

Electronic Supplementary Information for

A self-assembling induced emission system constructed by host-guest interaction of AIE-active building blocks

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Experimental Section

1. Materials and instruments

4-Bromobenzophenone was purchased from Alfa Aesar. Titanium tetrachloride, tetrakis(triphenylphosphine)palladium, and bis(triphenylphosphine) palladium(II) chloride were purchased from Aladdin. *N*-methylformanilide, and *n*-butyl lithium were purchased from J&K. Bis(pinacolato)diboron was purchased from Energy. Ceric ammonium nitrate was purchased from Acros. Benzylamine, and dibenzo[24]crown-8 were purchased from TCI. Other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetrahydrofuran (THF), dioxane and trimethylamine (Et₃N) were distilled under normal pressure with nitrogen to remove water and oxygen in the solvents prior to use.

¹H and ¹³C NMR spectra were measured on a Mercury plus 400 MHz NMR spectrometer in CDCl₃ or DMSO-*d*₆ using tetramethylsilane (TMS; $\delta = 0$ ppm) as the internal standard. FT-IR spectra were recorded on a Bruker Vector 22 spectrometer. UV-vis absorption spectra were obtained on a Varian CARY 100 Bio UV/Visible spectrophotometer. Photoluminescence (PL) spectra were recorded on a Shimadzu RF-5301PC spectrophotometer. High-resolution mass spectra (HRMS) were measured on a GCT Premier CAB 048 mass spectrometer operated in MALDI-TOF mode. SEM images were investigated on a Hitachi S4800 scanning electron microscope (5 kV, 10 μ A).

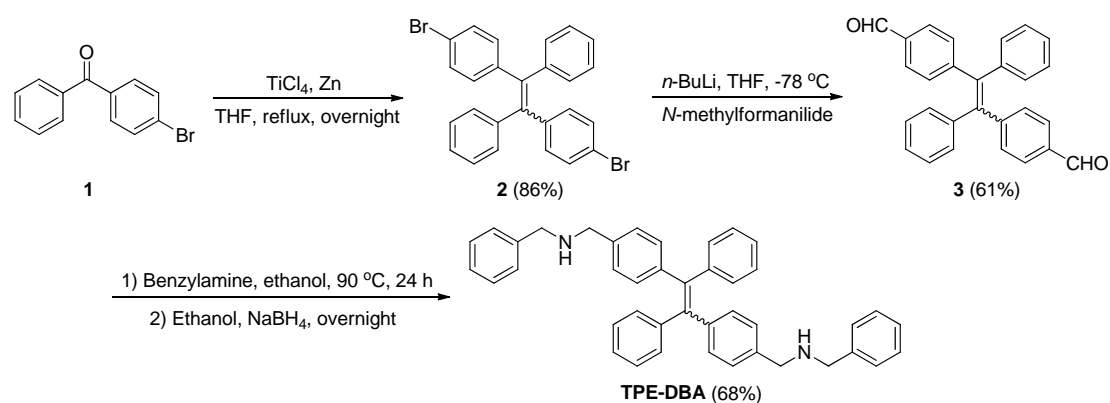
2. Synthesis.

All the TPE-based precursors were prepared according to the papers published by our group and by others previously.¹⁻³

2.1 Synthesis of TPE-DBA.

1,2-Bis(4-bromophenyl)-1,2-diphenylethene (2). Into a 500-mL two-necked round-bottom flask with a reflux condenser were placed 4-bromobenzophenone (**1**) (10.000 g, 38.3 mmol) and zinc powder (7.52 g, 114.9 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen three times. Anhydrous THF (120 mL) was added into the reaction system. The mixture was cooled down to 0 °C, then titanium

(IV) chloride (10.89 g, 6.4 mL, 57.4 mmol) was added dropwise into the reaction system. The ice bath was taken out and the mixture was stirred and refluxed overnight. After the reaction, the mixture was cooled to room temperature, filtered and washed with dichloromethane (DCM). The liquid was vaporized with reduced pressure. Then the filtrate was poured into dilute HCl solution (100 mL), and extracted by DCM three times. The organic layer was combined and dried over MgSO₄. After filtration and solvent evaporation, the crude product was purified by silica column chromatography using petroleum ether (PE) as eluent. White solid of 1,2-bis(4-bromophenyl)-1,2-diphenylethene (**2**) was obtained in 86% yield (8.079 g).



Scheme S1. Synthetic route to TPE-DBA.

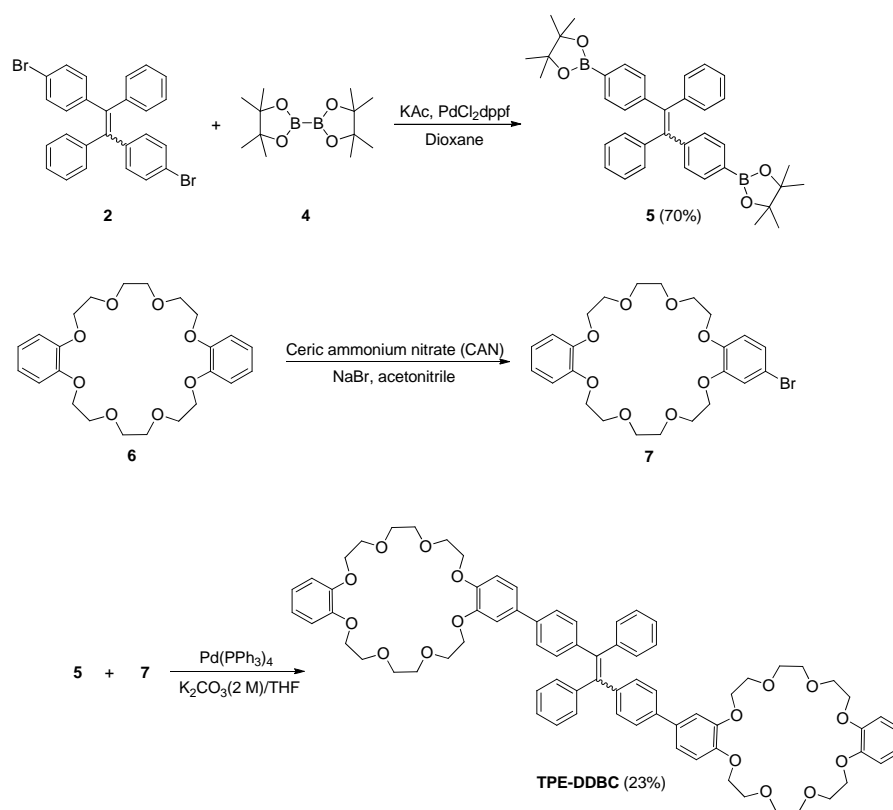
4,4'-(1,2-Diphenylethene-1,2-diyl)dibenzaldehyde (3). Into a 250 mL two-necked round-bottom flask was placed **2** (2.000 g, 4.08 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen three times. After anhydrous THF (100 mL) was added, *n*-BuLi (6.1 mL, 1.6 M, 9.79 mmol) was added dropwise at -78 °C. After the resulting solution was stirred at -78 °C for 2 h, *N*-methylformanilide (2.0 mL, 16.3 mmol, dissolved in 20 mL THF) was added dropwise with stirring. The mixture was reacted at -78 °C for 1 h and returned to room temperature for a 6-hour reaction. The reaction was then quenched by dilute HCl solution. The mixture was extracted with DCM and the organic layer was combined and dried over MgSO₄. Filtering and evaporating the solvent, the crude product was purified by silica column chromatography using PE/ethyl acetate (EA) mixture (20/1 by volume) as eluent. Light yellow solid of 4,4'-(1,2-diphenylethene-1,2-diyl)dibenzaldehyde (**3**) was obtained in 61% yield (0.970 g).

