPE.

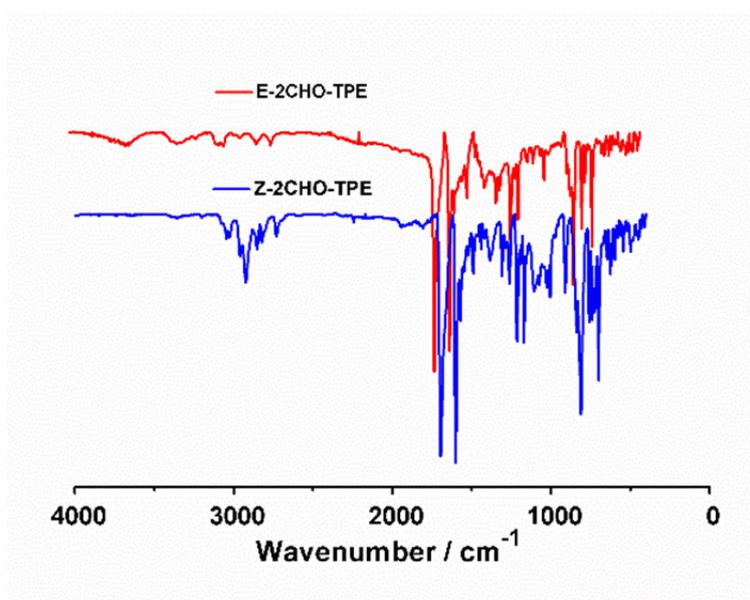


Fig. S30 FT-IR spectra of E-2CHO-TPE and Z-2CHO-TPE.

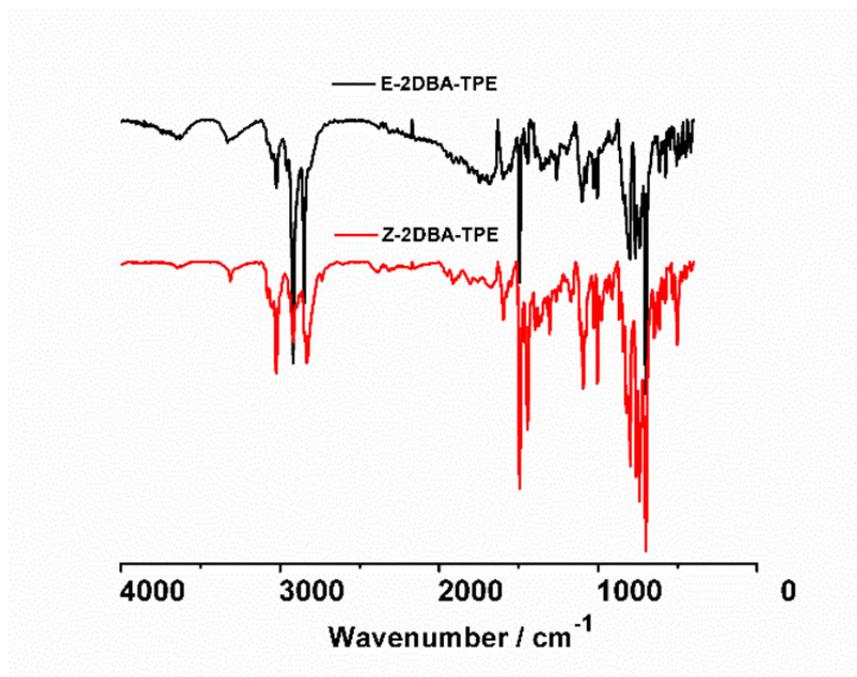


Fig. S31 FT-IR spectra of E-2DBA-TPE and Z-2DBA-TPE.

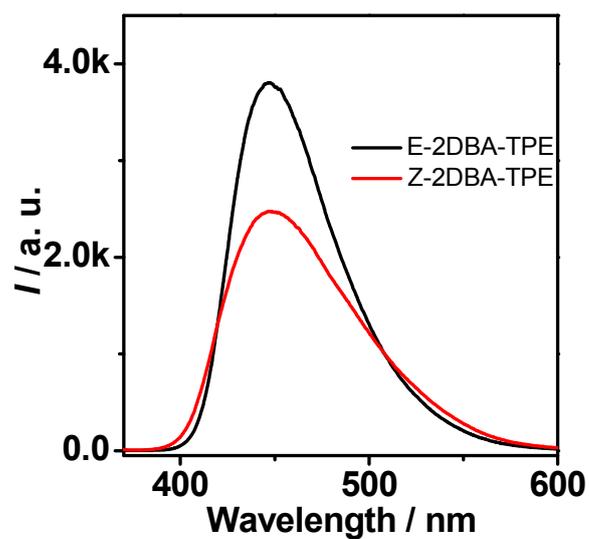


Fig. S32 Fluorescent spectra of solid E-2DBA-TPE (black) and Z-2DBA-TPE (red).

