

Electronic Supplementary Information

Fluorescence responsive conjugated poly(tetraphenylethene) and its morphological transition from micelle to vesicle†

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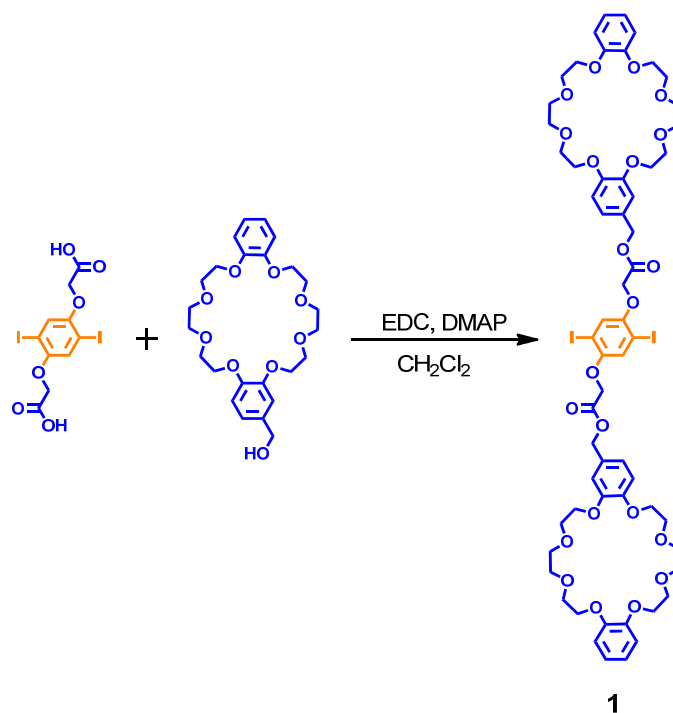
Instruments and Materials

All solvents and reagents were of reagent grade quality and purchased commercially. ^1H NMR, ^{13}C NMR were recorded on a JNM-ECS400 spectrometer, performing in CD_2Cl_2 , CDCl_3 , CD_3CN solutions and using TMS as an internal standard. Electrospray ionization mass spectra (ESI-MS) were performed with Bruker microTOF-Q II. UV-vis absorption spectra were recorded by using a SHIMADZU UV-2550 spectrophotometer. Luminescence measurements were made on a Hitachi F-7000 spectrofluorimeter with a xenon lamp as the excitation source. Dynamic light scattering (DLS) measurements were performed on a Brookhaven BI-200SM spectrometer. SEM measurements were performed on a field emission scanning electron microscope (JEOL JSM-6701F). TEM images were obtained with JEOL JEM-1230 and JEM-2100 operating at 120 kV and 200 kV respectively. All measurements were carried out at room temperature.

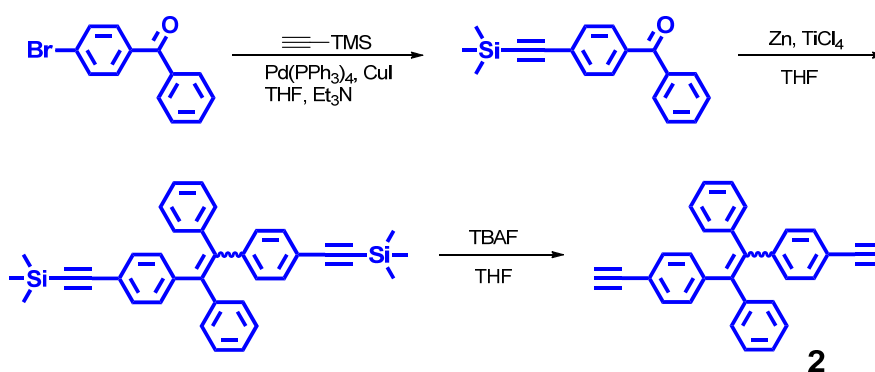
All water- and air-sensitive reactions were carried out under argon atmosphere.

Synthesis of AP-TPE

Compounds **1**¹ and **2**² were synthesized and showed identical ^1H NMR spectra to those reported therein.



Scheme S1 Synthesis of **1**



Scheme S2 Synthesis of **1,2-Bis(4-ethynylphenyl)-1,2-diphenylethene (2)**

4-(2-Trimethylsilylethynyl)benzophenone: Into a 100 mL schlenk tube were added bis(triphenylphosphine)palladium(II) chloride (0.4 mmol, 280.4 mg), copper(I) iodide (0.4 mmol, 76 mg) and 4-bromobenzophenone (10 mmol, 2.6 g), the tube was degassed with argon, then 5 mL THF and 50 mL Et₃N were added. After the catalysts were completely dissolved, 1.8 mL (13 mmol) of (trimethylsilyl)acetylene was injected into the flask and the mixture was stirred at reflux for 24 h. The formed solid was removed by filtration and washed with diethyl ether. The crude product was purified by column chromatography (silica gel) using hexane as eluent to give a pale brown solid in 88% yield.

^1H NMR (400 MHz, CDCl_3), δ = 7.76 (d, J = 7.2 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.57 (m, 3H), 7.47 (m, 2H), 0.27 [s, 9H, $\text{Si}(\text{CH}_3)_3$].

1,2-Bis{4-[2-(trimethylsilyl)ethynyl]phenyl}-1,2-diphenylethene: Into a 100 mL schlenk tube with a reflux condenser were added zinc dust (18 mmol, 12.1 g) and **4-(2-Trimethylsilylethynyl)benzophenone** (15 mmol, 4.18 g). The tube was argon degassed and 50 mL of THF was then added. The mixture was cooled to -78 °C and 1 mL (9 mmol) of TiCl_4 was slowly added. The mixture was slowly warmed to room temperature, stirred for 0.5 h, and then refluxed overnight. The reaction was quenched with 10% aqueous K_2CO_3 solution and large amount of water was added until the solid turned to grey or white. The mixture was extracted with DCM for three times. The organic layers were combined and washed with brine twice. After solvent evaporation, the crude product was purified by column chromatography (silica gel) using hexane as eluent. A yellow solid was obtained in 90% yield. ^1H NMR (400 MHz, CDCl_3), δ = 7.19 (m, 4H), 7.09 (m, 6H), 6.92 (m, 8H), 0.23 and 0.21 [s, 18H, $\text{Si}(\text{CH}_3)_3$].

1,2-Bis(4-ethynylphenyl)-1,2-diphenylethene: Into a 100 mL round bottom flask was added 40 mL of THF solution of **1,2-Bis{4-[2-(trimethylsilyl)ethynyl]phenyl}-1,2-diphenylethene** (3 mmol, 1.57 g), followed by addition of 12 mL of 1 M THF solution of TBAF. After stirring for 3 h, 40 mL of water was added and the mixture was extracted with 200 mL of DCM three times. The DCM solution was washed with brine twice. The mixture was dried over anhydrous sodium sulfate. After solvent evaporation, the crude product was purified by column chromatography (silica gel) using hexane as eluent. A light yellow solid of 17 was obtained in 92% yield. ^1H NMR (400 MHz, CDCl_3), δ = 7.21 (m, 4H), 7.10 (m, 6H), 6.95 (m, 8H), 3.06 and 3.04 (2H, $\text{HC}\equiv$).

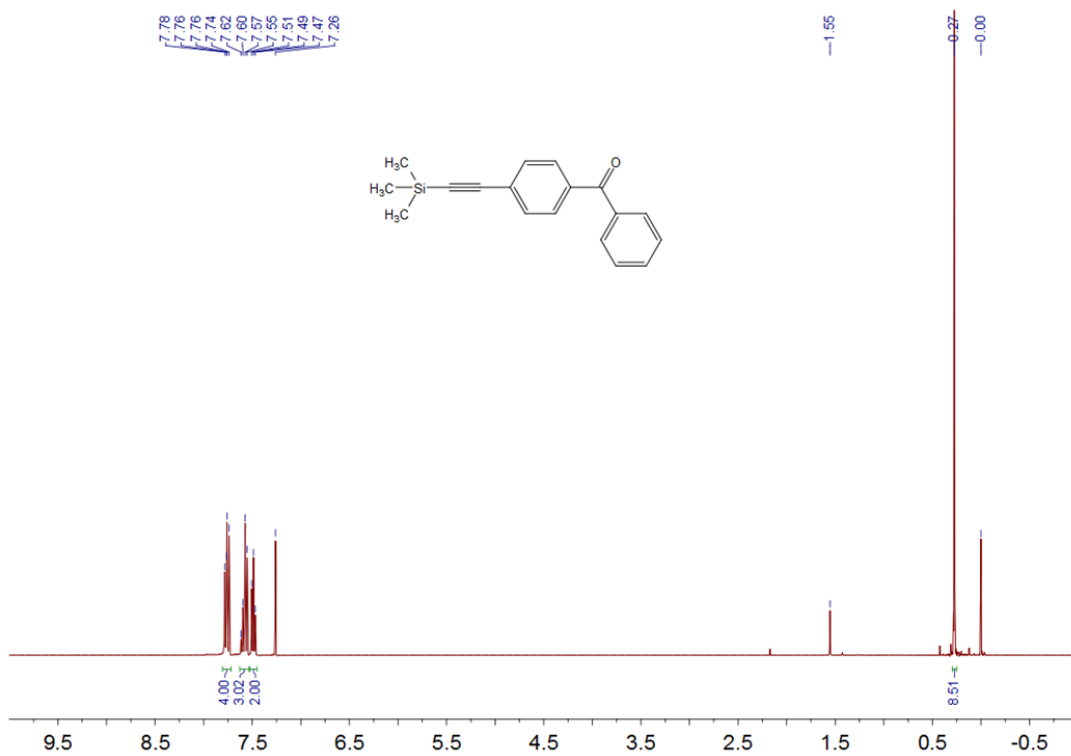


Fig. S1 ¹H NMR Spectrum of 4-(2-Trimethylsilylethynyl)benzophenone

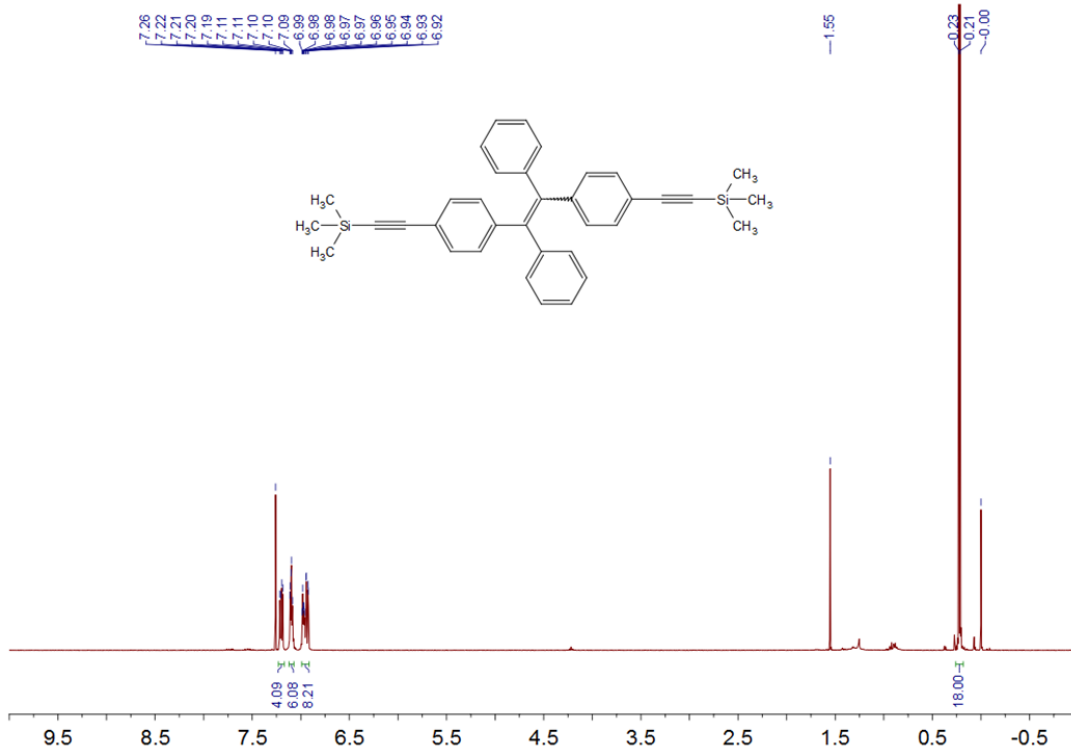


Fig. S2 ¹H NMR Spectrum of 1,2-Bis{4-[2-(trimethylsilyl)ethynyl]phenyl}-1,2-diphenylethene