N,N'-(((1,2-diphenylethene-1,2-diyl)bis(4,1-phenylene))bis(methylene))bis(1-phenylmethanamine) (**TPE-DBA**). Into a 250-mL round-bottom flask with a reflux condenser were placed benzylamine (166 mg, 1.54 mmol), **3** (300 mg, 0.773 mmol) and anhydrous ethanol (100 mL). The mixture was heated to 90 °C and refluxed for 24 h. After the Schiff's base reaction, the solution was cooled to room temperature. Into the reaction system was added sodium tetrahydridoborate (117 mg, 3.09 mmol). The mixture was stirred overnight. The resulting solution was vaporized with reduced pressure and the crude product was purified by silica column chromatography using DCM/methanol mixture (20/1 by volume). White and yellow solids (two isomers) of TPE-DBA were obtained in a total yield of 68% (301 mg), with the ratio of two isomers varying from batch to batch. IR (KBr), ν (cm⁻¹): 3419, 2918, 2850, 1635, 1446, 1263, 740, 700. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.40 – 7.31 (m, 8H), 7.29 (dd, J = 5.6, 1.6 Hz, 2H), 7.17 – 7.10 (m, 8H), 7.10 – 7.05 (m, 6H), 7.02 (d, J = 8.0 Hz, 4H), 3.79 (s, 4H), 3.74 (s, 4H), 1.83 (s, 2H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 145.0, 143.6, 141.8, 141.4, 139.4, 132.6, 132.5, 129.6, 129.4, 128.8, 128.6, 128.2, 127.6, 54.3, 54.0. HRMS (MALDI-TOF, DCTB, m/z), [M+H⁺] calculated: 571.3108, found: 571.3119.

2.2 Synthesis of TPE-DDBC

1,2-Diphenyl-1,2-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethane (5). Into a 250-mL two-necked round-bottom flask were placed **2** (1.000 g, 2.04 mmol), bis(pinacolato)boron (**4**) (1.140 g, 4.49 mmol), potassium acetate (1.262 g, 6.41 mmol), and PdCl₂dppf (92.4 mg, 0.063 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen three times. Then into the flask was added anhydrous 1,4-dioxane (40 mL). The reaction mixture was heated to 110 °C and refluxed overnight. The solution was cooled to room temperature after the reaction and extracted with DCM. The organic layer was combined and dried over MgSO₄. Filtering and evaporating the solvent, the crude product was purified by silica column chromatography using PE/DCM mixture (3/1 by volume) as eluent. White solid of 1,2-diphenyl-1,2-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethane (**5**) was obtained in 70% yield (842 mg). HRMS (MALDI-TOF, DCTB, m/z), [M⁺]

calculated: 584.3269, found: 584.3250.



Scheme S2. Synthetic route to TPE-DDBC.

2-Bromodibenzo[24]crown-8 (7). Into a 250-mL two-necked round-bottom flask were added dibenzo[24]crown-8 (6) (0.800 g, 1.78 mmol), and sodium bromide (0.183 g, 1.78 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen three times. Then 35 mL of acetonitrile was added into the reaction system. Meanwhile, ceric ammonium nitrate (1.173 g, 2.14 mmol) was dissolved by 15 mL of acetonitrile. This orange brown solution was then added into the reaction system really slowly. The duration should be longer than 30 min. The solution was reacted for 16 h and quenched by deionized water (50 mL). After that, the mixture was extracted with DCM and the organic layer was combined and dried over MgSO_4 . Filtering and evaporating the solvent, the crude product was purified by silica column chromatography using DCM/MeOH mixture (100/1 by volume) as eluent. The product was white solid with three different components after TLC analysis. We didn't conduct further purification and the product was utilized to the next reaction. However, the ^1H NMR spectrum and mass spectrum showed it was what we want. ^1H

NMR (400 MHz, CDCl₃), δ (TMS, ppm): 6.98 (d, J = 13.4 Hz, 2H), 6.88 (s, 4H), 6.72 (d, J = 11.1 Hz, 1H), 4.13 (dd, J = 12.7, 6.8 Hz, 8H), 3.90 (s, 8H), 3.85 – 3.70 (m, 8H). HRMS (MALDI-TOF, DCTB, m/z), [M+Na⁺] calculated: 549.1100 and 551.1080, found: 549.1100 and 551.1080.

1,2-Bis(4-(2-bromodibenzo[24]-crown-8)phenyl)-1,2-diphenylethene (TPE-DDBC).