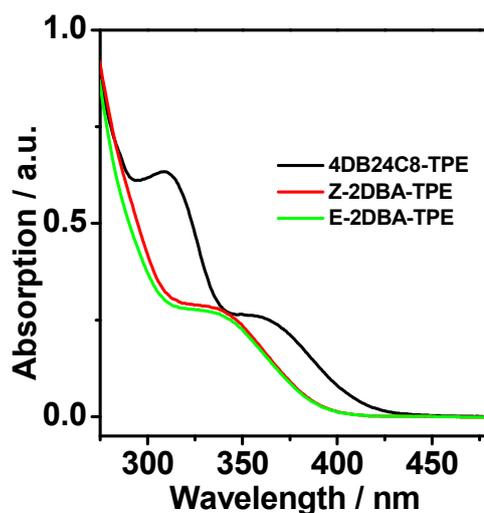


Fig. S33 Uv-vis absorption spectra of 4DB24C8-TPE, Z-2DBA-TPE and E-2DBA-TPE.

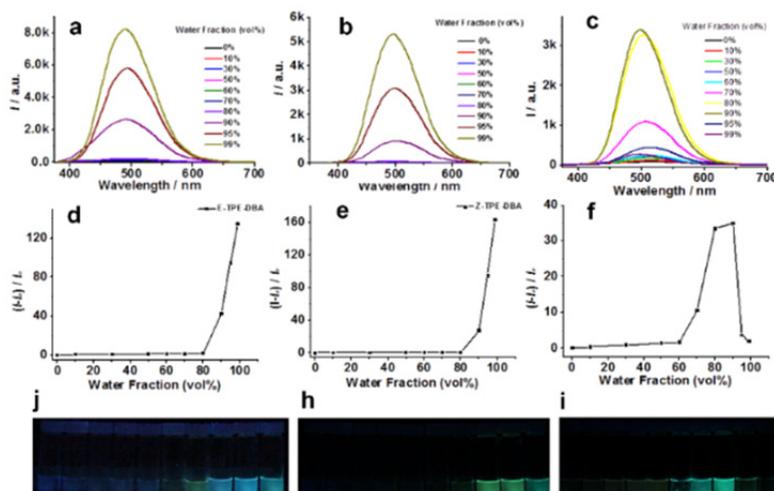


Fig. S34 Photoluminescence spectra and plots of emission intensities of 10 μM E-2DBA-TPE (a, d), Z-2DBA-TPE (b, e) and 4DB24C8-TPE (c, f) in THF-Water mixture solvents with different fractions of water. Photographs of E-2DBA-TPE (j), Z-2DBA-TPE (h) and 4DB24C8-TPE (i) in THF-Water mixture solvents under UV irradiation.

(Since water is a poor solvent for E/Z-2DBA-TPE and 4DB24C8-TPE, with the water content increase, which started to aggregate, which led to the enhanced emission. But compared to E/Z-2DBA-TPE, the 4DB24C8-TPE has larger hydrophobic groups, when the water content was increased to 95%, the solubility of 4DB24C8-TPE became much poorer and the large-sized aggregates were formed. These aggregates would further form the precipitation, thus decreased the effective 4DB24C8-TPE concentration in the solution and led to a decreased emission. Besides this, amorphous aggregates abruptly formed at 95% water content could trap the solvent molecules inside. In these loose aggregates, the TPE molecules had undergone partial intra-molecular motions, which also decreased the emission.)

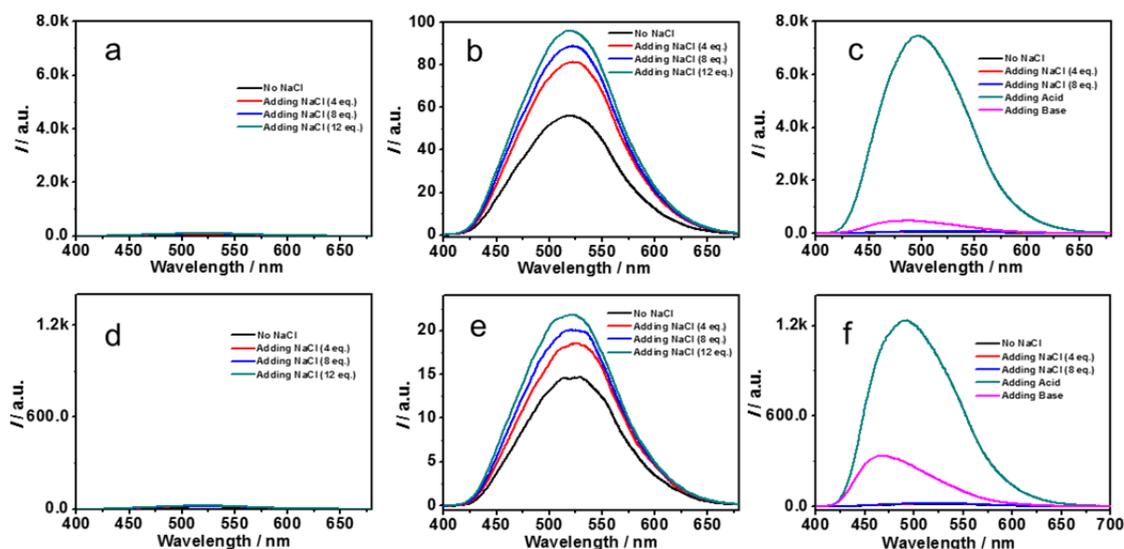


Fig. S35 Fluorescence spectra of E-2DBA-TPE (a, b, and c) and Z-2DBA-TPE (d, e and f) mixed with 4DB24C8-TPE in THF treated with NaCl (Relative to the amount of 4DB24C8-TPE). Fluorescence spectra of c and f were obtained under an acid condition.