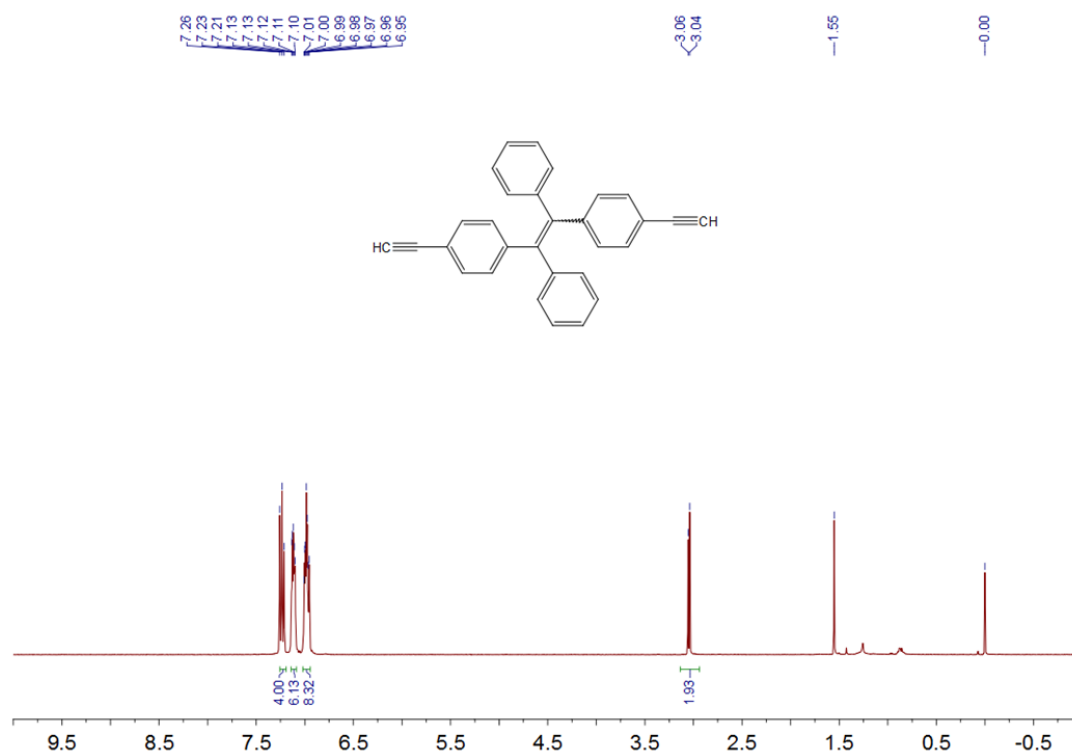
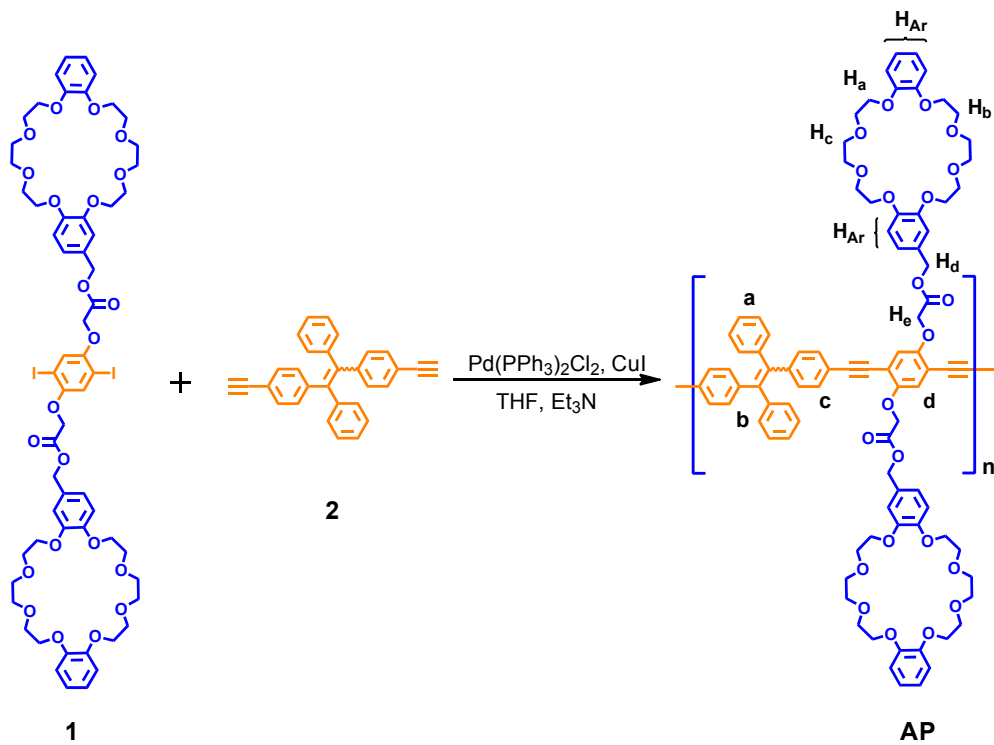


Fig. S3 ¹H NMR Spectrum of 1,2-Bis(4-ethynylphenyl)-1,2-diphenylethene



Scheme S3 Synthesis of AP-TPE

AP-TPE: To an argon degassed mixture of **1** (0.1 mmol, 140 mg) and compound **2** (0.1 mmol, 38 mg) in dry THF (10 mL) and dry triethylamine (5 mL) were added bis(triphenylphosphine)palladium(II) chloride (5 mol%) and copper(I) iodide (10 mol%) and the reaction mixture was stirred at reflux until TLC indicated complete conversion. After cooling to room temperature, the precipitated ammonia salt was filtered off and washed intensively with CHCl_3 . The solution was washed with sat. aq. $\text{NH}_4\text{Cl}/\text{EDTA}$ solution and dried over MgSO_4 . After removal of the solvents, the product was precipitated from methanol. Further purification was achieved by column chromatography (aluminum oxide, $\text{CH}_2\text{Cl}_2/\text{MeOH} = 5:1$ as eluent). ^1H NMR (CD_2Cl_2 , 400 MHz, δ): 7.50 (m, d), 7.18 (m, c), 7.06 (m, a), 6.94 (m, b), 6.79 (m, H_{Ar}), 5.03 (m, H_{d}), 4.62 (m, H_{e}), 4.00 (m, H_{a}), 3.75 (m, H_{b}), 3.66 (m, H_{c}).