Into a 100-mL two-necked round-bottom flask were placed **5** (88 mg, 0.15 mmol), **7** (187 mg, 0.33 mmol), and Pd(PPh₃)₄ (3.5 mg, 0.003 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen three times. At meantime, Potassium carbonate (2.764 g, 20 mmol) was dissolved in 10 mL of deionized water to make a K₂CO₃ solution (2 M). Then anhydrous THF (10 mL) and K₂CO₃ solution (2 M, 5 mL) were added into the reaction system using a needle tube. The mixture was heated to 80 °C and refluxed for 24 h. After the reaction, the mixture was cooled to room temperature and extracted with DCM. The organic layer was combined and dried over MgSO₄. Filtering and evaporating the solvent, the crude product was purified by silica gel column chromatography using DCM/MeOH mixture (50/1 by volume) as eluent. Yellowish white solid of 1,2-bis(4-(2-bromodibenzo[24]-crown-8)phenyl)1,2-diphenylethene (TPE-DDBC) was obtained in 23% yield (42 mg). IR (KBr), ν (cm⁻¹): 3415 (broad), 2925, 2870, 1591, 1500, 1452, 1255, 1212, 1124, 1053, 938, 747, 542. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.65 (ddd, J = 17.5, 9.5, 8.0 Hz, 4H), 7.59 – 7.42 (m, 6H), 7.15 – 7.02 (m, 6H), 6.98 (m, 6H), 6.93 – 6.82 (m, 8H), 6.70 (t, J = 9.8 Hz, 2H), 4.22 – 4.07 (m, 16H), 3.96 – 3.86 (m, 16H), 3.82 (m, 16H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 150.0, 149.2, 148.5, 132.5, 132.4, 129.0, 128.9, 124.3, 121.8, 117.5, 115.6, 114.4, 113.5, 71.6, 70.3, 70.2, 70.1, 70.0, 69.9, 69.7.

3. Fluorescent behaviours of the assembling/disassembling process

Into a flask, 5 mL dry THF, TPE-DBA and TPE-DDBC were added. A mixture solution was prepared. The concentrations of TPE-DBA and TPE-DDBC were 5×10⁻⁴ M. 10 μ L HCl aqueous solution (1.0 M) was added into the solution, white suspension was formed and its fluorescence spectrum was recorded immediately. Afterwards, 20

μL NaOH aqueous solution (1.0 M) was added into the mixture in two times (10 μL + 10 μL). The white precipitate totally disappeared after the addition of 20 μL of NaOH solution. The fluorescent emission of the solution vanished and the fluorescence spectrum was recorded. To check the reversibility of this fluorescence turn-on/turn-off process. Acid and base solutions were added into the mixture alternately, and the fluorescence spectra were recorded in each step. For three acid/base treatment cycles, the volumes of HCl aqueous solution added into the mixture were 10, 20, and 20 μL ; while the volumes of NaOH aqueous solution added successively into the mixture were 20, 20, and 20 μL . Consequently, after three cycles, the total water volume was approximately 110 μL . In the mixture containing 5 mL THF, the water fraction was approximately 2.2%. In such low water fraction, TPE-DBA and TPE-DDBC could not form precipitate individually. The suspension was ascribed to the host-guest interaction between TPE-DBA and TPE-DDBC, which induced the formation of poorly soluble supramolecular macromolecules.

References:

- [1] J. Tong, Y. Wang, J. Mei, J. Wang, A. Qin, J. Z. Sun and B. Z. Tang, *Chem. Eur. J.*, 2014, **20**, 4661.
- [2] B. T. Cho and S. K. Kang, *Tetrahedron*, 2005, **61**, 5725.
- [3] P. Mobian, N. Banerji, G. Bernardinelli and J. Lacour, *Org. Biomol. Chem.*, 2006, **4**, 224.

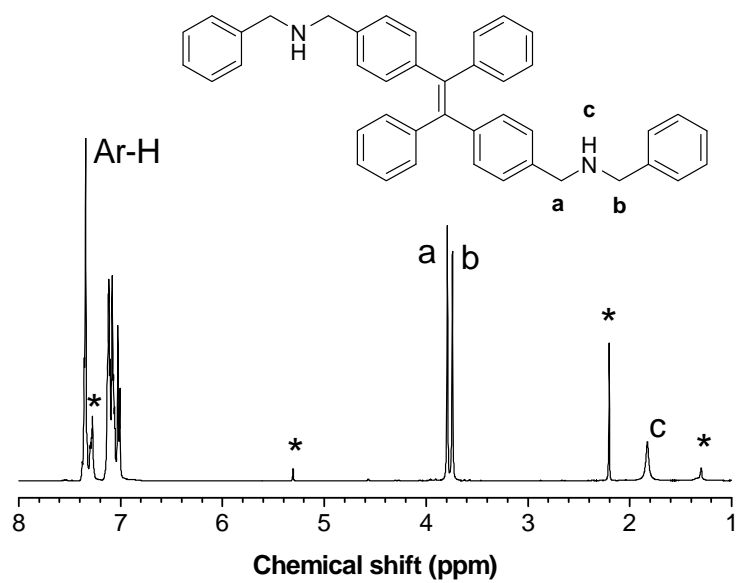


Fig. S1 ^1H NMR spectrum of TPE-DBA in CDCl_3 . The solvent peaks are marked with asterisks.

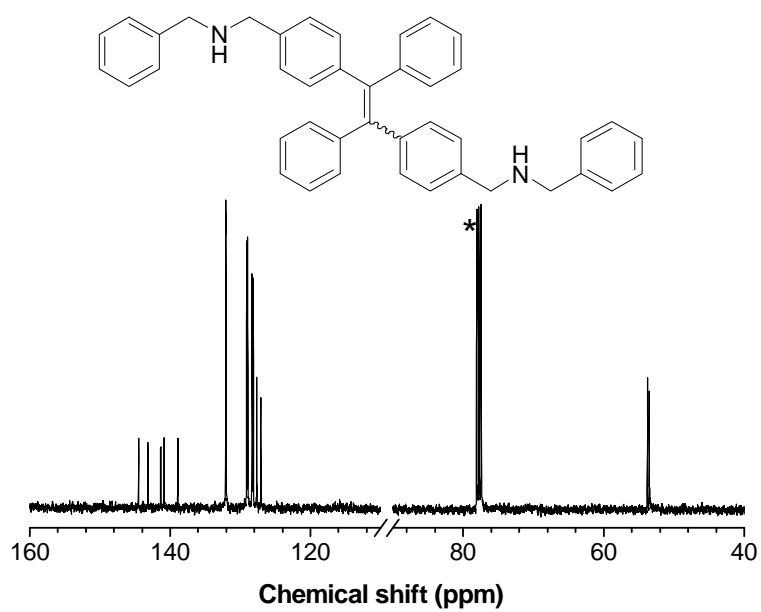


Fig. S2 ^{13}C NMR spectrum of TPE-DBA in CDCl_3 . The solvent peaks are marked with asterisks.