Results and discussion: To explain the reason of stepwise emission enhancements and blue shifts as “could be due to a synergic interaction of the host–guest recognition of DB24C8 and dibenzylammonium moieties together with the salting-out effect”, we have carried out several control experiments. (1) 12.0 equivalents of NaCl were gradually added to the THF solution of 2 equivalents of E-2DBA-TPE (Figure S35a and b) and Z-2DBA-TPE (Figure S35d and e) mixed with 4DB24C8-TPE. In the case of E-2DBA-TPE, the fluorescence intensities increased only slightly with a factor of 1.4, 1.6, and 1.7 at the first, second, and third adding NaCl, respectively. Similarly, the fluorescence of Z-2DBA-TPE was only enhanced to 1.2, 1.3, and 1.5 folds. (2) Furthermore, 4.0 Equivalents of HCl were added to the THF solutions containing E-2DBA-TPE (Figure S35c) or Z-2DBA-TPE (Figure S35f) mixed with 4DB24C8-TPE and 8.0 equivalents of NaCl. The fluorescence intensities increased to 129 and 78 times for E-2DBA-TPE and Z-2DBA-TPE, respectively, close to those values after the third acidification (157 and 97 times). These results revealed that the host–guest interaction between the protonated DBA and DB24C8 and the salting-out effect played a leading role in the enhancement of emission. According to the previous work,⁶ when the TPE moieties adopted a tighter packing in ordered structures, the intramolecular motion was restricted more efficiently, leading to the stronger and larger blue-shifted emissions. In this study, the emission peaks of E-2DBA-TPE and Z-2DBA-TPE showed clear blue shifts of 67 and 38 nm, respectively, indicating more and more compact packing of TPE groups. The pH values of the original solution and the solutions after successive addition of HCl and NaOH were (7.41, 5.43, and 13.82) for E-2DBA-TPE and (7.42, 5.43, and 13.82) for Z-2DBA-TPE, respectively.

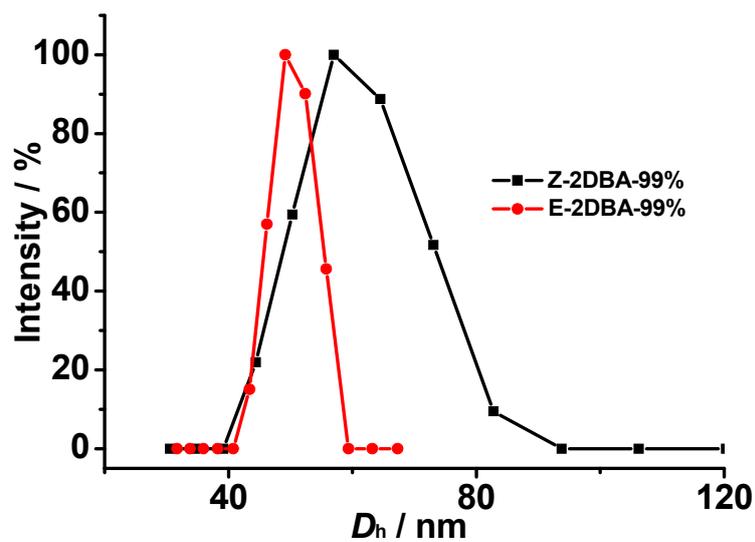


Fig. S36 DLS plots of 10 μ M E-2DBA-TPE (red), Z-2DBA-TPE (black) in THF-Water mixture solvent with 99% water content.

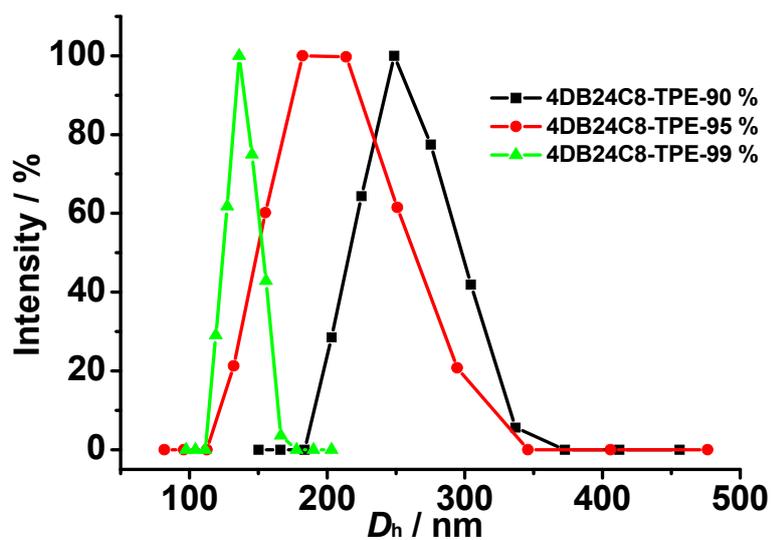


Fig. S37 DLS plots of 4DB24C8-TPE in THF-Water mixture solvent (10 μ M) with 90%, 95%, 99% water content, respectively.