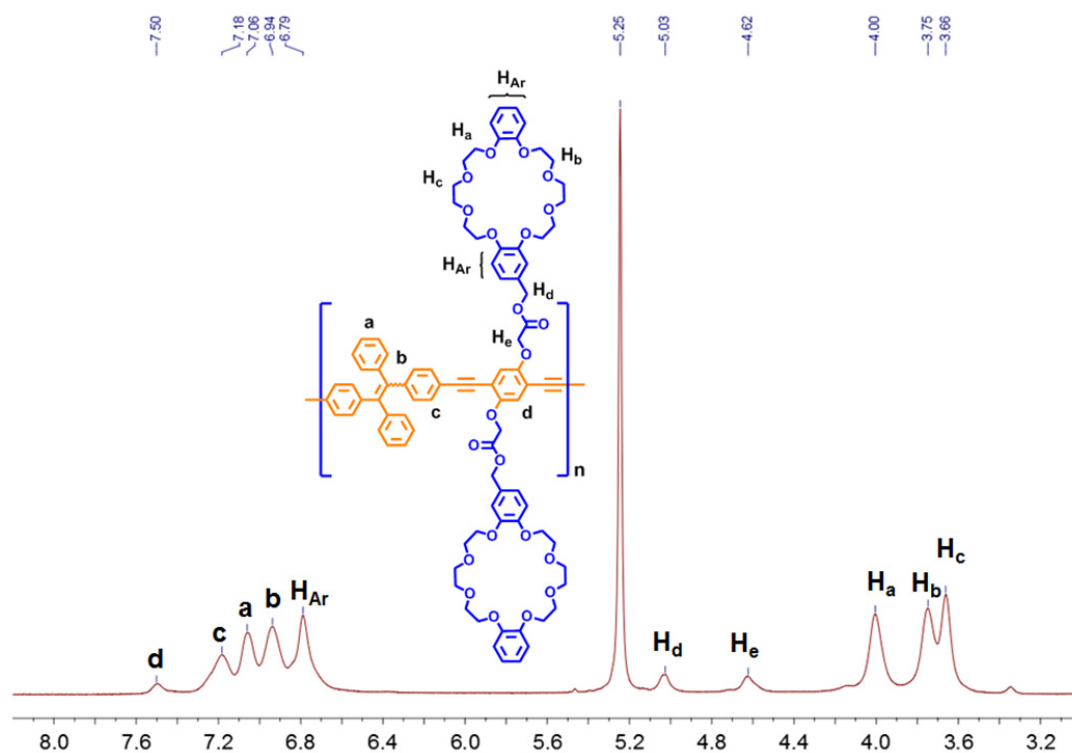


Fig. S4 ^1H NMR Spectrum of AP-TPE

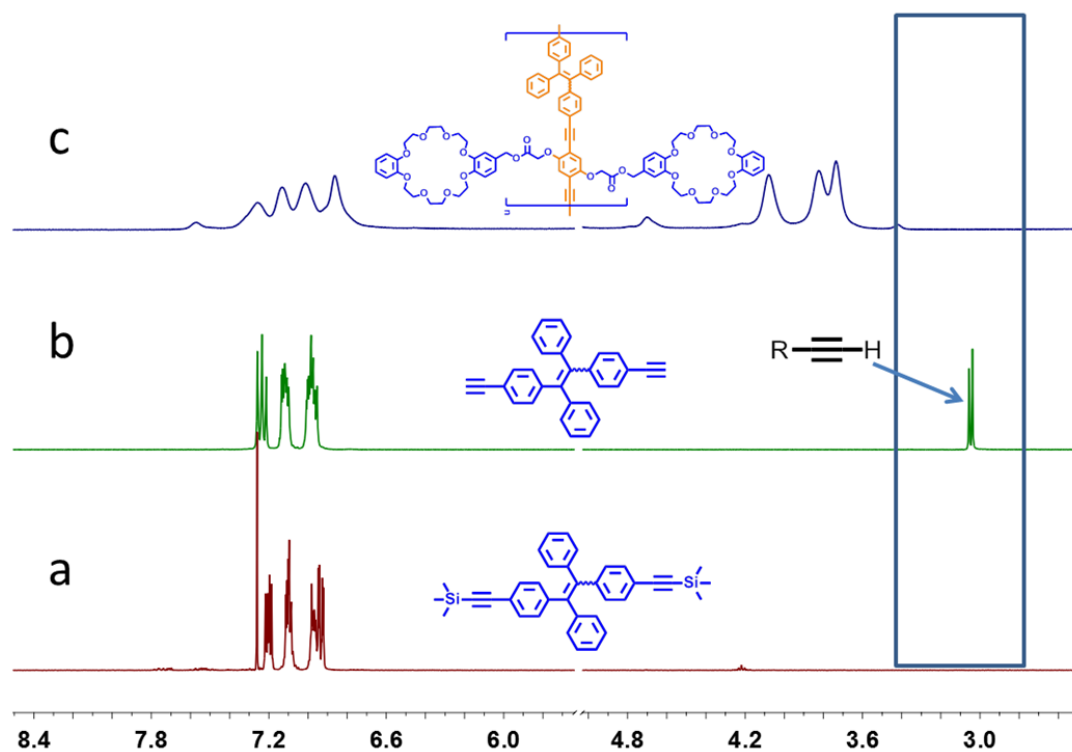
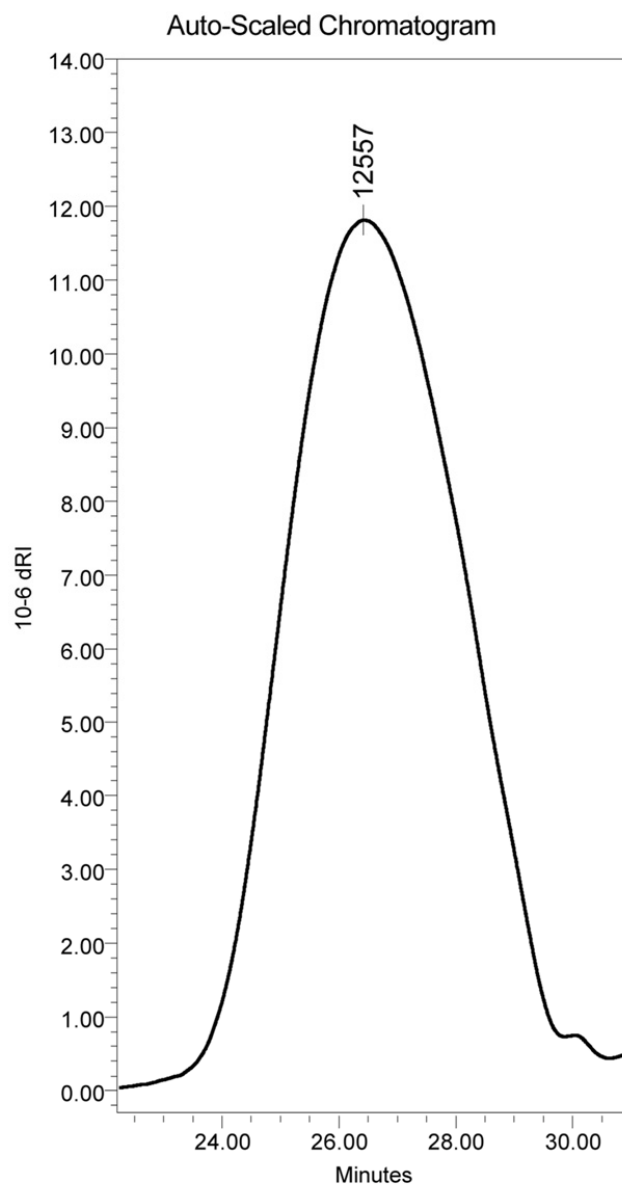


Fig. S5 ¹H NMR Spectrum of (a) 1,2-Bis{4-[2-(trimethylsilyl)ethynyl]phenyl}-1,2-diphenylethene, (b) 1,2-Bis(4-ethynylphenyl)-1,2-diphenylethene, (c) AP-TPE.



GPC Results

	SampleName	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Area ($\mu\text{V}\cdot\text{sec}$)
1	0529_AP	8385	13690	12557	20391	27415	1.632610	2264138

Fig. S6 GPC result of AP-TPE

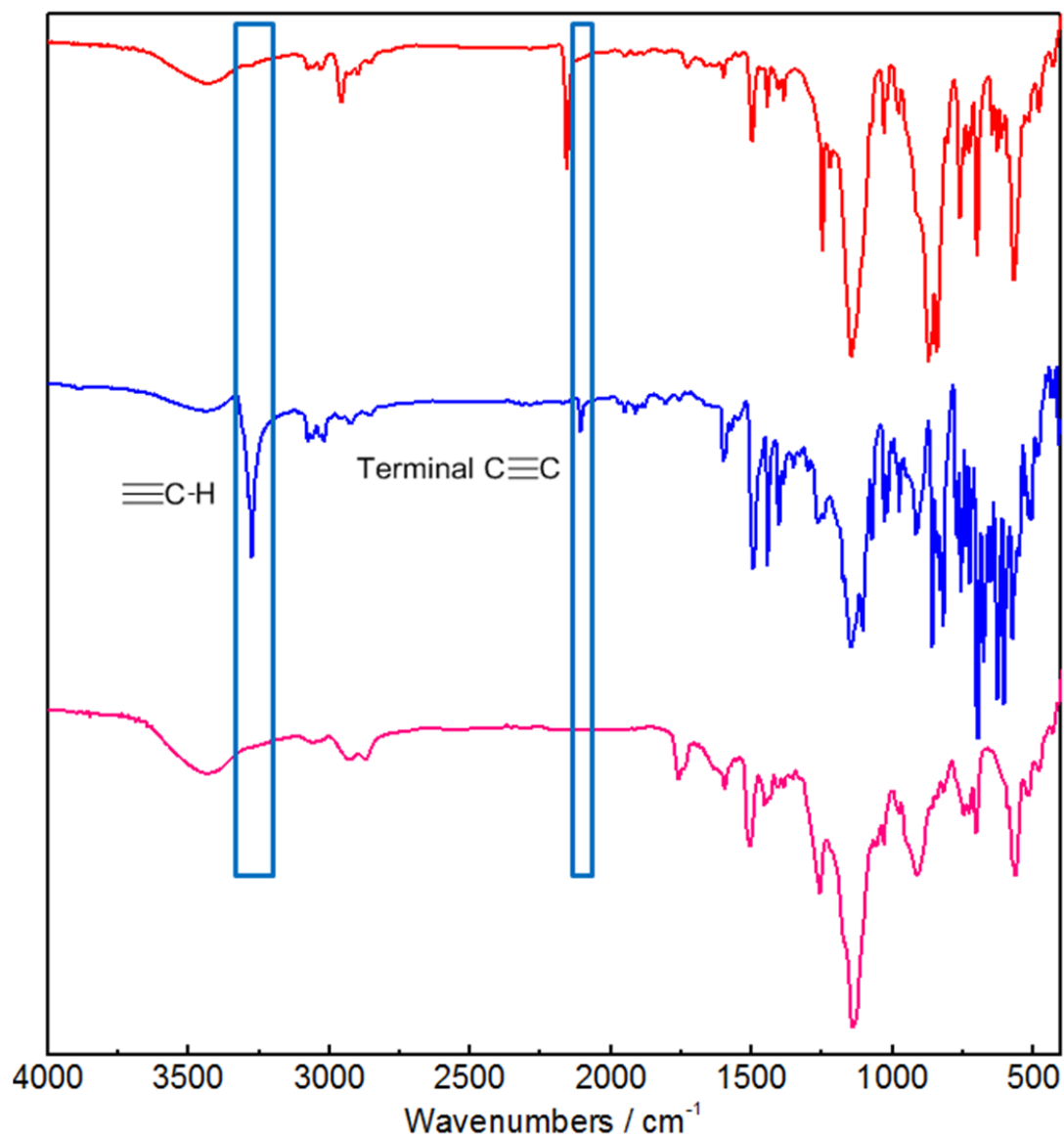


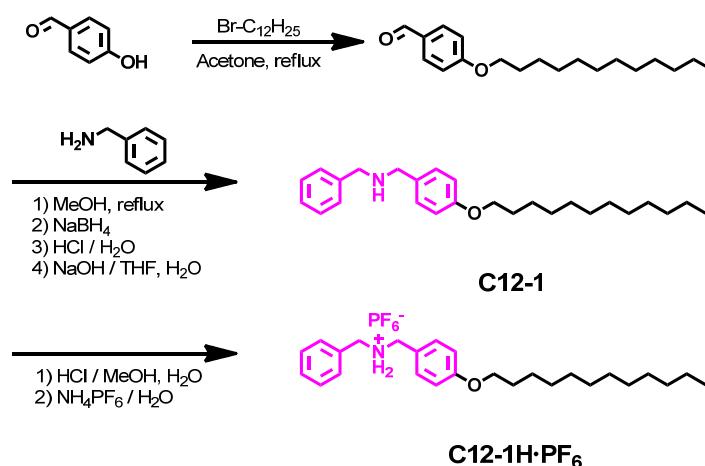
Fig. S7 FT-IR spectrum of **1,2-Bis{4-[2-(trimethylsilyl)ethynyl]phenyl}-1,2-diphenylethene** (red), **1,2-Bis(4-ethynylphenyl)-1,2-diphenylethene** (blue), **AP-TPE** (violet).

Discussion:

On account of the complete absence of the terminal alkynyl proton signal ($\delta = 3.06$ ppm, Fig. S5) and the typical detection limit of ^1H NMR spectroscopy ($\approx 5\%$),³ we deemed AP-TPE should consist of more than 20 repeated units and its molecular weight was roughly estimated to be 30.46 kDa. Meanwhile, the GPC data calibrated with standard polystyrenes revealed a relatively low molecular weight ($M_n = 8.385$ kDa) and a low polydispersity ($M_w/M_n = 1.63$) (Fig. S6). This value was much lower than that based on the ^1H NMR analysis, which might result from the absence of TPE-polymer standard samples. Additionally, further analysis by infrared spectra gave the same result as ^1H NMR.

The stretching vibration peaks of $\equiv\text{C-H}$ (3275 cm^{-1}) and terminal $\text{C}\equiv\text{C}$ (2107 cm^{-1}) were not detected, suggesting all monomers had been consumed after polymerization (Fig. S7).

Syntheses of Ghost C12-1 and C12-1H·PF₆



Scheme S4 Synthesis of **C12-1** and **C12-1H·PF₆**

4-(dodecyloxy)benzaldehyde: To a mixture of 4-hydroxybenzaldehyde (10 mmol, 1.22 g) and KCO_3 (30 mmol, 4.14 g) in acetone (80 mL) was added 1-bromododecane (15 mmol, 3.75 g) and the reaction mixture was stirred at reflux overnight. The mixture was cooled to room temperature, filtered off and washed intensively with CHCl_3 . After removal of the solvents, the residue was purified by column chromatography (petroleum ether/ethyl acetate, 7:1 v/v) to afford 4-(dodecyloxy)benzaldehyde as a white solid (2.32 g, 80%). $^1\text{H NMR}$ (CDCl_3 , 400 MHz, δ): 9.87 (s, 1H), 7.82-7.84 (d, 2H), 6.98-7.00 (d, 2H), 3.97-4.01 (t, 2H), 1.72-1.95 (m, 2H), 1.28-1.44 (m, 18H), 0.88-0.91 (t, 3H).

C12-1: 4-(dodecyloxy)benzaldehyde (1.16 g, 4.0 mmol) and phenylmethanamine (430 mg, 4.0 mmol) were dissolved in methanol (50 mL) and heated at reflux under argon atmosphere overnight. Then NaBH_4 (380 mg, 10.0 mmol) was added to the solution in small portions and the mixture was stirred at room temperature for another 12 h. Water (10 mL) was added to quench the remaining NaBH_4 and 2M HCl was added to acidify the amine. The solvent was removed to give a white solid. Then the solid was dispersed into THF and treated with 4.0 equivalent NaOH aqueous solution. The suspension was stirred vigorously for 3 hours, the solution thus turned transparent. After removal of the solvent, the mixture was extracted with DCM for three times. The crude product was purified by column chromatography (silica gel) to give a waxy product (96%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 7.31 (m, 4H), 7.24 (m, 4H), 6.83 (d, 2H), 3.93 (t, 2H), 3.78 (s, 2H), 3.73 (s, 2H), 1.76 (m, 2H), 1.43 (m, 2H), 1.29 (m, 16H), 0.87 (t, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , δ): 158.33, 140.57, 132.39, 129.42, 128.52, 128.29, 127.03, 114.52, 68.17, 53.21, 52.74, 32.07, 29.81, 29.78, 29.75, 29.73, 29.56, 29.50,

29.46, 26.21, 22.84, 14.28. HRMS (m/z), [M+H]⁺ calculated: 382.3104, found: 382.3107.