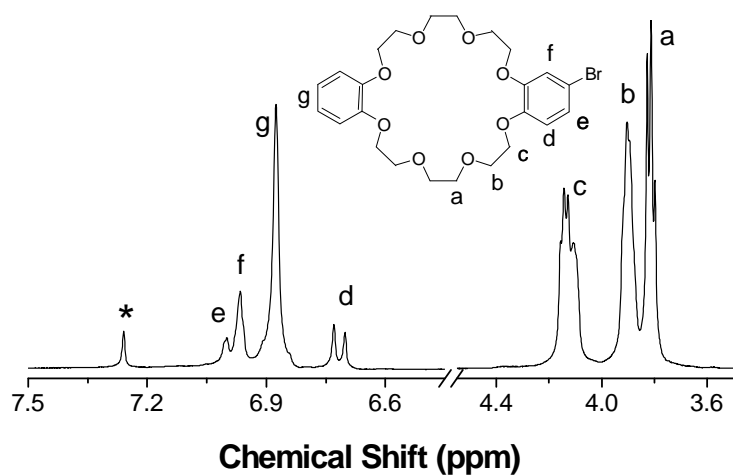


Fig. S3 ^1H NMR spectrum of 2-bromodibenzo[24]crown-8 (**7**) in CDCl_3 . The solvent peaks are marked with asterisks.

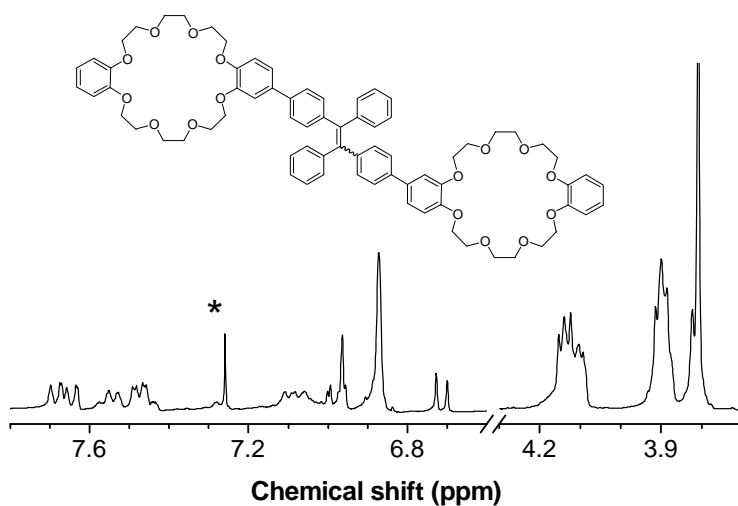


Fig. S4 ^1H NMR spectrum of TPE-DDBC in CDCl_3 . The solvent peaks are marked with asterisks.

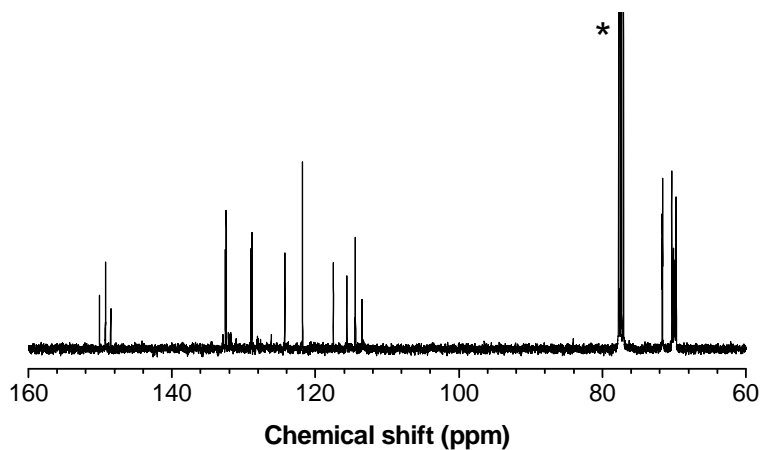


Fig. S5 ^{13}C NMR spectrum of TPE-DDBC in CDCl_3 . The solvent peaks are marked with asterisks.

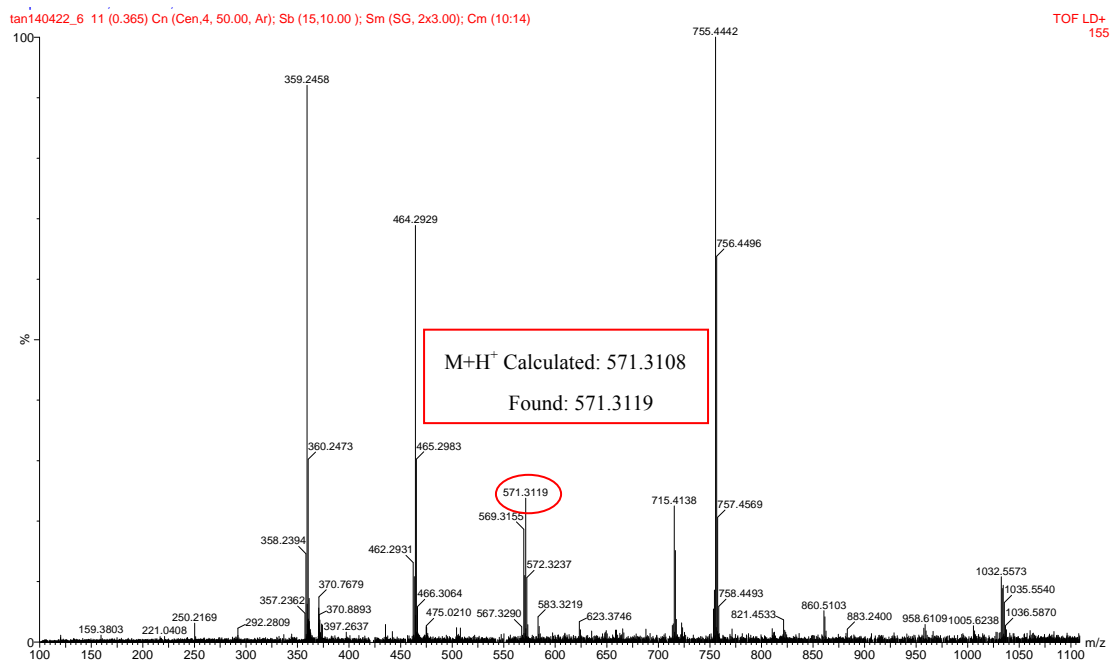


Fig. S6 High-resolution mass spectrum of TPE-DBA.

