Supplementary Information

A helical polydiacetylene with enhanced thermochromic reversibility temperature from self-assembly of diacetylene-containing rosettes

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1. Materials and methods

Materials. 10,12-Pentacosadiynoic acid (PCDA) was bought from GFS Chemicals (USA). 4-Nitrobenzaldehyde, Tin (II) chloride dihydrate, 4-Aminobenzaldehyde and propylphosphonic anhydride were bought from Sigma-Aldrich (Korea). Triethylamine was purchased from DAEJUNG (Korea). Barbituric acid was bought from Tokyo Chemical Industry (Korea). All additional chemicals used in this study were of analytical grade quality.

Instruments. Scanning electron microscopy (SEM) analysis was performed with a Hitachi S-4800 FE-SEM. Transmission electron microscopy (TEM) imaging was conducted using a JEOL JEM-2100 microscope. FT-IR spectra were acquired on a Thermo Nicolet iS50 FT-IR equipped with an ATR accessory (Thermo Fisher Scientific, Inc.). XRD spectra were recorded with a miniFlex600 (Rigaku). The UV–vis spectra were measured using a USB2000 miniature fiber-optic spectrometer (Ocean Optics). Raman spectra were obtained with LabRAM HR Evolution Raman spectrometer (Horiba Scientific) equipped with a 785 nm laser source. ^{1}H and ^{13}C NMR spectra were measured on a Varian VNMRS (600 MHz) spectrometer at 298 K using $CDCl_3$ and dimethyl sulfoxide (DMSO)-d_6 as solvents. Melting points were determined using an Auto-DSC Q20 (TA Instruments). The high-resolution electrospray ionization mass spectra (HR-ESI MS) were recorded on a SYNAPT G2 Q-TOF mass spectrometer (U.K.).

Fabrication of Nanohelices Structures. PCDA-ABA (10 mg) was dissolved in 1 mL of tetrahydrofuran by sonication and heating at 50 ^{o}C until a clear solution was obtained, serving as the stock solution. The pre-heated stock solution was allowed to cool to room temperature for 1

min and 12 mL of ethanol was injected into the stock solution, resulting in the self-assembly of **PCDA-ABA** nanohelices as a white precipitate.

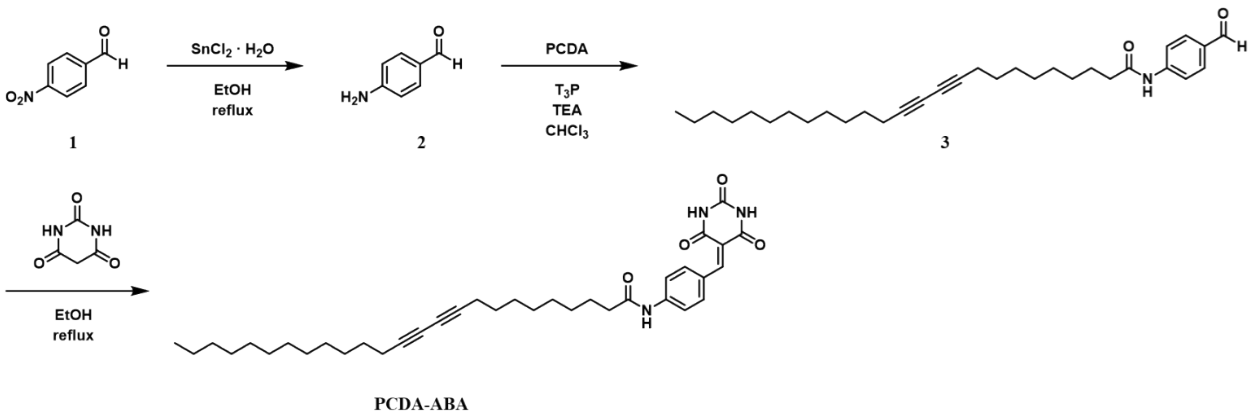
Thermochromic Studies. For investigation of colorimetric thermo-response, **P(PCDA-ABA)** nanohelices were placed on slide glass. The blue-phase **P(PCDA-ABA)** nanohelices were gradually heated on a hot plate at the rate of 10 ^{o}C/min and monitored for thermochromic color transitions.

pH-induced colorimetric response

The blue-phase P(PCDA-ABA) nanohelices (20 mg) were dispersed in ethanol (20 mL) under ambient conditions. The dispersion was aliquoted into 4 mL glass vials, with 1 mL transferred into each vial. Subsequently, 1 mL of buffer solution with pH values ranging from 1 to 13 was added to each vial and mixed gently.