C12-1H·PF₆: C12-1 (1.53g, 4 mmol) was dissolved in methanol (50 mL) and 2M HCl (3 equivalents) was added to acidify the amine. Then a saturated aqueous solution of NH₄PF₆ (10 equivalents) was added to afford a white precipitate, which was filtered off and washed with deionized water to afford **C12-1H·PF₆** as a white solid (1.90 g, 90%). ¹H NMR (400 MHz, CD₃CN, δ): 7.46 (s, 5H), 7.37-7.39 (d, 2H), 6.95-6.97 (d, 2H), 4.21 (s, 2H), 4.17 (s, 2H), 3.97-4.01 (t, 2H), 1.72-1.95 (m, 2H), 1.28-1.44 (m, 18H), 0.87-0.90 (t, 3H). ¹³C NMR (CD₃CN, δ): 161.25, 132.87, 131.44, 131.15, 130.76, 130.08, 122.93, 115.80, 69.01, 52.19, 52.10, 32.65, 30.37, 30.35, 30.31, 30.29, 30.07, 30.06, 29.87, 26.68, 23.40, 14.40. HRMS (m/z), [M-PF₆]⁺ calculated: 382.3104, found: 382.3106.

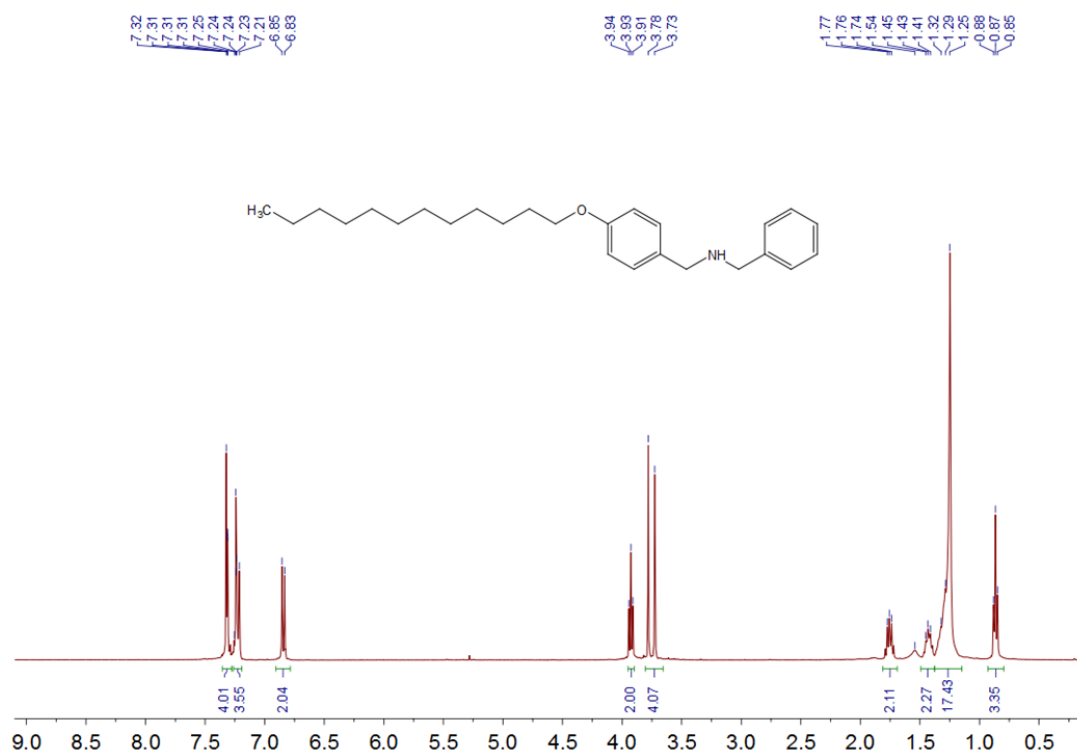


Fig. S8 ¹H NMR Spectrum of C12-1

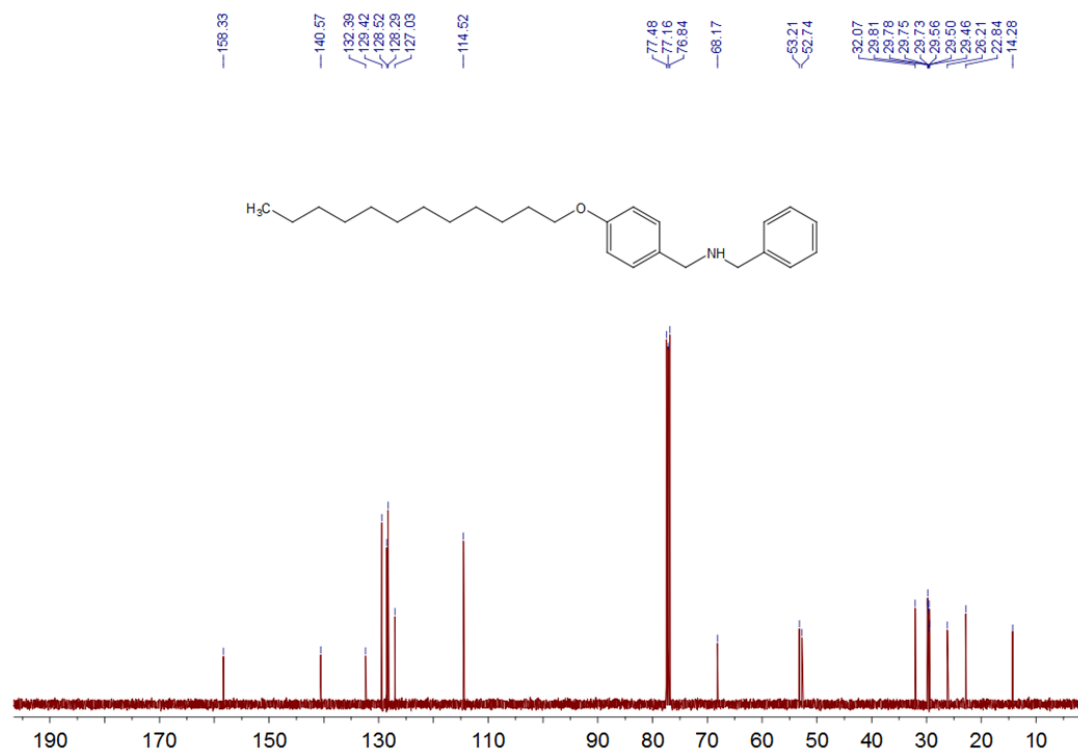


Fig. S9 ¹³C NMR Spectrum of C12-1

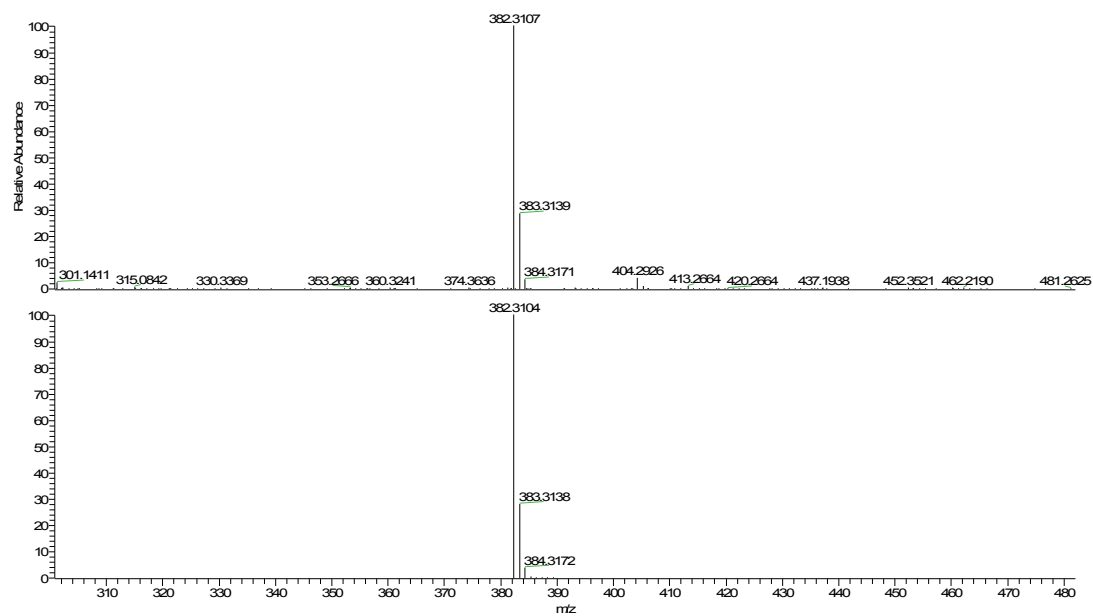


Fig. S10 High-resolution mass spectrum of C12-1

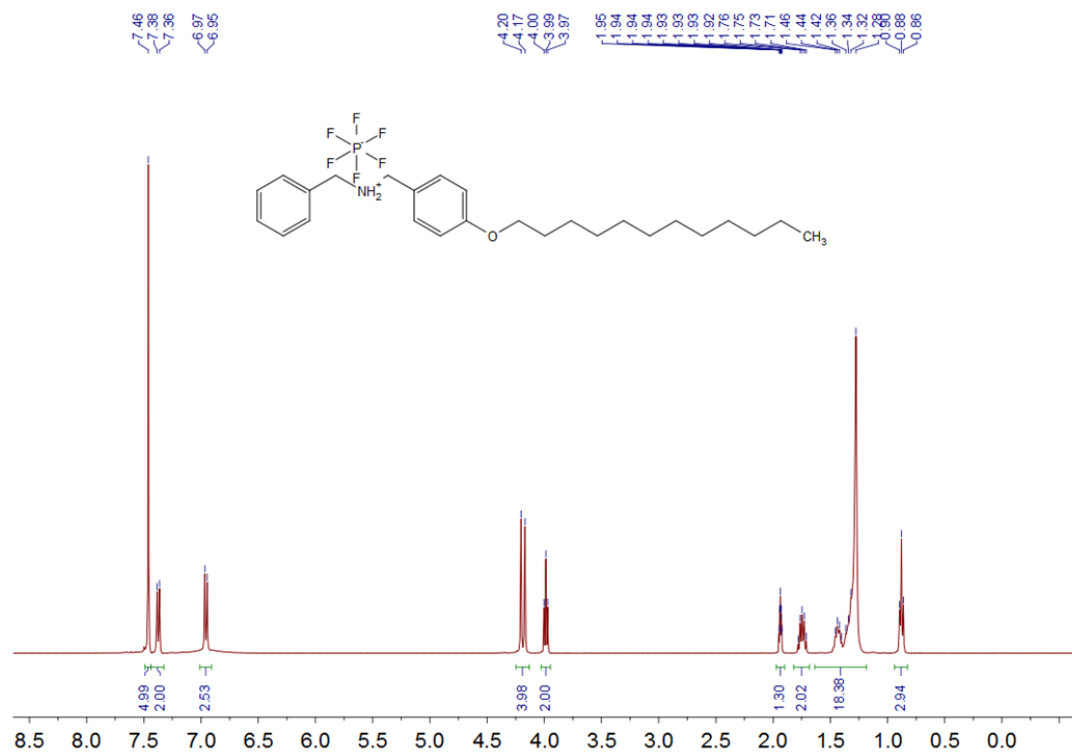


Fig. S11 ¹H NMR Spectrum of C12-1H·PF₆

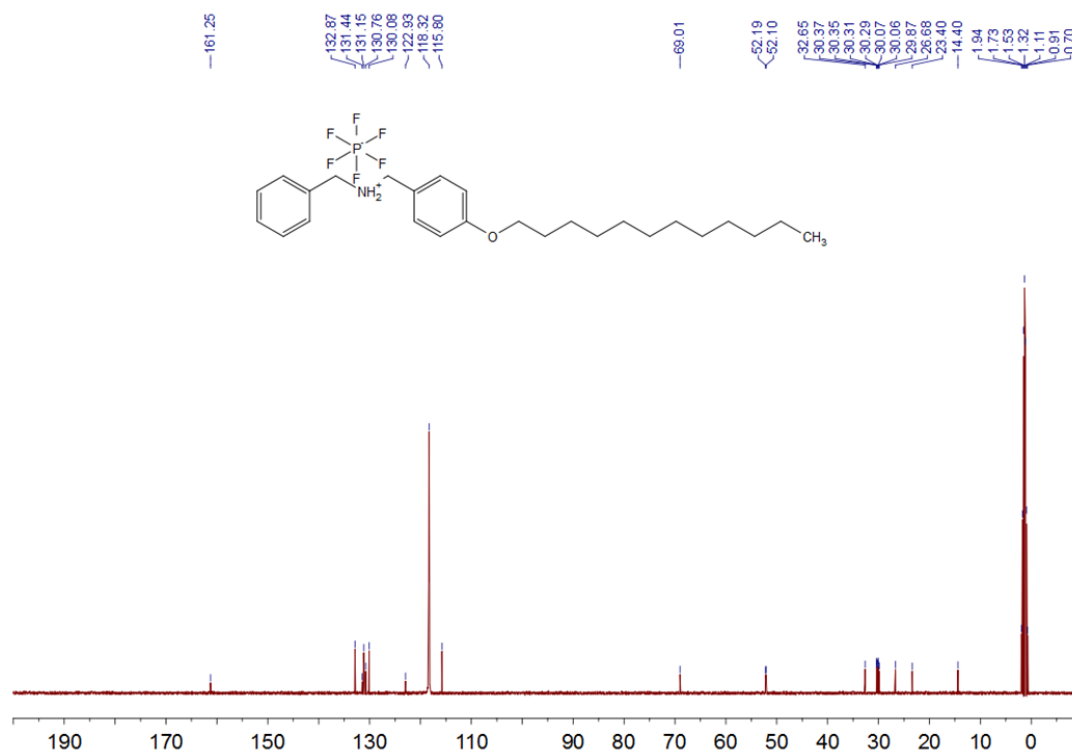


Fig. S12 ¹³C NMR Spectrum of C12-1H·PF₆

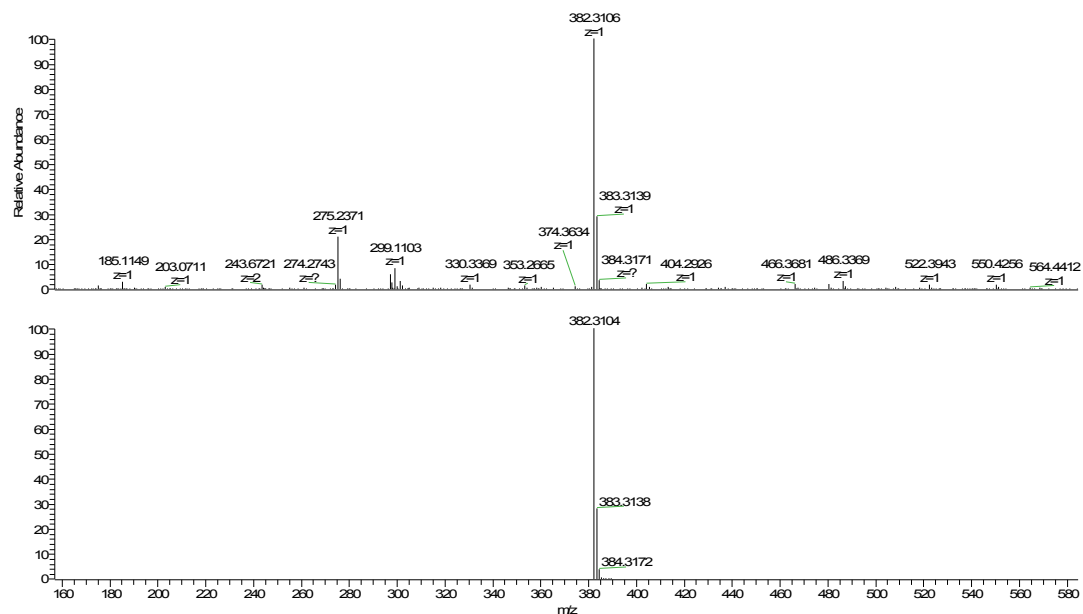
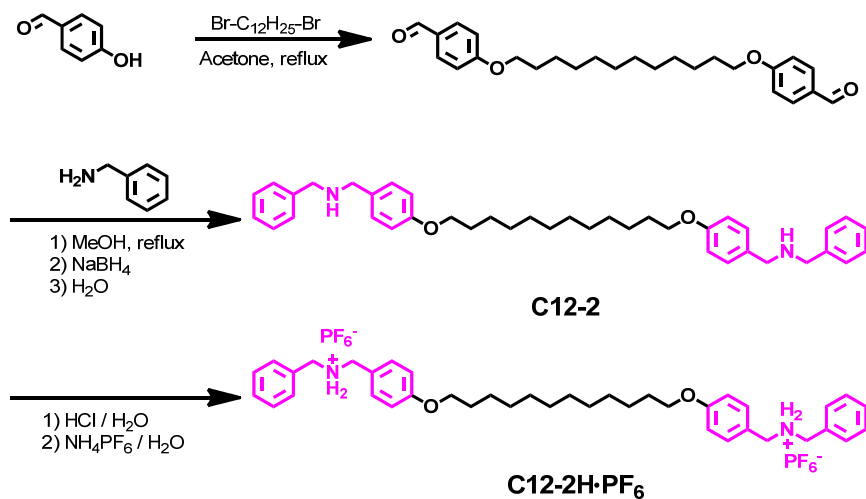


Fig. S13 High-resolution mass spectrum of C12-1H·PF₆

Syntheses of C12-2 and C12-2H·PF₆



Scheme S5 Syntheses of C12-2 and C12-2H·PF₆

4,4'-(dodecane-1,12-diylbis(oxy))dibenzaldehyde: To a mixture of 4-hydroxybenzaldehyde (20 mmol, 2.44 g) and KCO₃ (60 mmol, 8.28 g) in acetone (160 mL) was added 1,12-dibromododecane (10 mmol, 3.28 g) and the reaction mixture was stirred at reflux for 24 h. The mixture was cooled to room temperature, filtered off and washed intensively with CHCl₃. After removal of the solvents, the