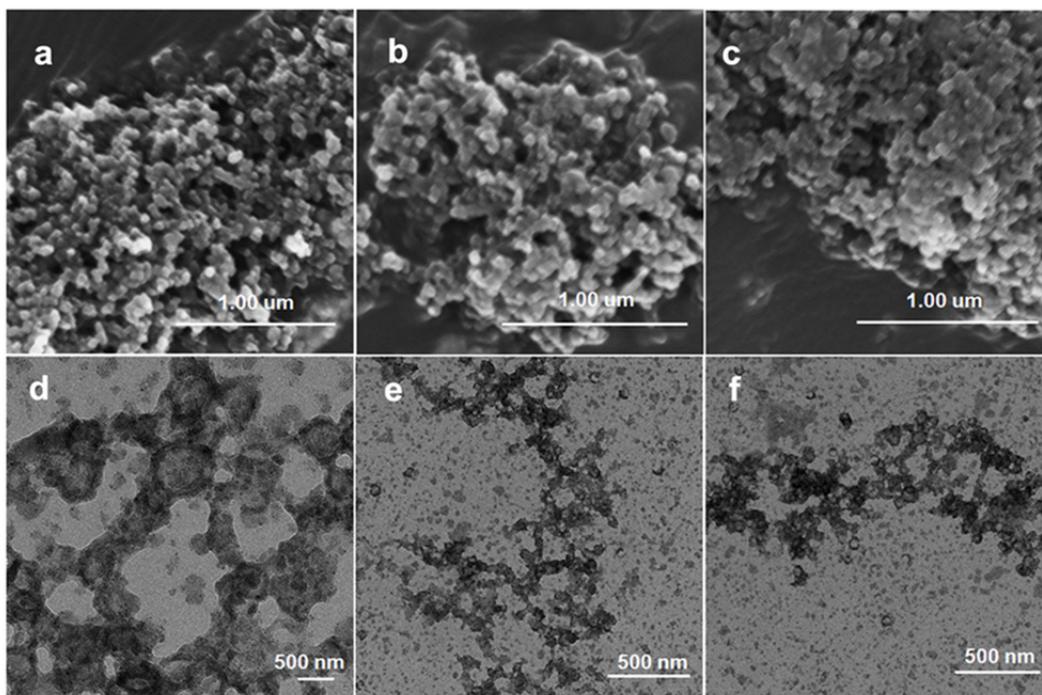


Fig. S38 SEM and TEM images of 10 μM E-2DBA-TPE (a, d), Z-2DBA-TPE (b, e) in THF-Water mixture solvent with 99% water content, and 4DB24C8-TPE (c, f) in THF-Water mixture solvent with 90% water content.