For the reversibility experiment, the sample treated with pH 13 buffer (deprotonated state) was used. After standing to allow the solid to settle, the supernatant ethanol/buffer mixture was carefully removed by decantation. The precipitate was washed by dispersing it in ethanol (1 mL) and deionized water (1 mL). After settling, the supernatant was removed again, and the solid was dispersed in ethanol (1 mL). A pH 1 buffer solution (1 mL) was then added to induce reprotonation. The reversibility of the pH-induced color transition was subsequently monitored.

2. Synthesis of PCDA-ABA



Scheme S1. Synthetic route for the synthesis of **PCDA-ABA.**

Synthesis of PCDA-fPh-amide (3). To a solution of 10,12-pentacosadiynoic acid (4.133 g, 11 mmol) in chloroform (70 mL) was added 4-aminobenzaldehyde (1.123 g, 9.19 mmol), followed by the addition of propylphosphonic anhydride (T_3P, 12 mL, 18.8 mmol) and triethylamine (3.1 mL, 22.1 mmol). The mixture was allowed to stir at ambient temperature overnight. After the reaction completion, the solvent was removed using vacuum evaporation. The crude residue was extracted with ethyl acetate (EA) and $NaHCO_3$ solution. The organic layer was dried over magnesium sulfate, filtered, and concentrated under *vacuo*. The crude product was purified through column chromatography on silica gel (60-120 mesh) using ethyl acetate-hexane mixture (3-10 %) to yield compound **3** as a white solid (3 g, 58.3 %). m.p.: 79-80 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.91 (s, 1H), 7.83 (t, J = 9.4 Hz, 3H), 7.73 (d, J = 8.5 Hz, 2H), 2.40 (t, J = 7.6 Hz, 2H), 2.22 (t, J = 7.0 Hz, 4H), 1.72 (p, J = 7.5 Hz, 2H), 1.48 (dt, J = 14.2, 7.0 Hz, 4H), 1.38 – 1.19 (m, 27H), 0.86 (t, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 191.24, 172.07, 143.86, 132.19, 131.36, 131.22, 119.40, 119.24, 77.83, 77.58, 65.46, 65.34, 38.07, 37.94, 37.81, 32.02, 29.75, 29.73, 29.71, 29.58, 29.45, 29.24, 29.20, 28.97, 28.81, 28.45, 28.34, 25.48, 22.79, 19.39, 19.30, 19.27, 19.18, 14.37, 14.28, 14.19, 1.12; FTIR (ATR) v cm^{-1}: 3287, 2954, 2918, 2847, 1686, 1663, 1603, 1592, 1533, 1465, 1417, 1403, 1392, 1320, 1306, 1252, 1213, 1175, 1162, 1096, 1008; MS(HR-ESI-TOF, m/z): calcd. for $C_{32}H_{47}NO_2$ $[M+Na]^+$ 500.34, found 500.35.