residue was purified by column chromatography (petroleum ether / ethyl acetate, 5:1 v / v) to afford 4,4'-(dodecane-1,12-diylbis(oxy))dibenzaldehyde as a white solid (2.05 g, 50%). ¹H NMR (CDCl₃, 400 MHz, δ): 9.88 (s, 2H), 7.82-7.84 (d, 4H), 6.98-7.00 (d, 4H), 4.02-4.06 (t, 4H), 1.79-1.85 (m, 4H), 1.43-1.47 (m, 4H), 1.30 (m, 12H).

C12-2: 4,4'-(dodecane-1,12-diylbis(oxy))dibenzaldehyde (1.64 g, 4.0 mmol) and phenylmethanamine (860 mg, 8.0 mmol) were dissolved in methanol (50 mL) and heated at reflux under argon atmosphere overnight. Then NaBH₄ (760 mg, 20.0 mmol) was added to the solution in small portions and the mixture was stirred at room temperature for another 12 h. Water (10 mL) was added to quench the remaining NaBH₄. The mixture was filtered off and washed with methanol and deionized water to afford **C12-2** as a white solid (2.12 g, 60%). ¹H NMR (400 MHz, CDCl₃, δ): 7.33 (m, 8H), 7.254 (m, 8H), 6.85 (d, 4H), 3.94 (t, 4H), 3.79 (s, 4H), 3.73 (s, 4H), 1.77 (m, 4H), 1.44 (m, 4H), 1.28 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, δ): 158.33, 140.53, 132.36, 129.43, 128.53, 128.30, 127.04, 114.52, 68.16, 53.21, 52.74, 29.71, 29.54, 29.45, 26.20. HRMS (m/z), [M+H]⁺ calculated: 593.4102, found: 593.4105.

C12-2H·PF₆: C12-2 (500 mg, mmol) was dispersed in methanol (40 mL), and 2M HCl (6 equivalents) was added to acidify the amine. The solvent was removed to give a white solid, which was dissolved in deionized water/methanol (60 mL, 5:1, v/v). A saturated aqueous solution of NH₄PF₆ (20 equivalents) was added to afford a white precipitate, which was filtered off and washed with deionized water to afford **C12-2H·PF₆** as a white solid (2.12 g, 60%). ¹H NMR (400 MHz, CD₃CN, δ): 7.46 (s, 4H), 7.36-7.38 (d, 4H), 6.95-6.97 (d, 4H), 4.20 (s, 4H), 4.16 (s, 4H), 3.97-4.00 (t, 4H), 1.73-1.77 (m, 4H), 1.42-1.44 (s, 4H), 1.27 (s, 12H). ¹³C NMR (CD₃CN, δ): 161.20, 132.83, 131.60, 131.11, 130.07, 123.10, 118.32, 69.01, 52.21, 52.10, 30.32, 30.10, 29.89, 26.70. HRMS (m/z), [M-2PF₆]²⁺ calculated: 297.2087, found: 297.2092.