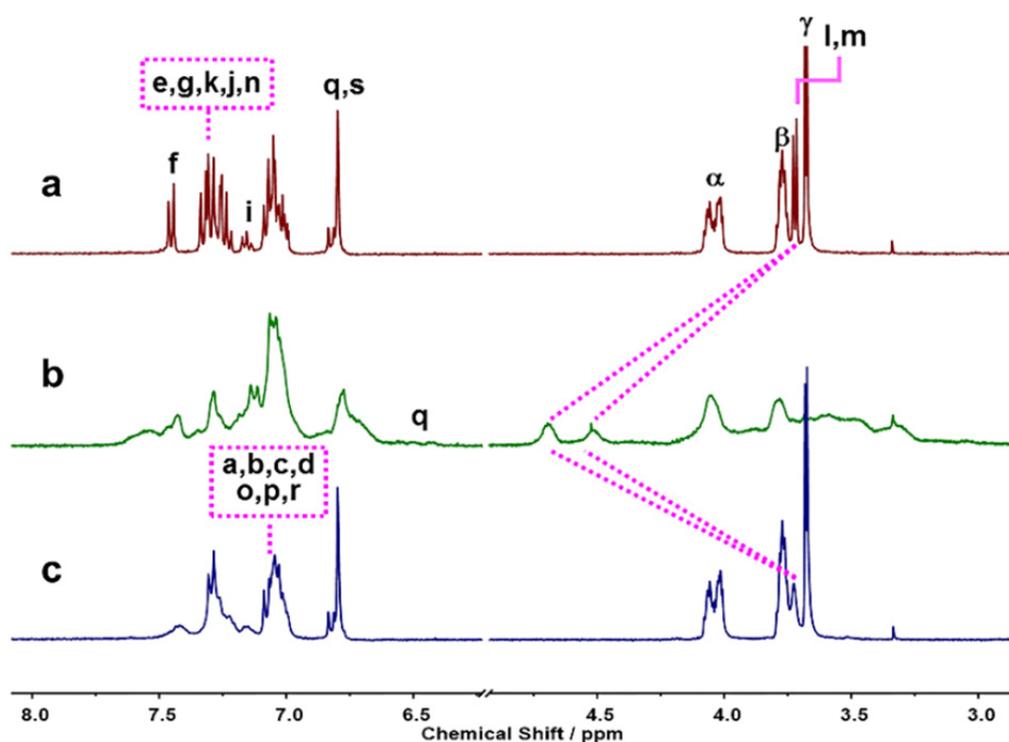
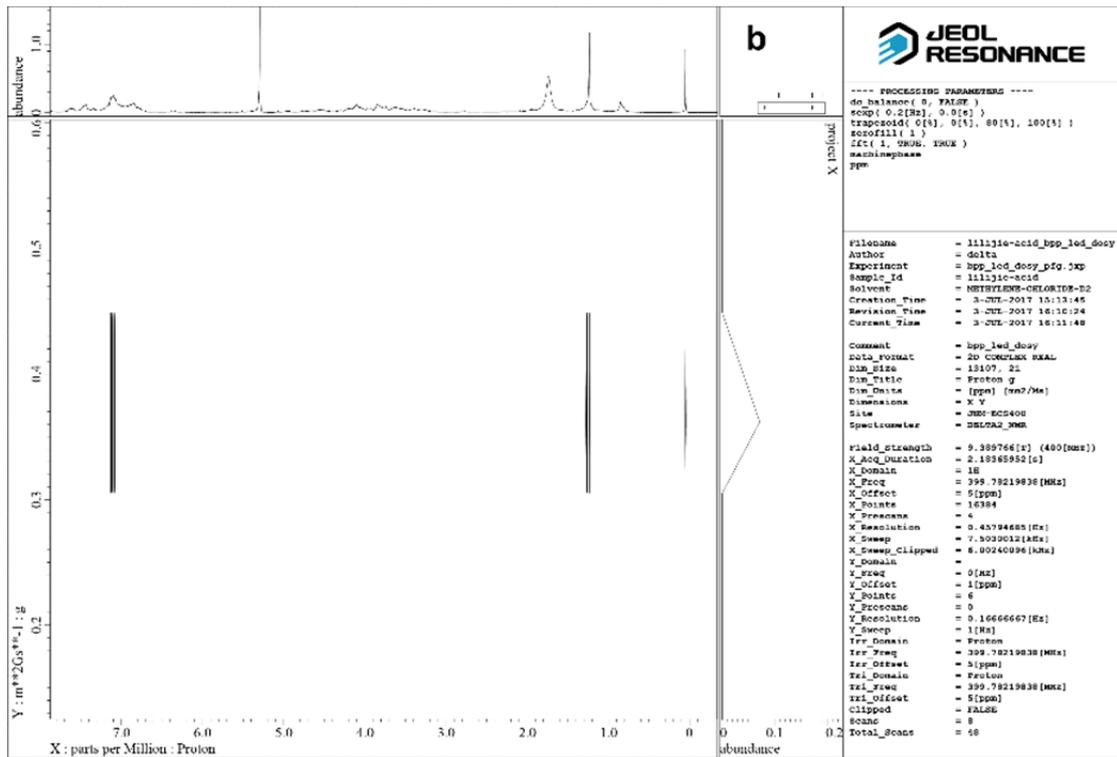
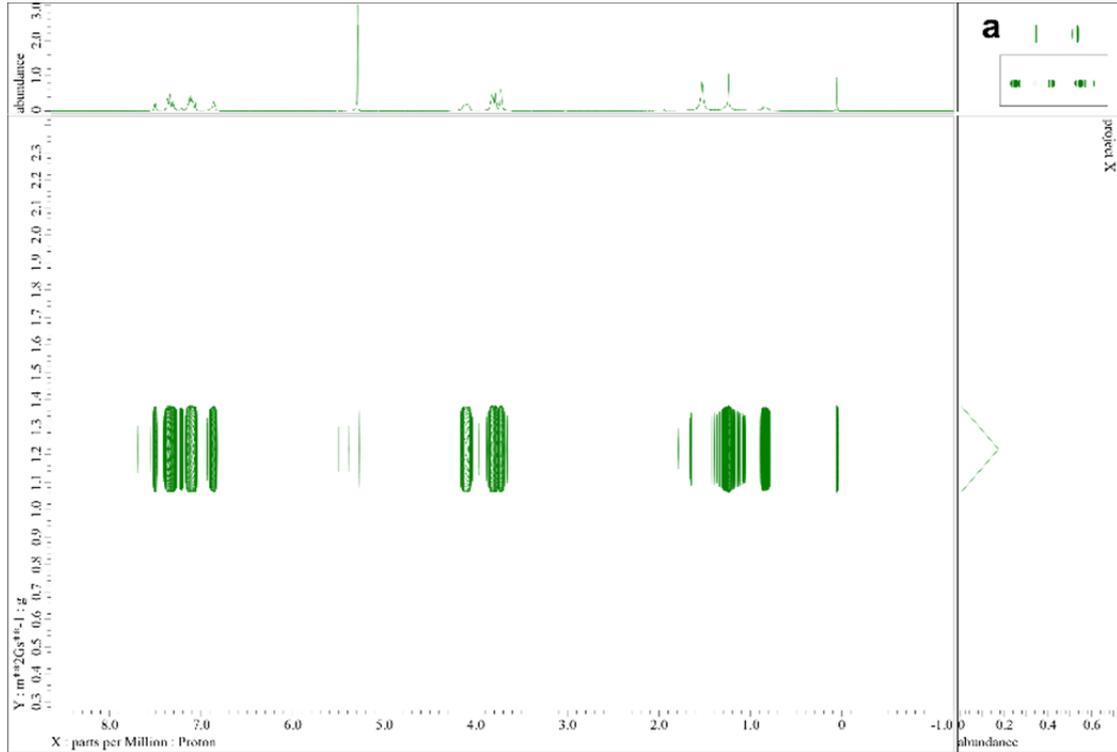