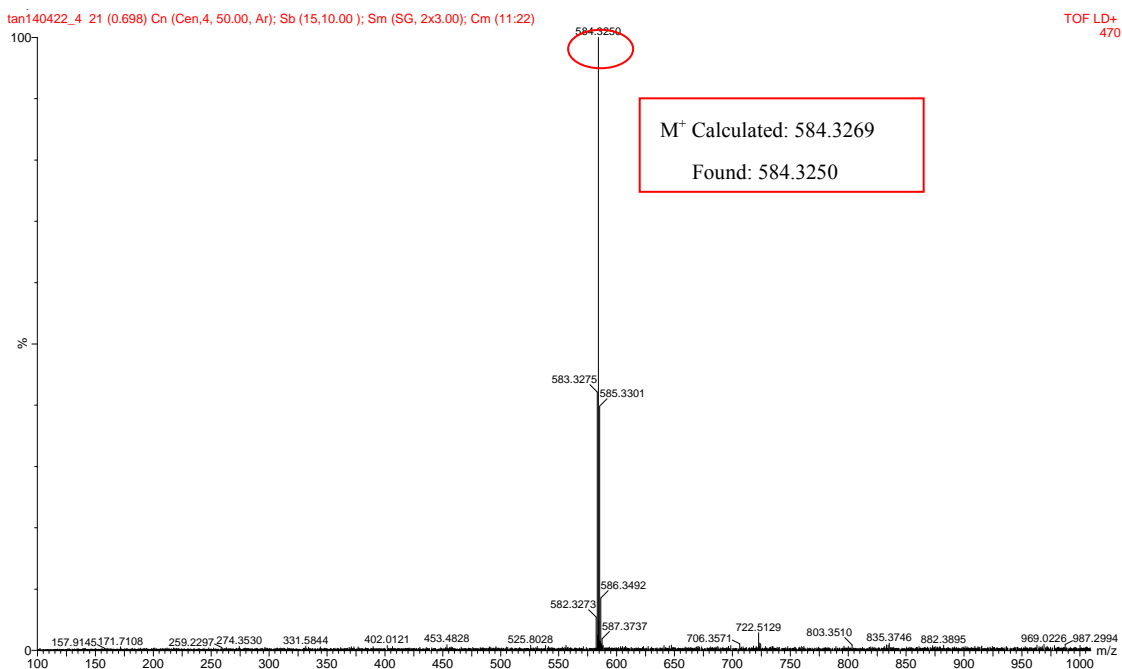


Fig. S7 High-resolution mass spectrum of 1,2-diphenyl-1,2-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethane (**5**).

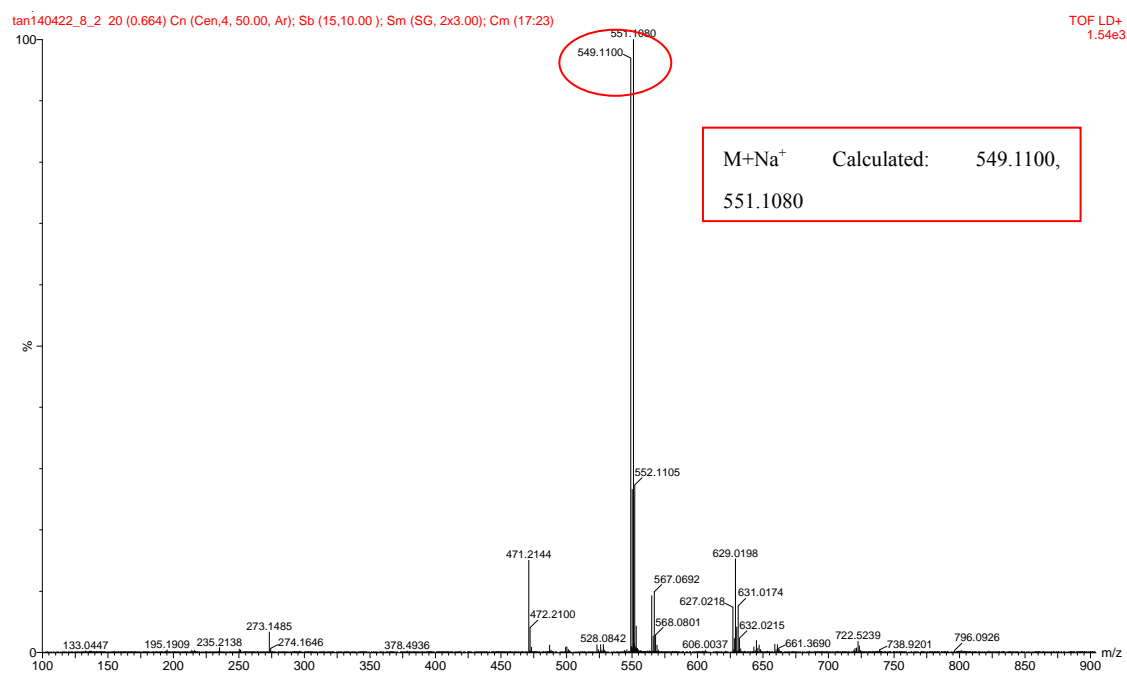


Fig. S8 High-resolution mass spectrum of 2-bromodibenzo[24]crown-8 (7).