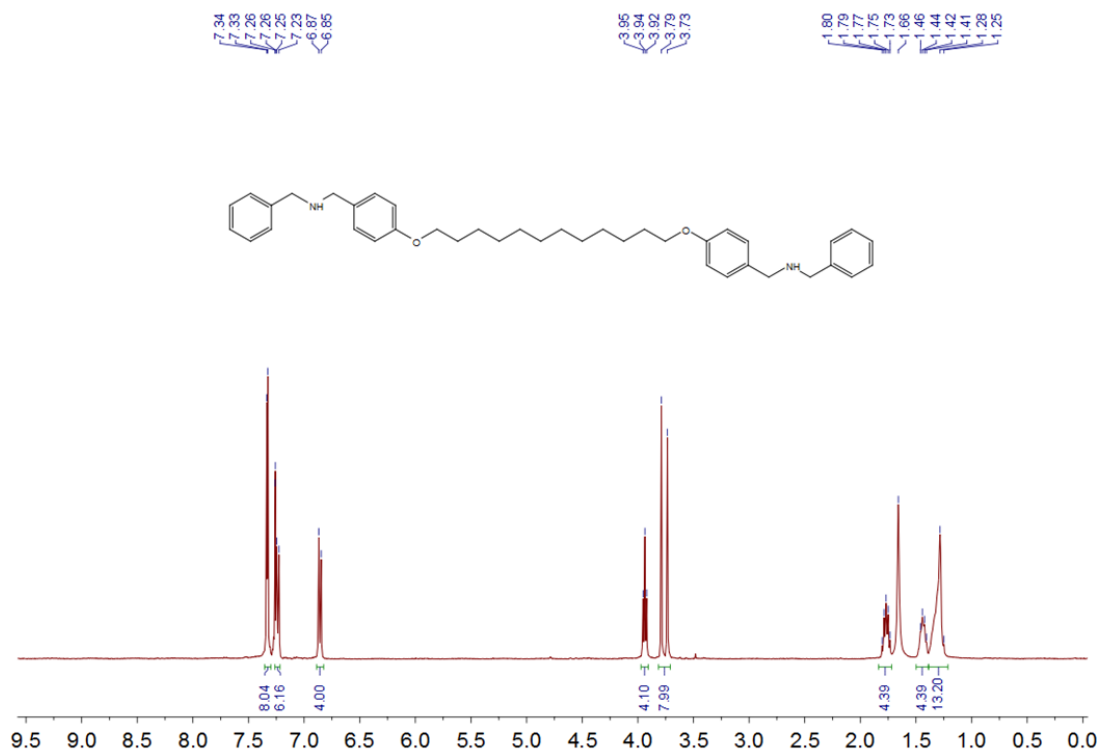


Fig. S14 ¹H NMR Spectrum of C12-2

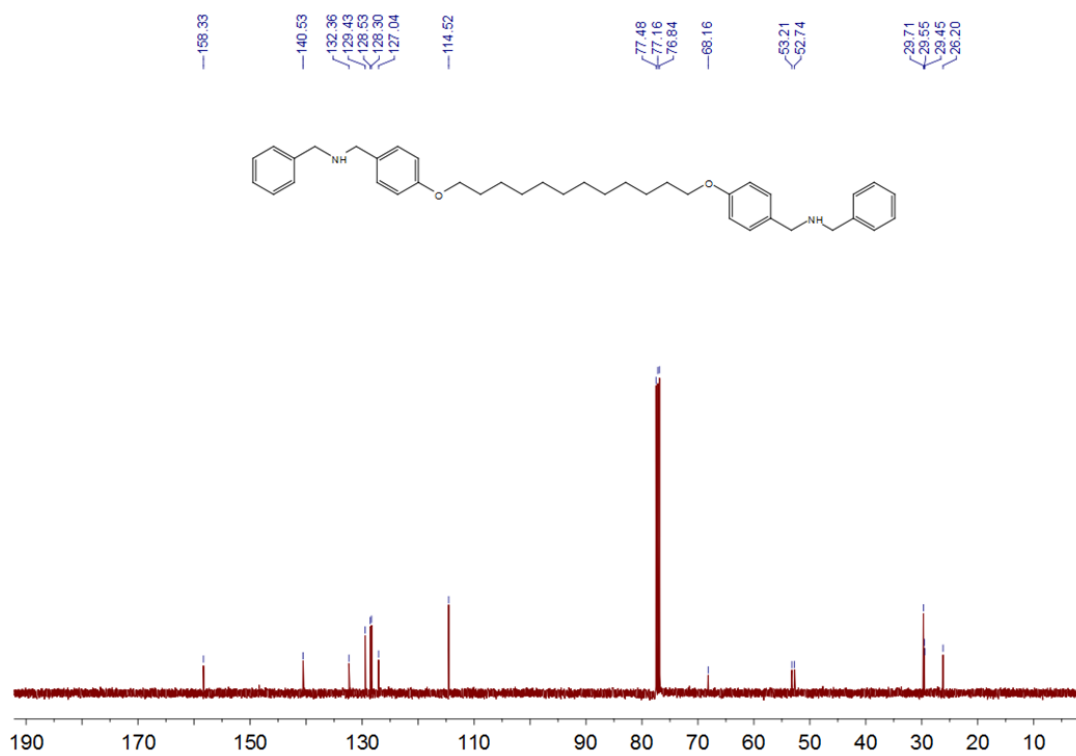


Fig. S15 ¹³C NMR Spectrum of C12-2

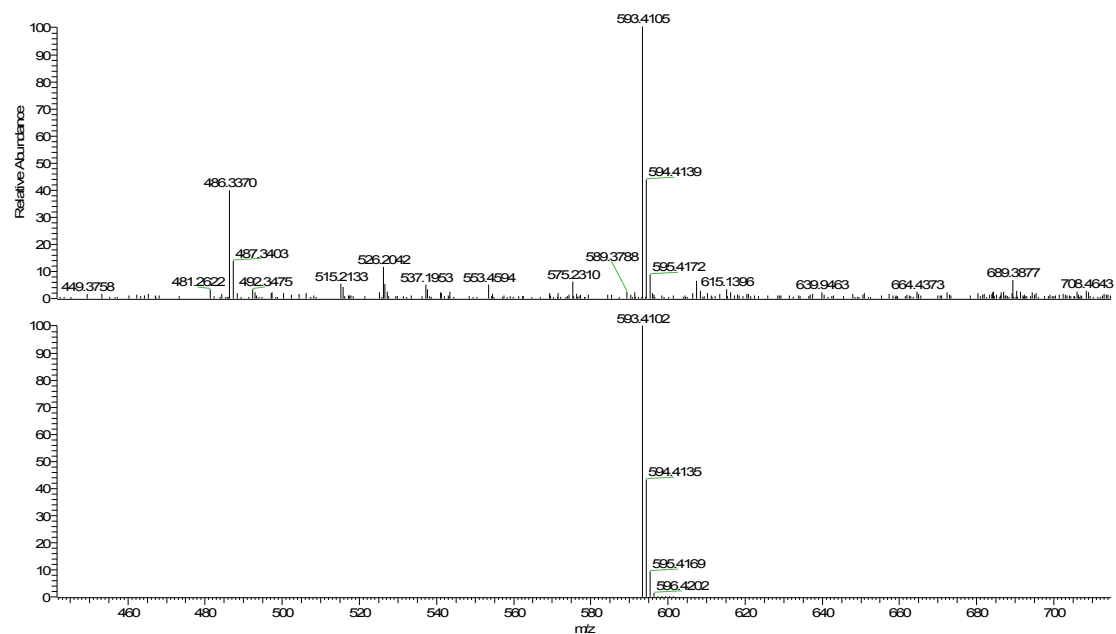


Fig. S16 High-resolution mass spectrum of C12-2

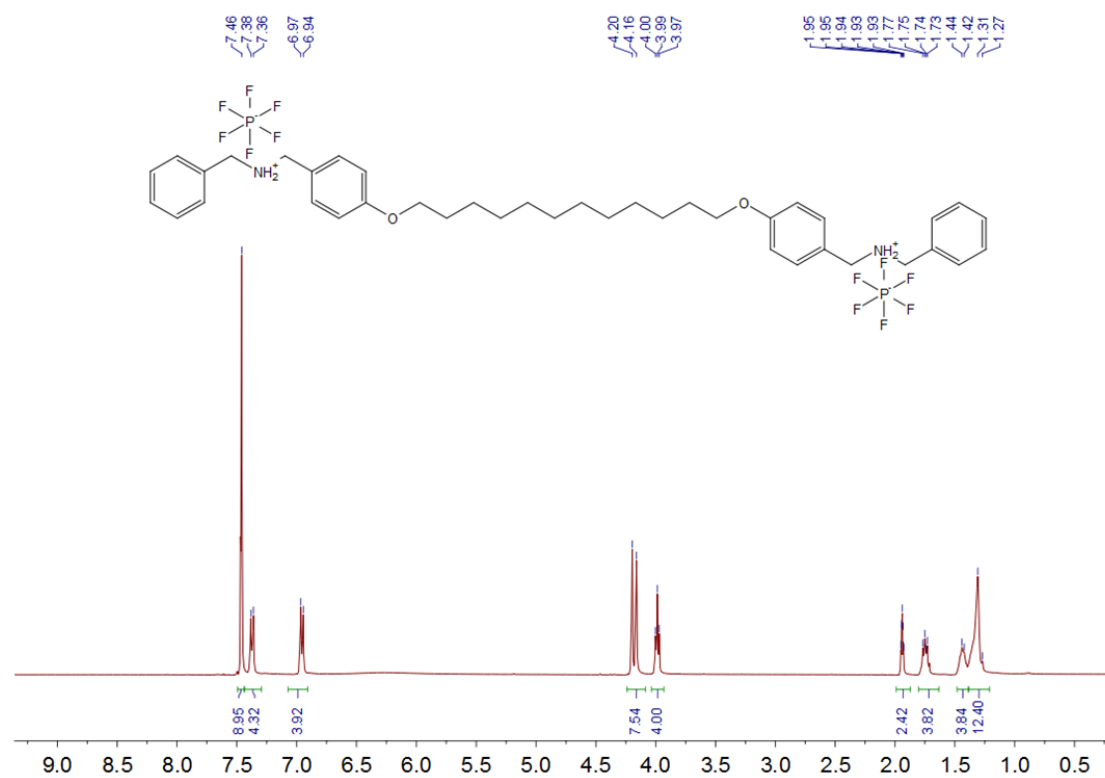
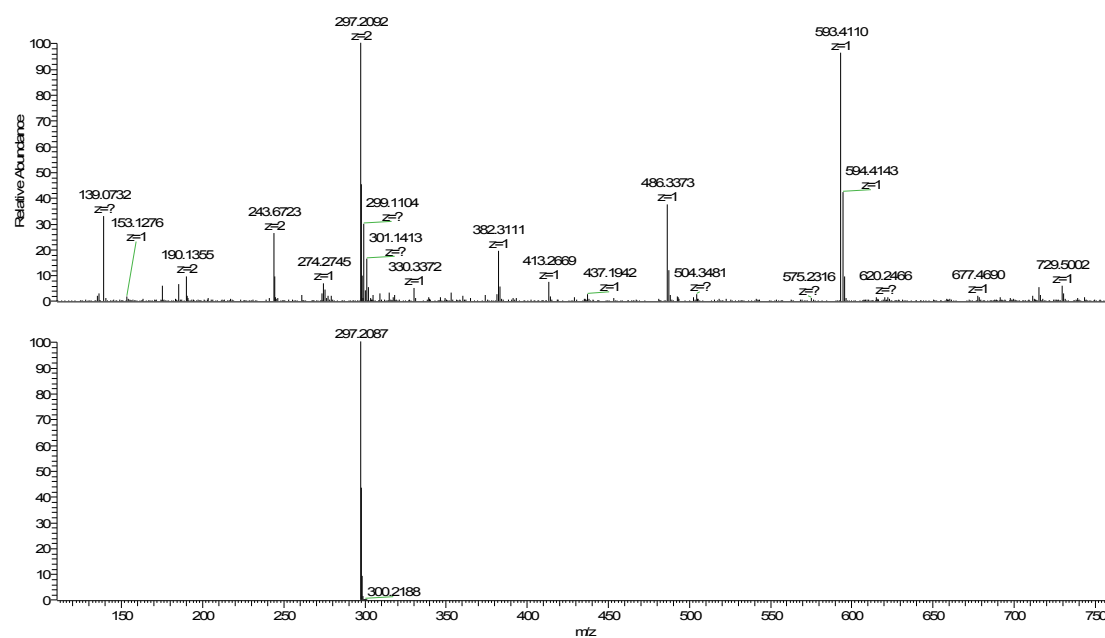


Fig. S17 ¹H NMR Spectrum of C12-2H·PF₆



Additional Experimental Data and Figures

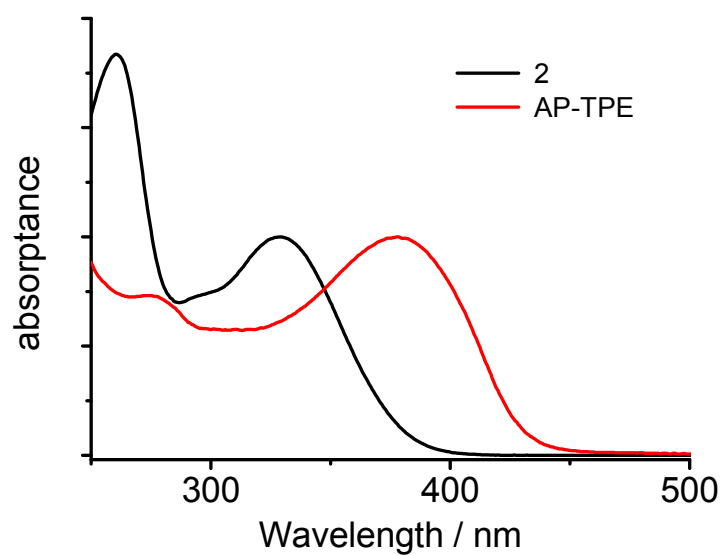


Fig. S20 Uv-vis absorption spectrum of **2** and **AP-TPE** (10 μ M, THF)

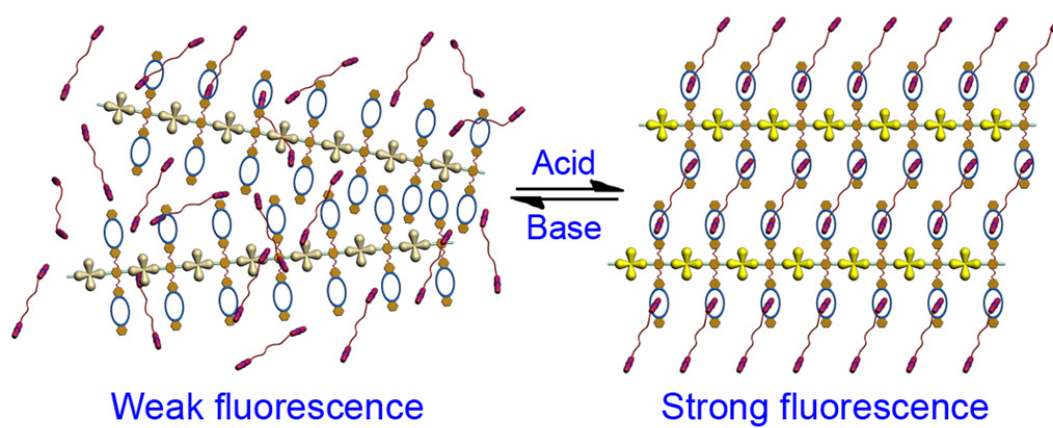


Fig. S21 Cartoon representation of assembly/disassembly of **AP-TPE** and **C12-2H•PF₆** by performing acid/base reactions.