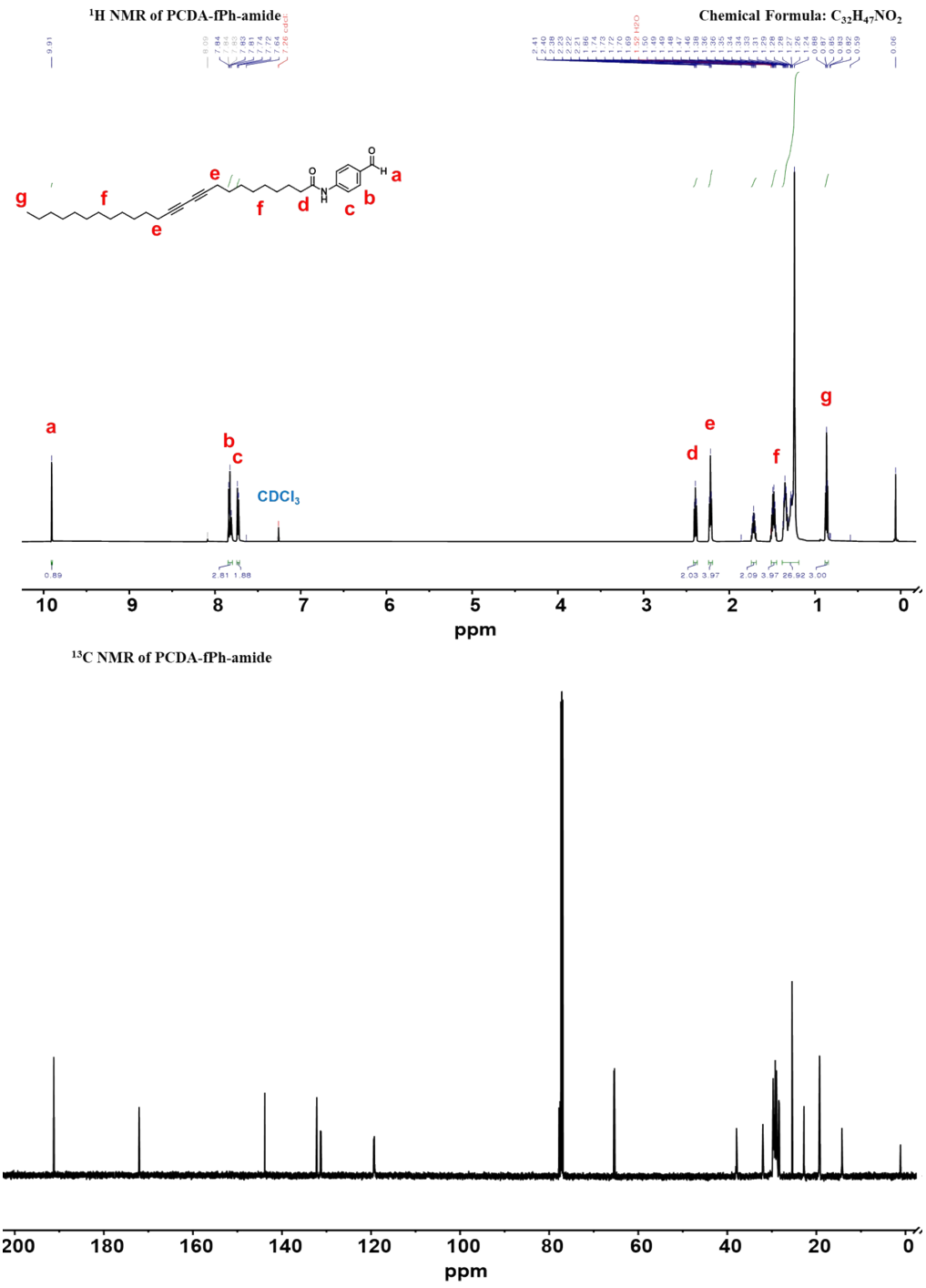


Fig. S1. ^{1}H (top, 600MHz) and ^{13}C (bottom, 151MHz) NMR spectra of **PCDA-fPh-amide** in $CDCl_3$.

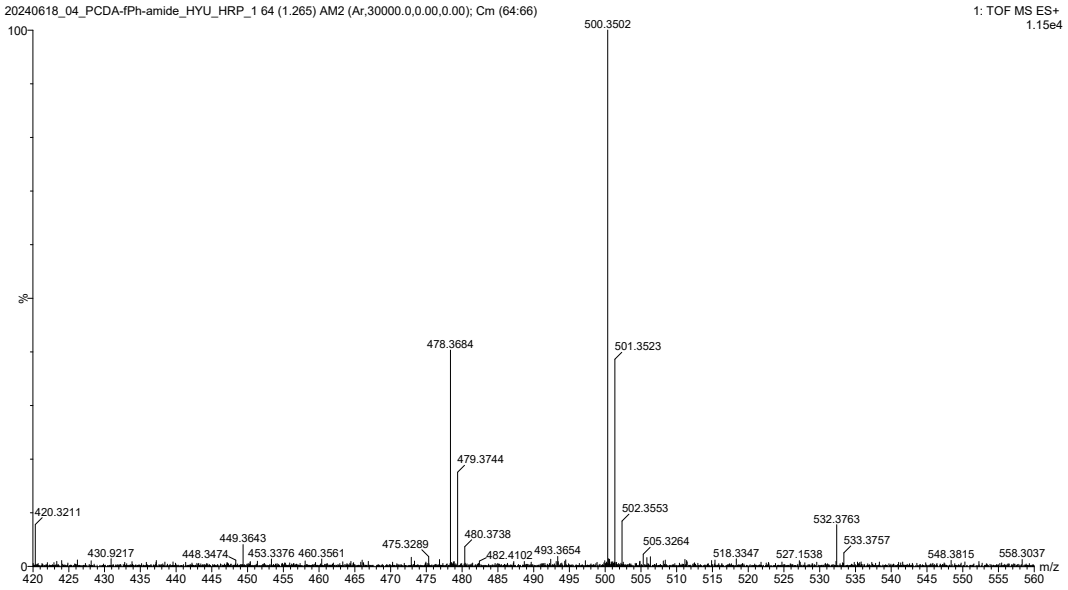


Fig. S2. HR-ESI-TOF spectrum of **PCDA-fPh-amide**. MS(HR-ESI-TOF, m/z): calcd. for $C_{32}H_{47}NO_2$ $[M+Na]^+$ 500.34, found 500.35.