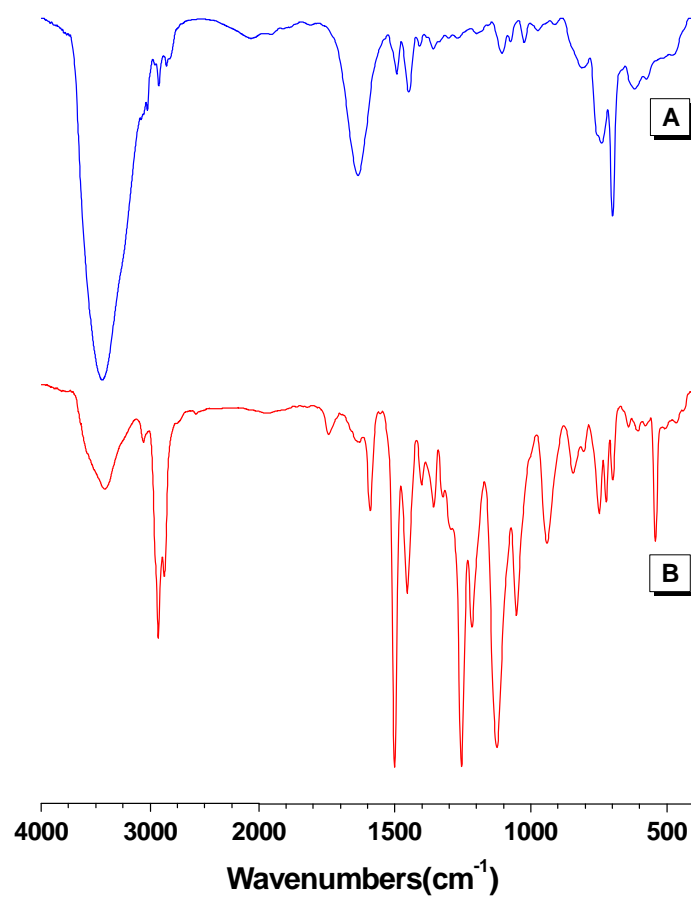


Fig. S9 FT-IR spectra of (A) TPE-DBA and (B) TPE-DDBC.

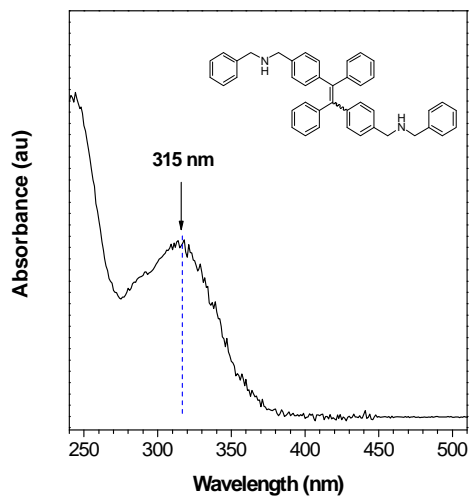


Fig. S10 UV-vis absorption spectrum of TPE-DBA in THF. TPE-DBA concentration: 10^{-5} M.

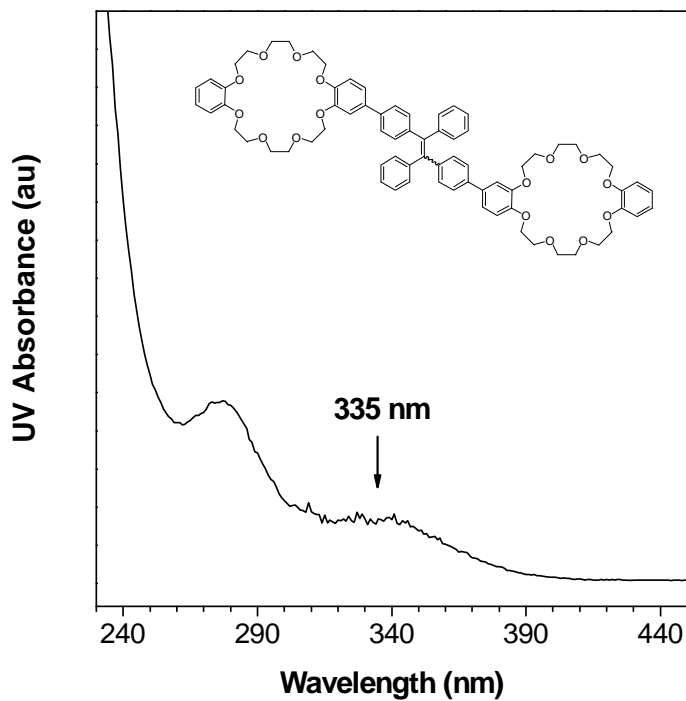
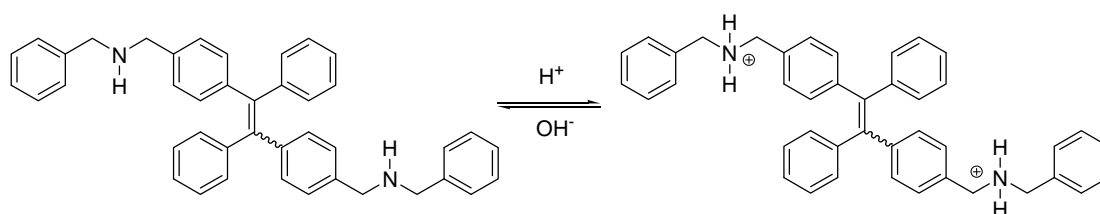


Fig. S11 UV-vis absorption spectrum of TPE-DDBC in THF. TPE-DDBC concentration: 10^{-5} M.



Scheme S3. Schematic representation of the pH responsiveness of TPE-DBA.

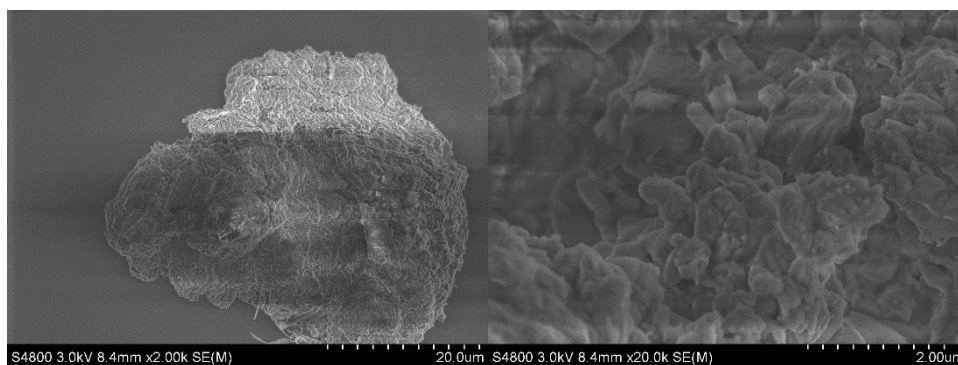


Fig. S12 SEM images of the mixture of TPE-DBA and TPE-DDBC with no acid/base treatment (N, neutral THF solution).