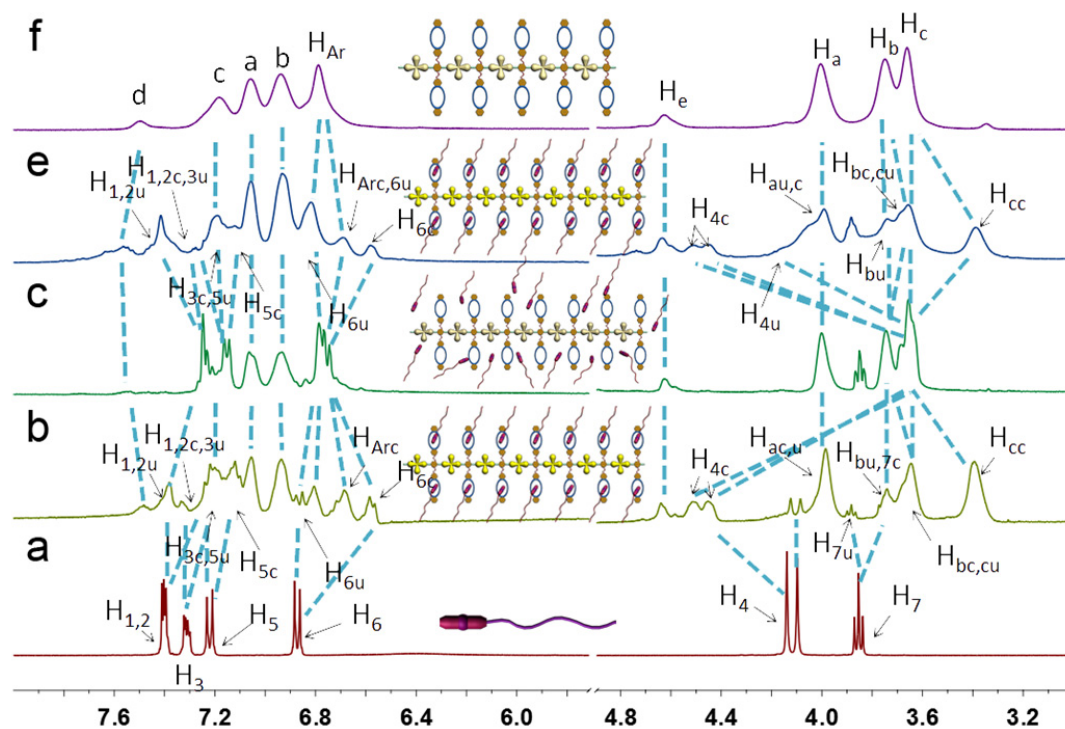


Fig. S22 Partial ^1H NMR spectra (400 MHz, CD_2Cl_2) of (a) C12-1H-PF_6 , (b) 0.5 mM AP-TPE (monomer concentration) and 2.0 equivalents of C12-1H-PF_6 (DBA/DB24C8 1:1 molar ratio), (c) obtained by addition 2.0 equivalents of $\text{P}_1\text{-}t\text{Bu}$ to (b), (d) obtained by addition 2.0 equivalents of CF_3COOH to (c), (e) 0.5 mM AP-TPE . Here “u” and “c” denote uncomplexed and complexed moieties, respectively.

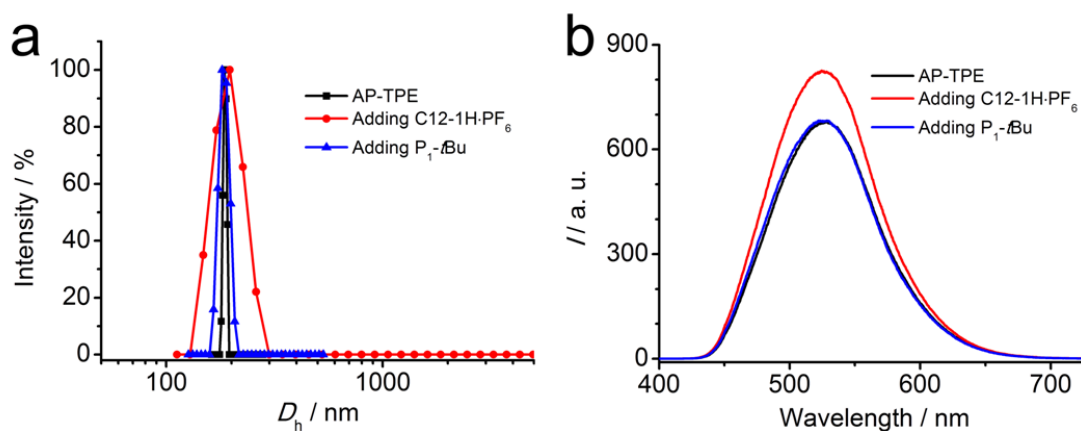


Fig. S23 (a) DLS plot of AP-TPE and (b) Fluorescence responsiveness of AP-TPE upon treatment with C12-1H-PF_6 (CH_2Cl_2 , 0.5 mM).

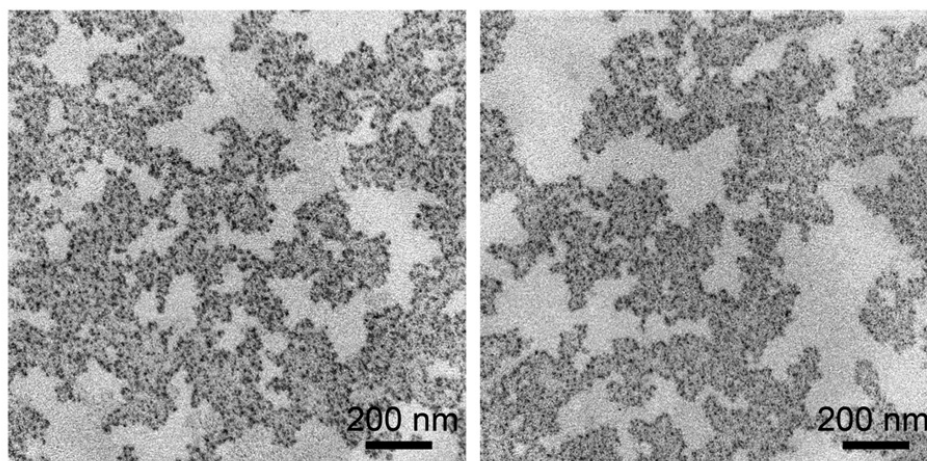


Fig. S24 TEM images of AP-TPE (CH_2Cl_2 , 0.5 mM)

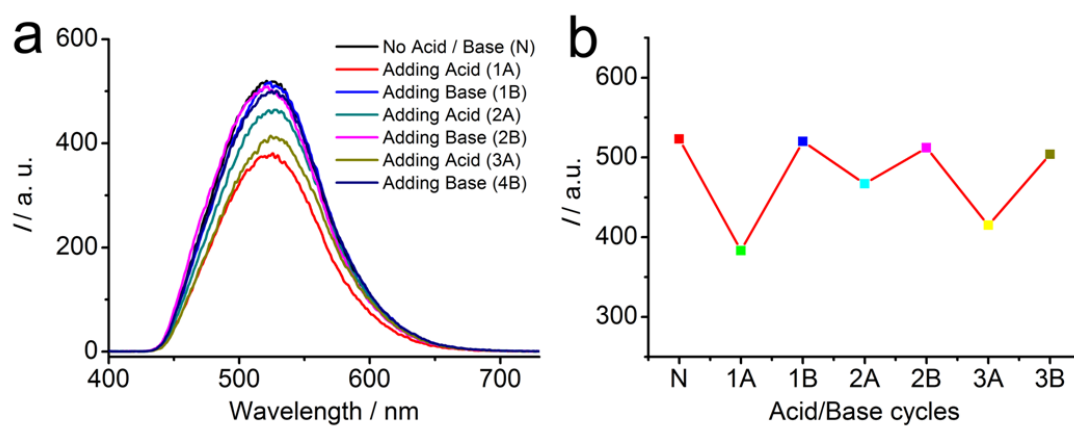


Fig. S25 Fluorescence spectrum of AP-TPE/C12-1 upon treatment with HCl/NaOH repeatedly.



Fig. S26 Photographs of AP-TPE/C12-2 (a) without treatment and (b) upon treatment with HCl.

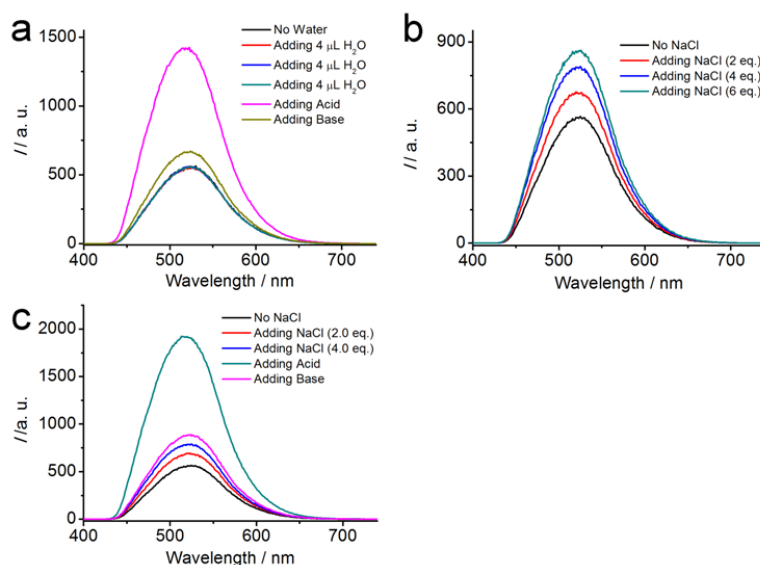


Fig. S27 Fluorescence spectra of AP-TPE/C12-2 in THF treated with water (a), NaCl (b, c).

Discussion:

To explain the emission enhancement better, we had carried out several control experiments.

(a) A trace of water (12 μL) was added into the THF solution of AP-TPE and C12-2 (0.5 mM, 2 mL, the concentration referred to the monomer concentration). As shown in Fig. S27a, the fluorescence didn't show any increase in the intensity. The slight decrease in the concentration of AP-TPE (0.5 mM vs 0.497 mM) have no effect on the emission intensity. Then 2.0 equivalents of HCl was added, the fluorescence intensity increased 2.5 times, which was parallel with that after the first acidification (2.2 times, Fig. 4b). Subsequent addition of 2.0 equivalents of NaOH led to a decreased fluorescence.

(b) 6.0 equivalents of NaCl were gradually added into the THF solution of AP-TPE/C12-2. As shown in Fig. S27b, the fluorescence intensities showed 1.23, 1.41 and 1.54 times increase, respectively. This situation was due to the salting-out effect on AP-TPE leading to the increase in the polymer aggregates. What is more, the experiment had explained successfully why the fluorescence intensity didn't recover to the original level after the acid-base cycles. NaCl generated by the acid-base reactions slightly enhanced the emission of AP-TPE/C12-2.

(c) Furthermore, 2.0 equivalents of HCl were added into the THF solution containing AP-TPE, C12-2 and 4.0 equivalents of NaCl (Fig. S27c). The fluorescence intensity increased nearly 3.5 times, which was almost consistent with that after the third acidification (4.3 times).