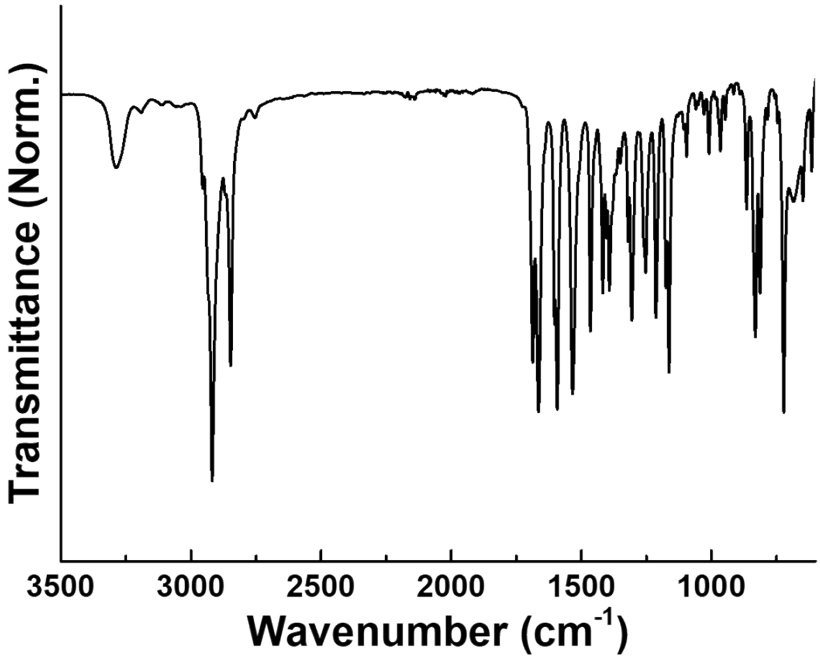


Fig. S3. FT-IR spectrum of **PCDA-fPh-amide**.

Synthesis of PCDA-ABA. A mixture of **PCDA-fPh-amide** (0.4 g, 0.84 mmol) and barbituric acid (0.322 g, 2.51 mmol) in ethanol (15 mL) was refluxed for 12 h under argon. After cooling the reaction mixture to room temperature, the precipitates were filtered and washed multiple times with hot ethanol (70 °C), yielding pure **PCDA-ABA** as a yellow solid (0.227 g, 46.1 %). m.p.:63-65 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ 11.32 (d, J = 2.0 Hz, 1H), 11.19 (d, J = 1.9 Hz, 1H), 10.32 (s, 1H), 8.31 – 8.24 (m, 2H), 8.20 (s, 1H), 7.74 – 7.67 (m, 2H), 2.35 (t, J = 7.5 Hz, 2H), 2.26 (td, J = 6.9, 3.3 Hz, 4H), 1.59 (p, J = 7.2 Hz, 2H), 1.43 (h, J = 7.4 Hz, 4H), 1.36 – 1.16 (m, 25H), 0.84 (t, J = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 172.09, 167.78, 163.82, 162.04, 154.61, 151.68, 150.21, 143.82, 136.19, 126.87, 117.85, 116.20, 77.97, 77.94, 65.35, 36.56, 31.31, 29.03, 28.97, 28.88, 28.73, 28.66, 28.59, 28.40, 28.38, 28.33, 28.25, 28.20, 28.18, 27.75, 27.71, 27.70,

24.89, 22.12, 18.28, 18.27, 13.96; FTIR (ATR) ν cm^{-1}: 3419, 3384, 3221, 3092, 2954, 2918, 2847, 1737, 1703, 1693, 1670, 1584, 1572, 1560, 1513, 1497, 1468, 1448, 1431, 1407, 1395, 1352, 1330, 1303, 1252, 1213, 1190, 1175, 1162, 1122, 1096, 1085, 1075, 1048; MS(HR-ESI-TOF, m/z): calcd. for $C_{36}H_{49}N_3O_4$ $[M+Na]^+$ 610.37, found 610.36.