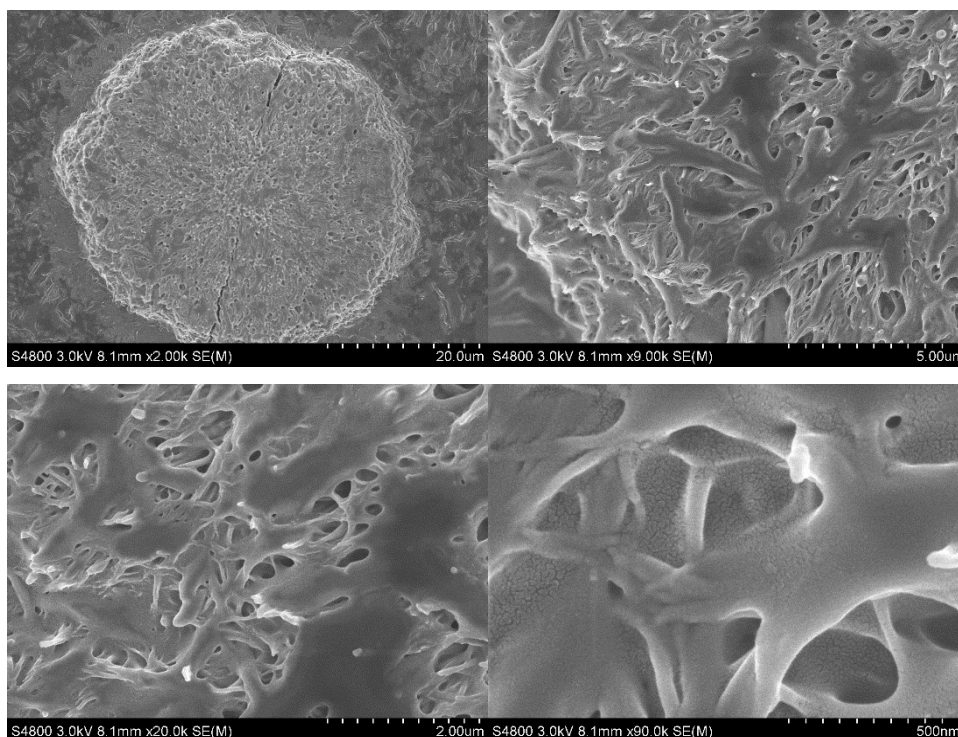


Fig. S13 SEM images taken at different length scales showing the morphology of the supramolecular self-assemblies between TPE-DBA and TPE-DDBC in THF solution after treated with adequate amount of HCl solution (A1).

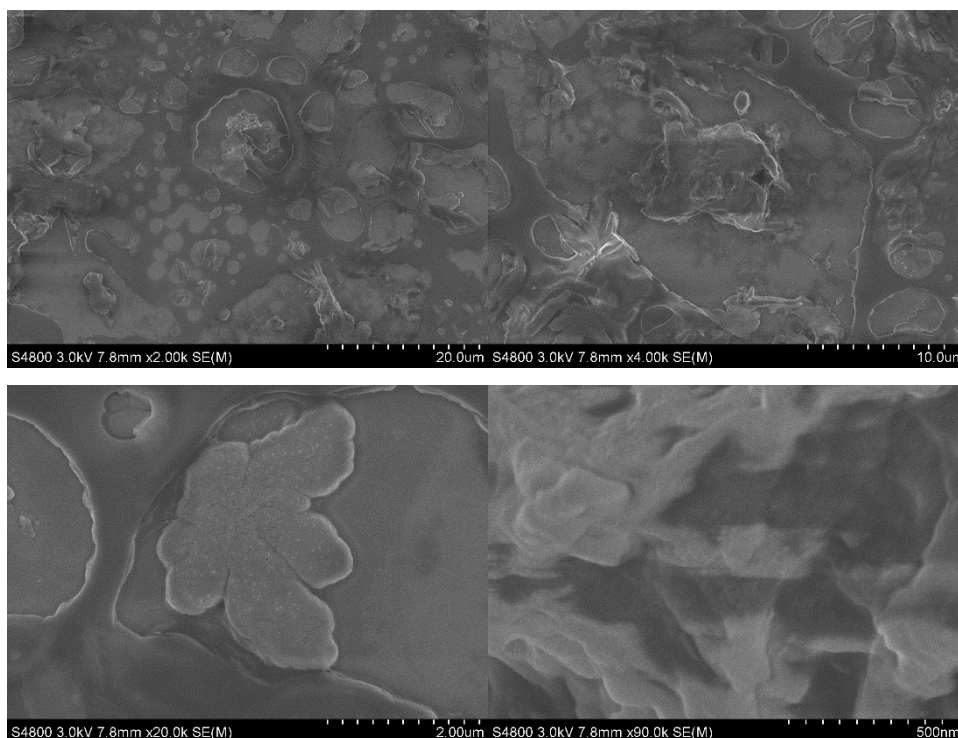


Fig. S14 SEM images taken at different length scales showing the morphology of the supramolecular self-assemblies between TPE-DBA and TPE-DDBC in THF solution after treated with an excess amount (2 equiv. to HCl) of NaOH solution (B1).