These results and discussions revealed that the interaction between DB24C8 and DBA and salting-out effect played a leading role in the enhancement of emission. According to the previous works¹¹, when the TPE moiety took a tighter packing in crystals or highly ordered structures, the intramolecular motion was restricted more completely, thus leading to stronger and blue-shifted emission.

In our system, the blue-shift of the emission peak from 523 to 514 nm had certified more and more compact packing of AP-TPE molecules.

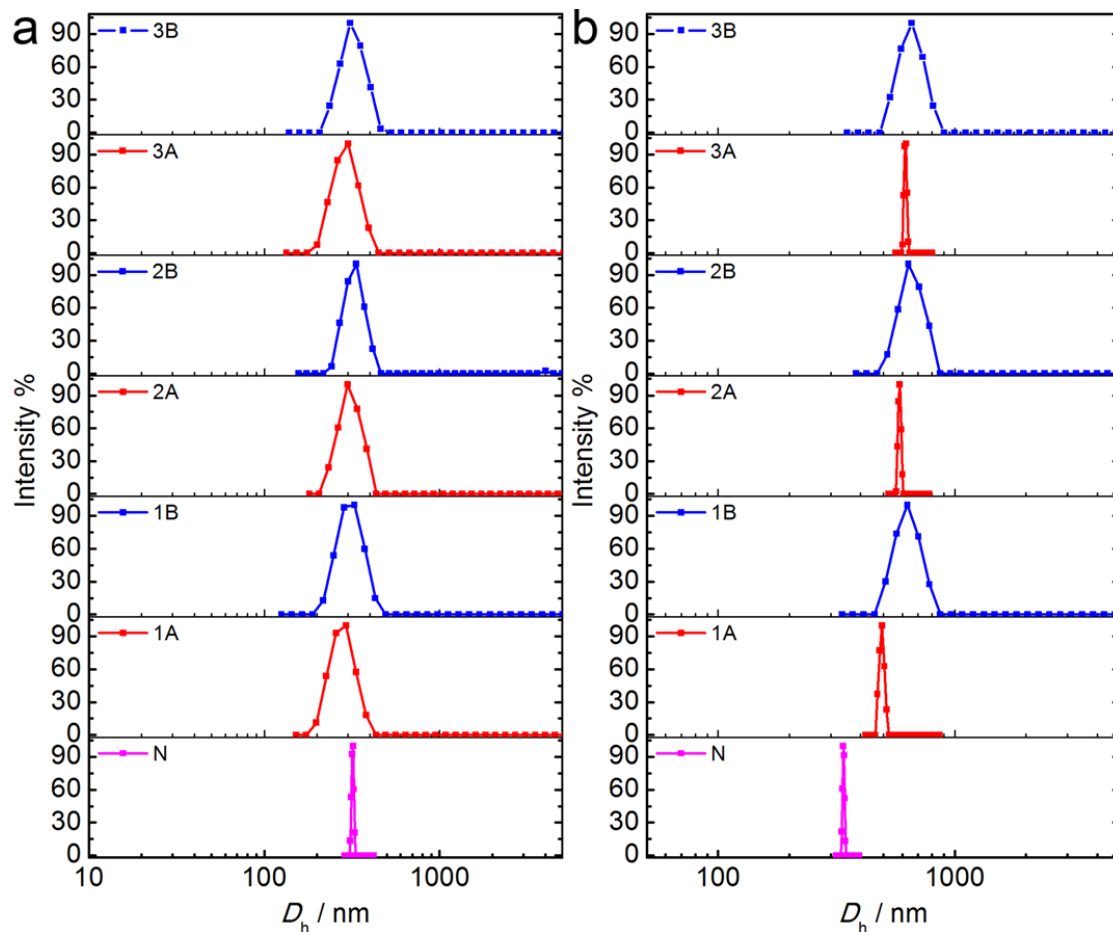


Fig. S28 D_h s of AP-TPE/C12-1 (a) and AP-TPE/C12-2 (b) upon treatment with acid and base repeatedly (0.5 mM, THF)

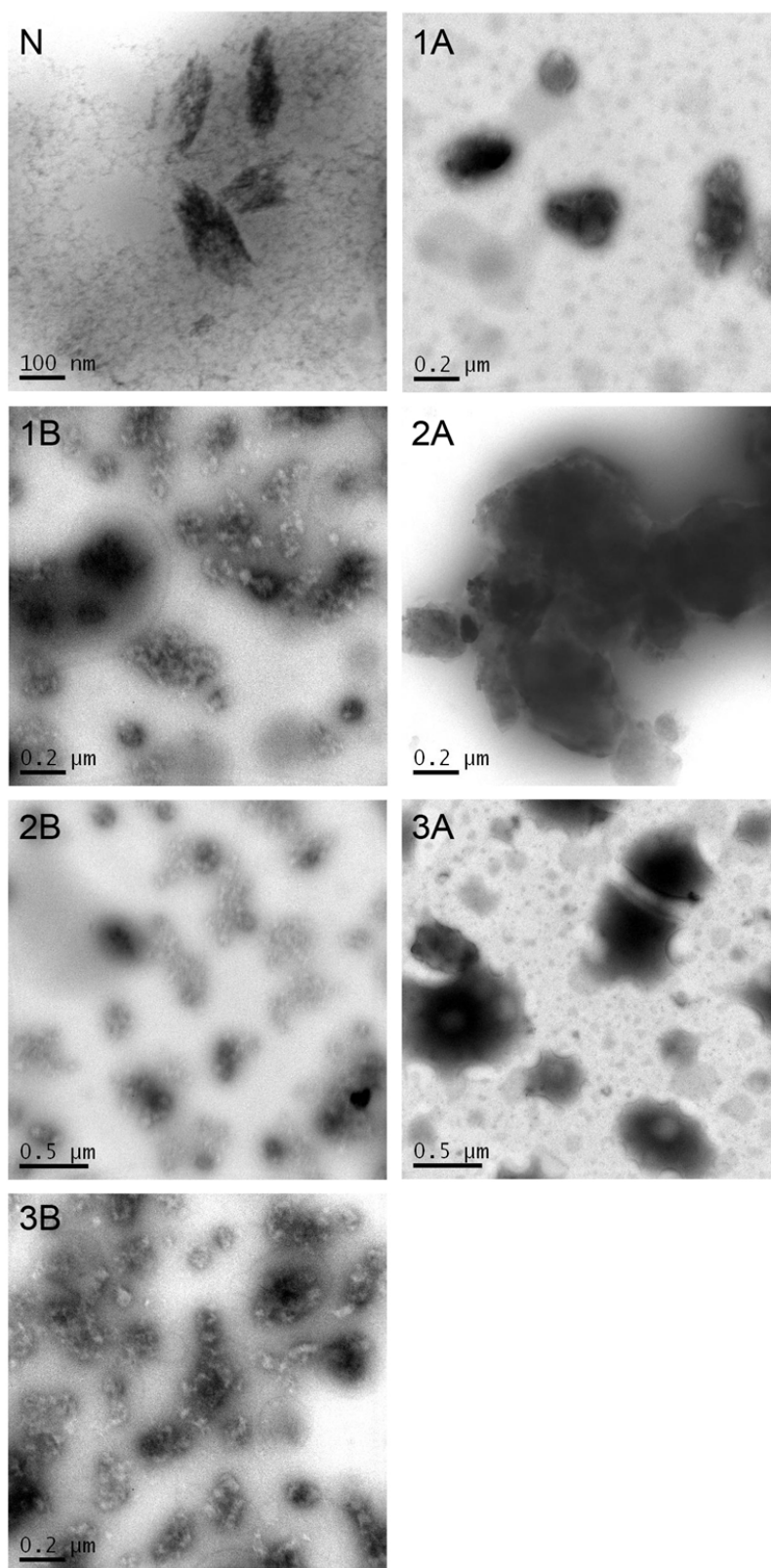


Fig. S29 TEM images of AP-TPE/C12-1 upon treatment with HCl and NaOH (0.5 mM, THF).

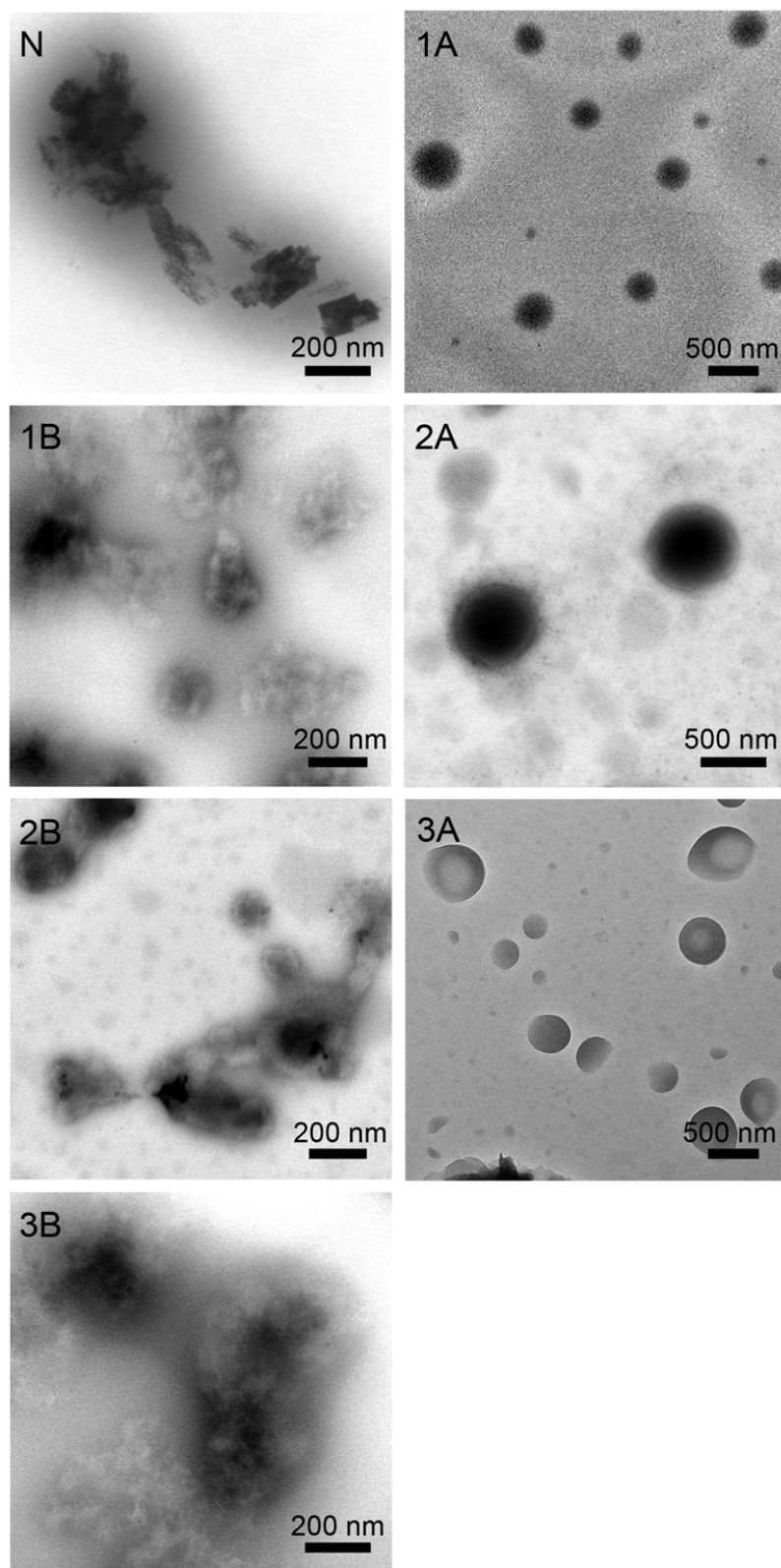


Fig. S30 TEM images of AP-TPE/C12-2 upon treatment with HCl and NaOH (0.5 mM, THF).

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