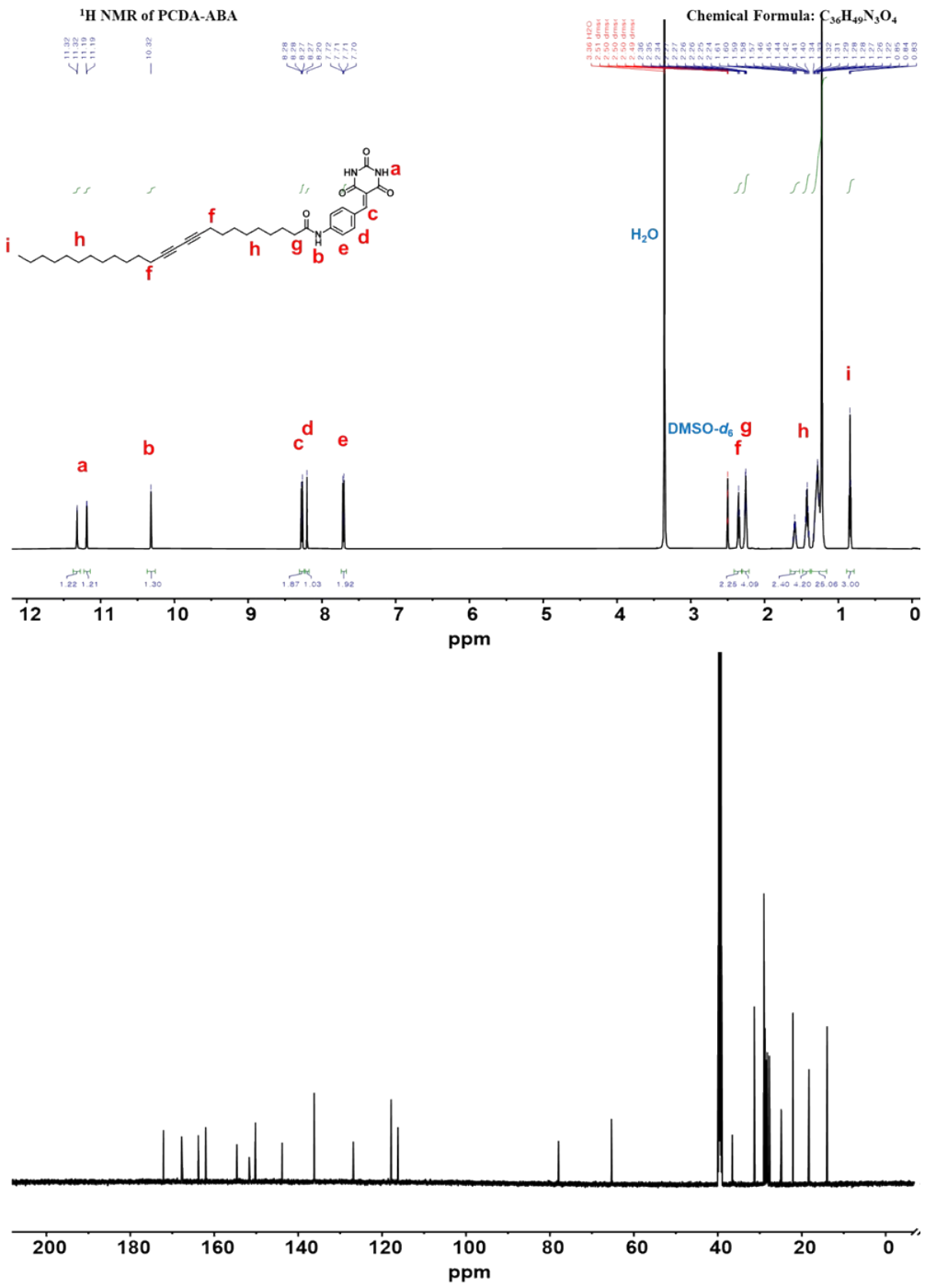


Fig. S4. ^{1}H (top, 600MHz) and ^{13}C (bottom, 151MHz) NMR spectra of **PCDA-ABA** in DMSO-d_6.