Fig. S39 Partial ^1H NMR spectra (400 MHz, CD_2Cl_2 , a) of 0.5 mM 4DB24C8-TPE and 1.0 mM Z-2DBA-TPE, (b) obtained by adding 2.4 equivalents of HPF_6 to the solution of (a), and (c) obtained by adding 2.8 equivalents of $\text{P}_1\text{-}t\text{Bu}$ to the solution of (b).



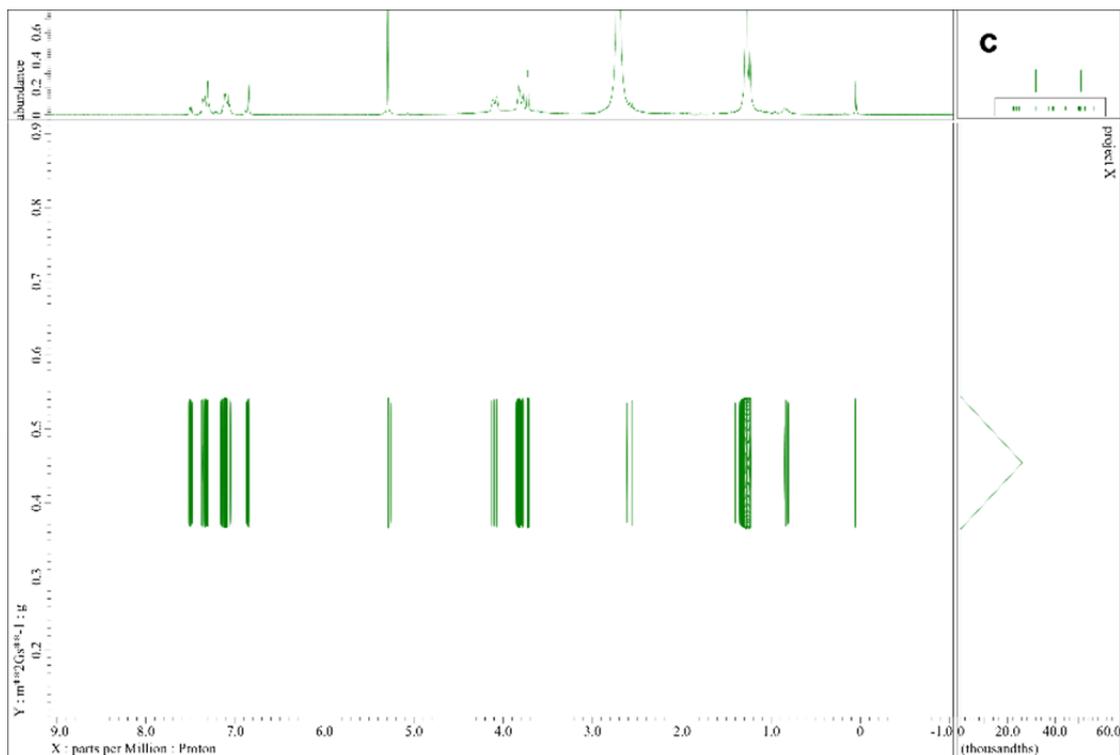
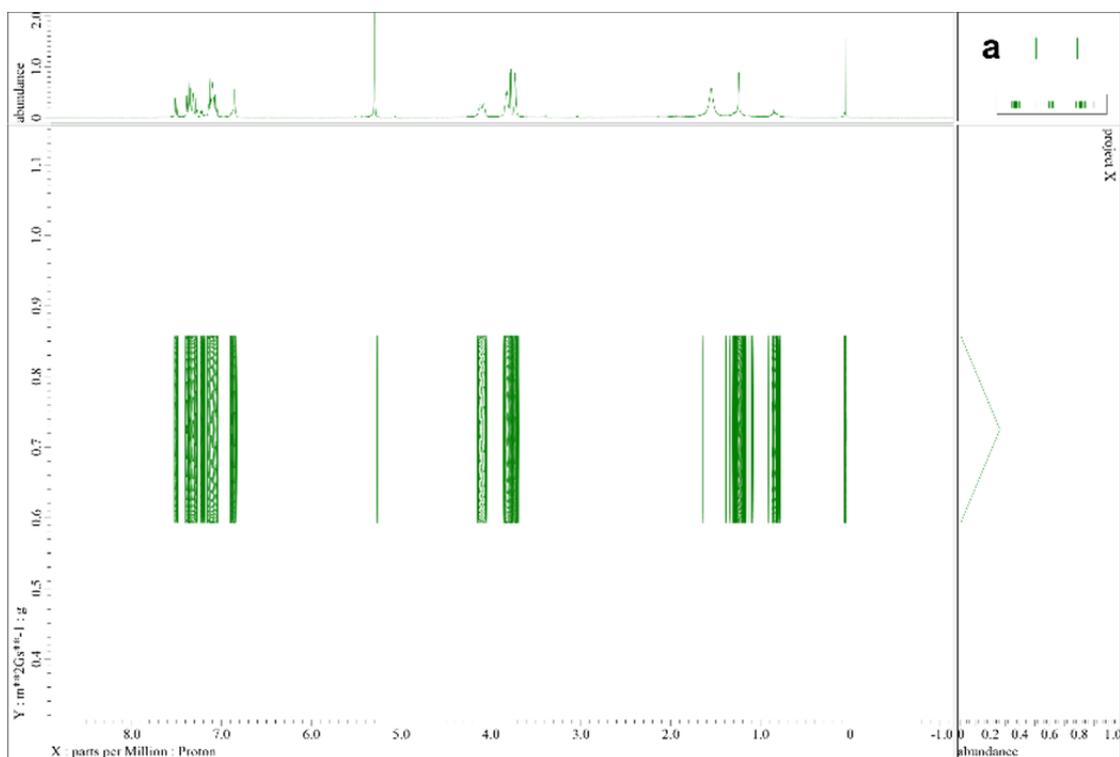