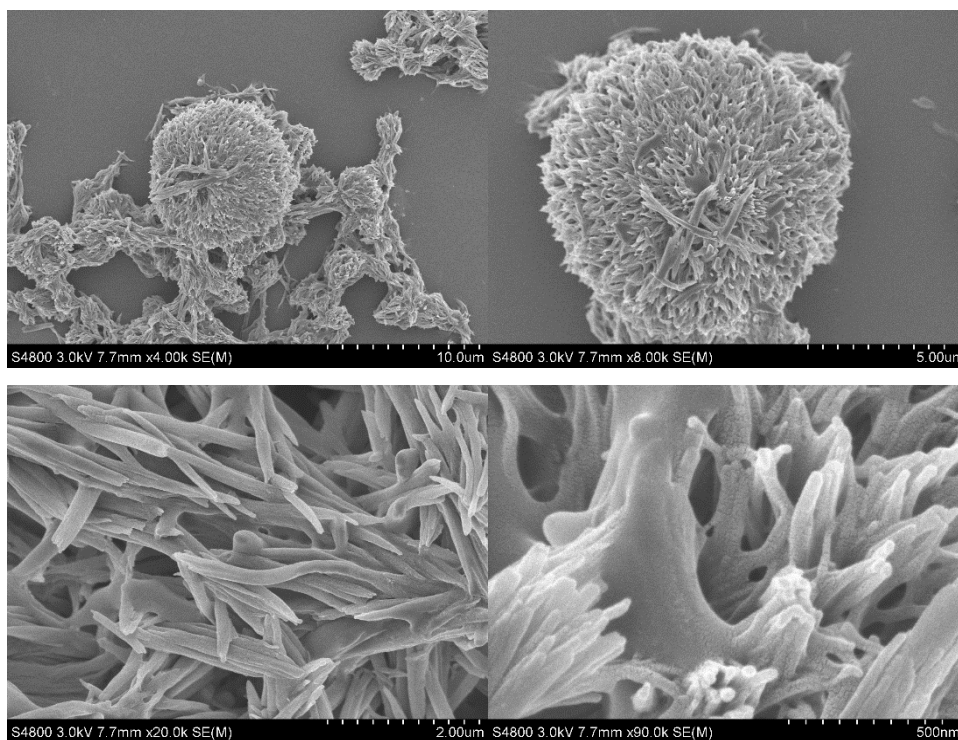


Fig. S15 SEM images taken at different length scales showing the morphology of the supramolecular self-assemblies between TPE-DBA and TPE-DDBC in THF solution after treated with an excess amount (2 equiv. to NaOH) of HCl solution (A2).

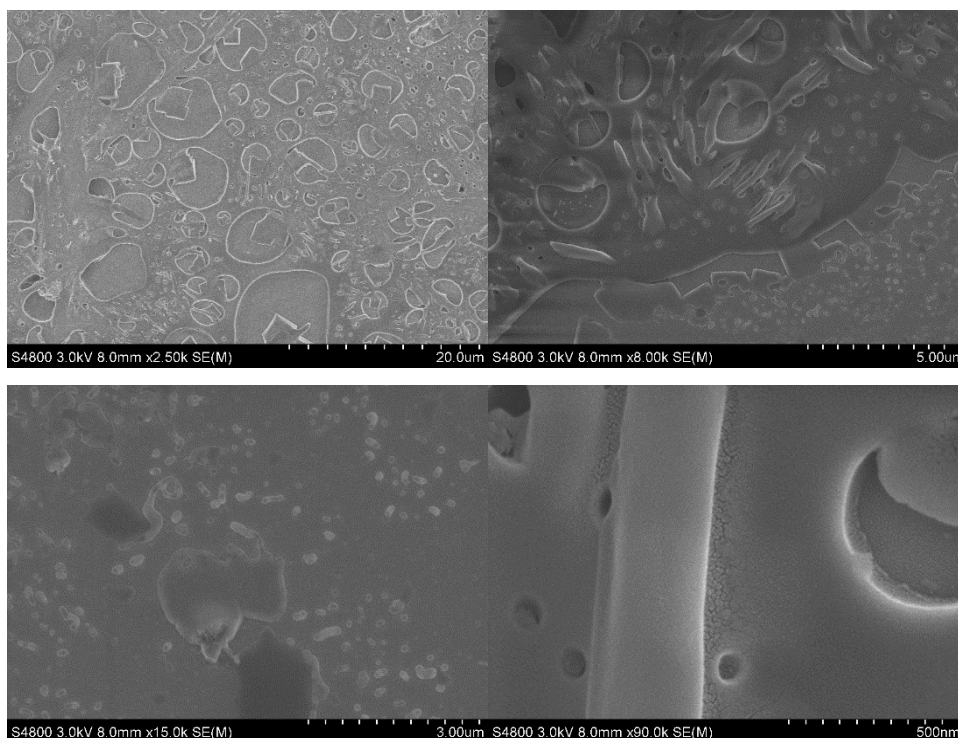


Fig. S16 SEM images taken at different length scales showing the morphology of the supramolecular self-assemblies between TPE-DBA and TPE-DDBC in THF solution after treated with an excess amount (2 equiv. to HCl) of NaOH solution (B2).

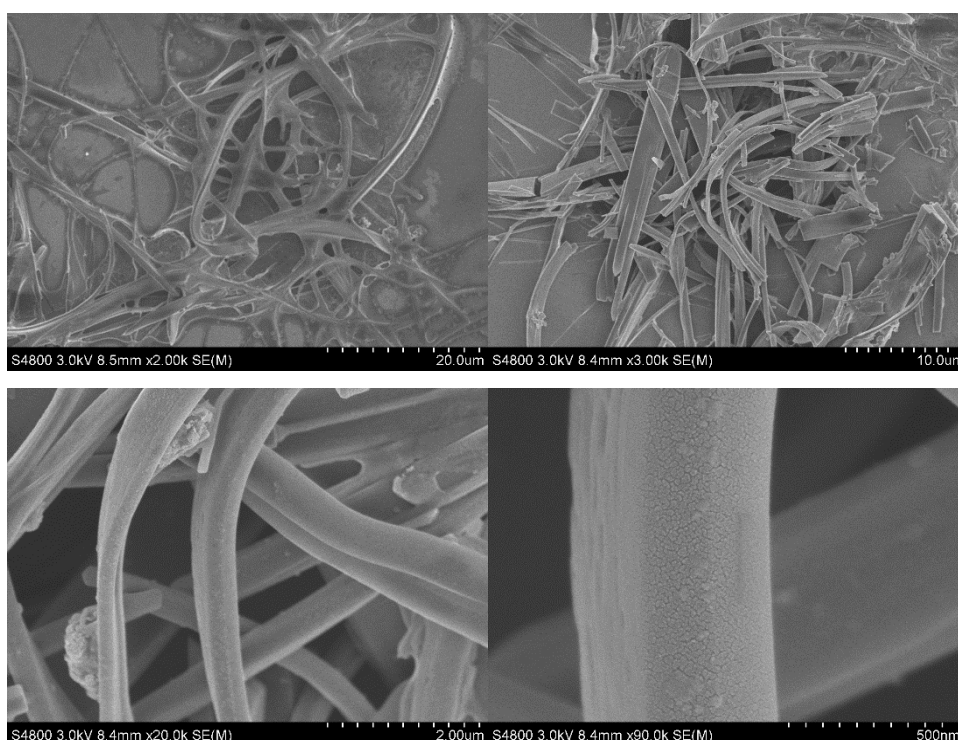


Fig. S17 SEM images taken at different length scales showing the morphology of the supramolecular self-assemblies between TPE-DBA and TPE-DDBC in THF solution after treated with an excess amount (2 equiv. to NaOH) of HCl solution (A3).