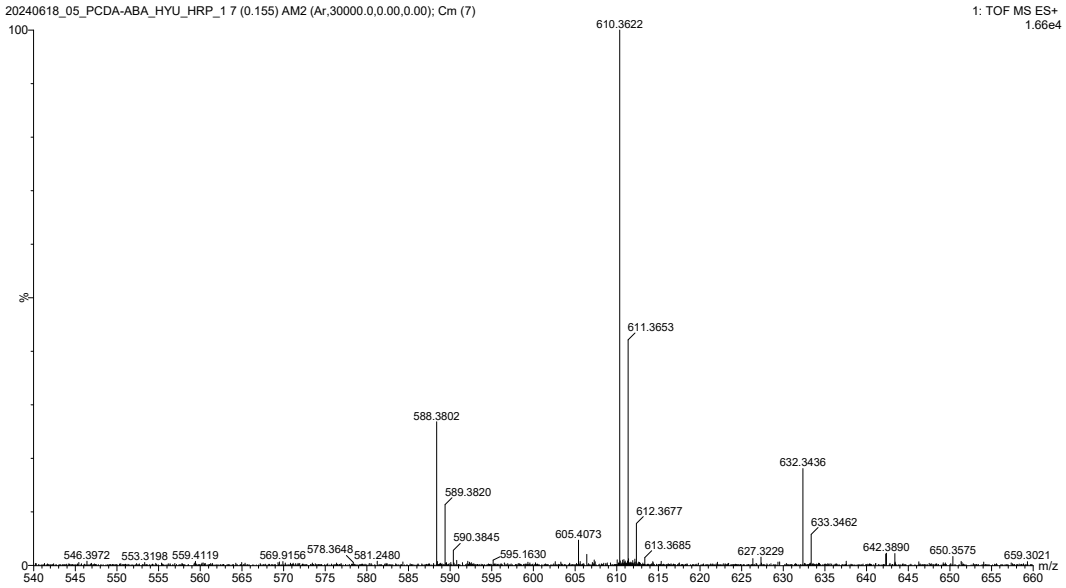


Fig. S5. HR-ESI-TOF spectrum of **PCDA-ABA**. MS(HR-ESI-TOF, m/z): calcd. for $C_{36}H_{49}N_3O_4$ $[M+Na]^+$ 610.37, found 610.36.

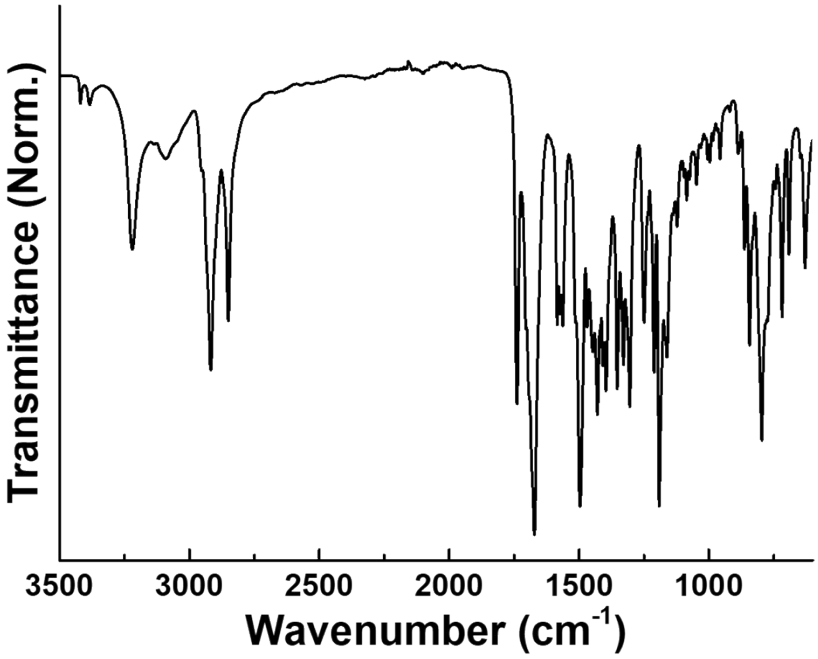


Fig. S6. FT-IR spectrum of **PCDA-ABA**.