Fig. S40 Diffusion-ordered NMR spectra (DOSY) of (a) 0.5 mM 4DB24C8-TPE and 1.0 mM E-2DBA-TPE, (b) obtained by adding 2.4 equivalents of HFA to the solution of (a), (c) obtained by adding 2.8 equivalents of P₁-*t*Bu to the solution of (b).



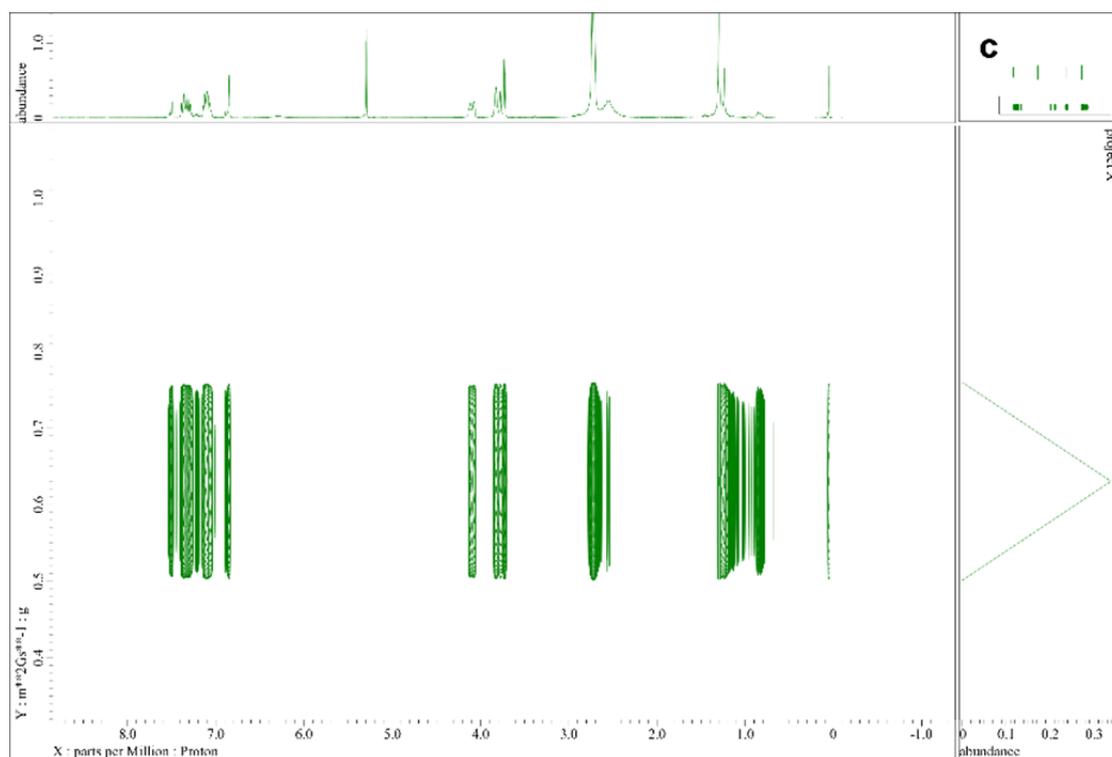
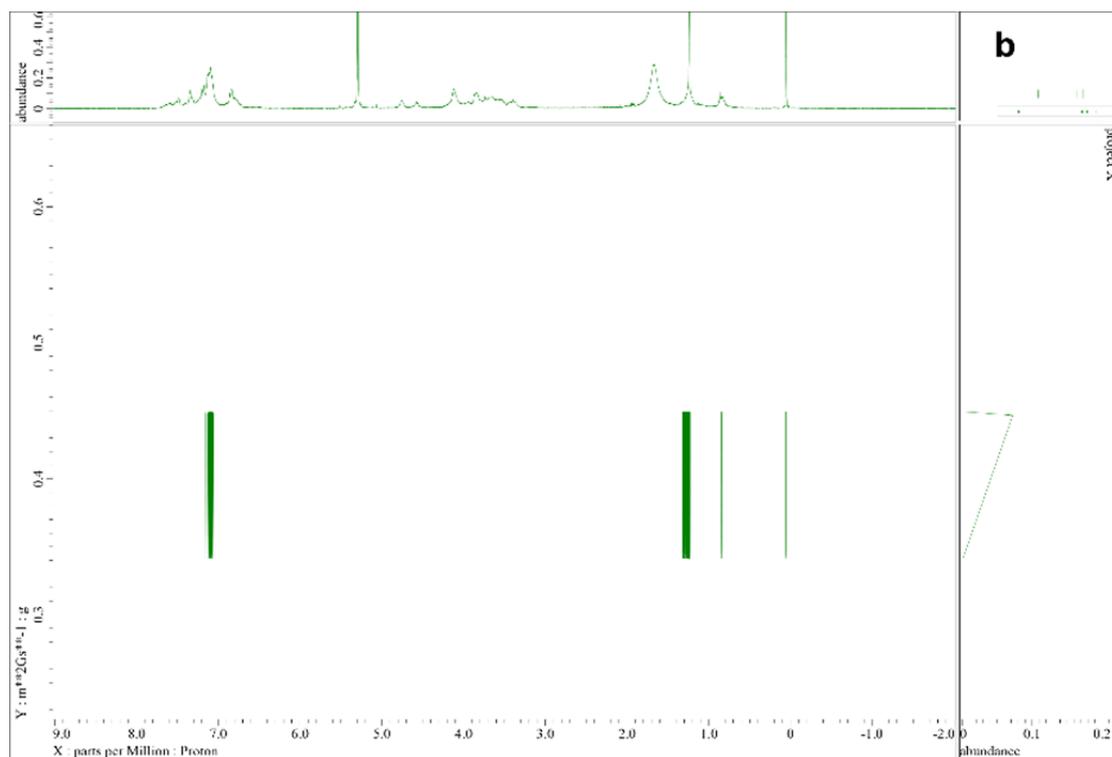


Fig. S41 Diffusion-ordered NMR spectra (DOSY) of (a) 0.5 mM 4DB24C8-TPE and 1.0 mM Z-2DBA-TPE, (b) obtained by adding 2.4 equivalents of HFA to the solution of (a), (c) obtained by adding 2.8 equivalents of P₁-*t*Bu to the solution of (b).

Additional results and discussion:

We have carried out DOSY NMR experiments to measure the diffusion coefficients (Fig. S40 and S41). At a concentration of 0.5 mM 4DB24C8-TPE and 1.0 mM E-2DBA-TPE, single bands occurred at $\log D = -8.91$ and -9.46 for the neutral solution and its acid treatment, respectively, demonstrating an appreciable size increase from monomer to the SHP as a result of the successful supramolecular polymerization (Fig. S40a and b). When slightly excessive P_1-tBu (2.8 equiv.) was added to the above solution, the $\log D$ was -9.30 and became smaller than that obtained under the acid condition (Fig. 40c), indicative of the reversible formation of the SHP. A similar acid-base controlled SHP was also fabricated by mixing 4DB24C8-TPE and Z-2DBA-TPE (Fig. S41). The values of $\log D$ for the acid-base cycle were determined to be -9.13 , -9.40 , and -9.20 , respectively, again suggesting that the the formation of the SHP was reversible.

Table S1. Luminescence lifetime (τ_1 and τ_2) and (fluorescence quantum yield Φ) for E-2DBA-TPE (Solid) and Z-2DBA-TPE (Solid).

Sample	τ_1 [ns]	RW %	τ_2 [ns]	RW %	Φ (%)
E-2DBA-TPE	2.54	55.73	3.93	44.27	77.26
Z-2DBA-TPE	1.57	50.49	3.30	49.51	53.56

References

- S1 R. Daik, W. J. Feast, A. S. Batsanov, J. A. K. Howard, *New J. Chem.*, 1998, **22**, 1047.
- S2 J. Zhang, K. Zhang, X. Huang, W. Cai, C. Zhou, S. Liu, F. Huang, Y. Cao, *J. Mater. Chem.*, 2012, **22**, 12759.