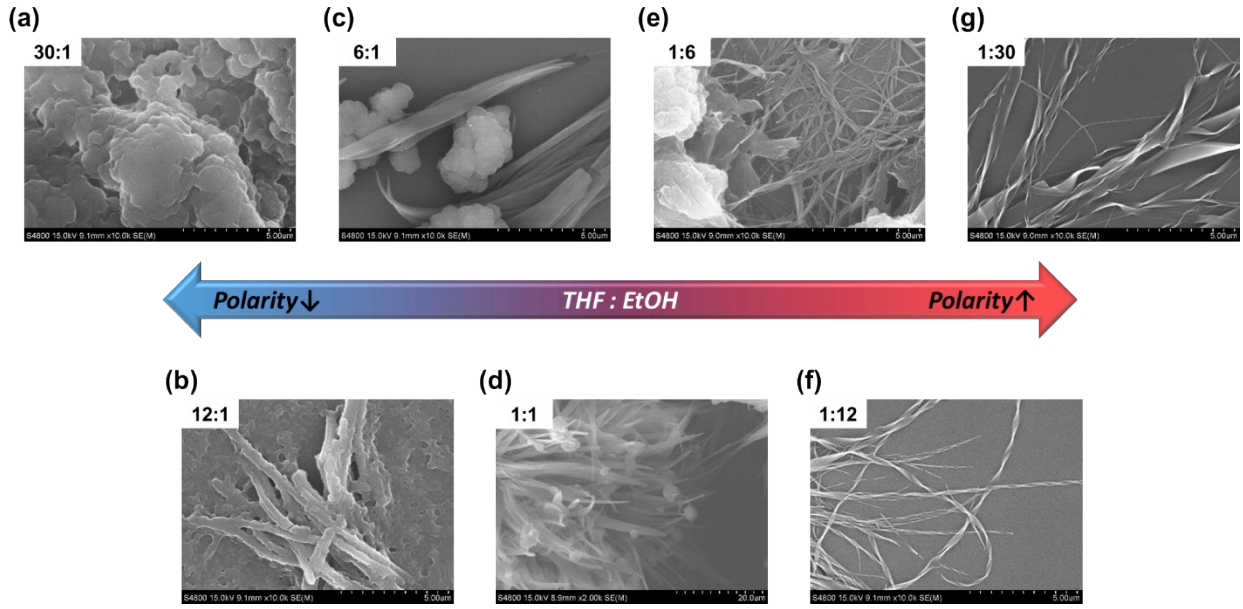


Fig. S7. SEM images of the different morphologies of **PCDA-ABA** at varying THF : ethanol polarity ratio. (a) 30 : 1, (b) 12 : 1, (c) 6 : 1, (d) 1 : 1, (e) 1 : 6, (f) 1 : 12, (g) 1 : 30.

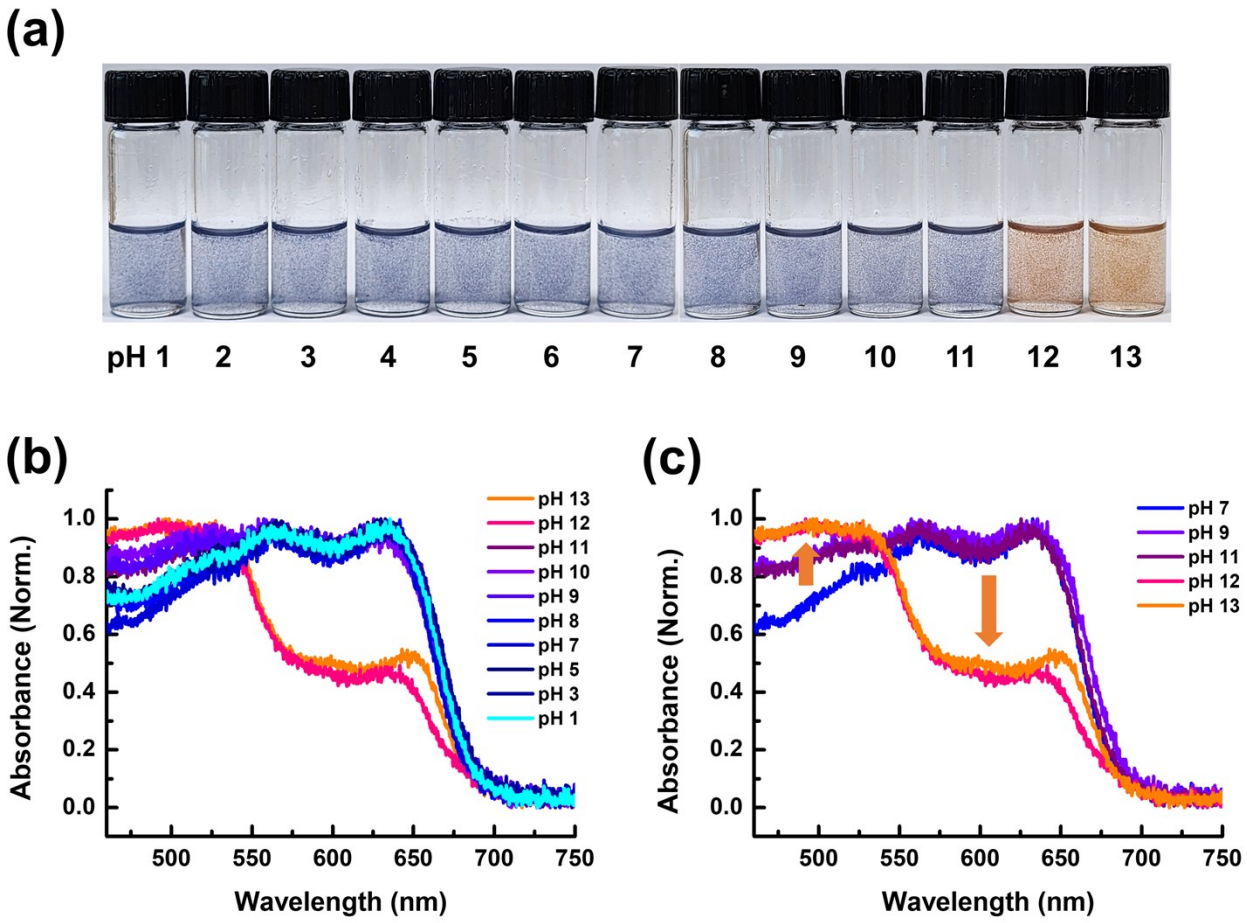


Fig. S8. (a) Colorimetric response of P(PCDA-ABA) over a pH range of 1-14; (b) UV-vis absorption spectra of P(PCDA-ABA) at pH 1, 3, 5, 7, 9, 10, 11, 12, and 13; (c) UV-vis absorption spectra of P(PCDA-ABA) at pH 7, 9, 11, 12, and 13.

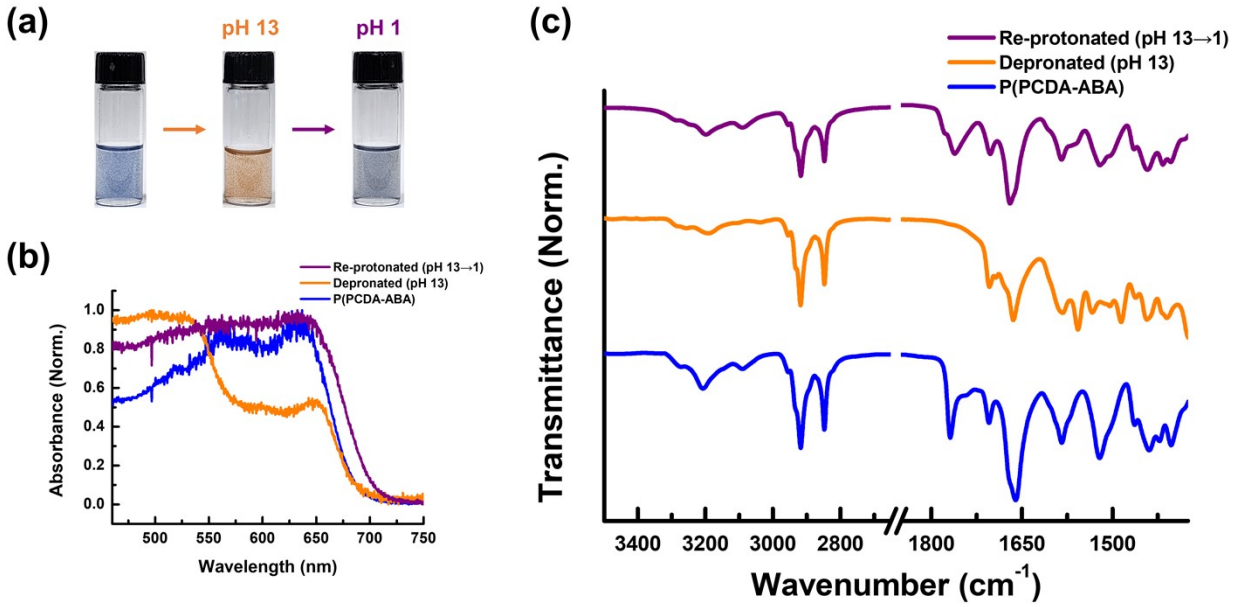


Fig. S9. (a) Reversible colorimetric response of P(PCDA-ABA) upon modulating pH between 1 and 13 via protonation and deprotonation processes; (b) UV–vis absorption spectra; (c) FT-IR spectra.