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Supporting Information

Enantiomeric filtration separation of supramolecular framework membranes

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Contents

S1. Materials

The general chemicals, 1,2-dibromoethane, 1,4-dimethoxybenzene, 4-methoxyphenol, 4-hydroxybenzaldehyde, paraformaldehyde, 5-bromopentanenitrile, boron fluoride ethyl ether [$BF_3{\cdot}O(C_2H_5)_2$], pyrrole, tris(hydroxymethyl)aminoethane, tetrabutylammonium bromide, *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (EEDQ), propargylamine, *L*-ascorbic acid sodium salt, (8*S*,9*R*)-(-)-*N*-benzylcinchonidinium chloride, amberlyst 15 hydrogen form, (*R*)-(+)-1-penylethylamine, (*S*)-(-)-1-penylethylamine, (1*S*,2*S*)-(-)-1,2-diphenyl-1,2-ethanediamine, (1*R*,2*R*)-(+)-1,2-diphenyl-1,2-ethanediamine, (*S*)-(-)-1,1′-binaphthyl-2,2′-diamine, (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine, (*S,S*)-(-)-hydrobenzoin, (*R,R*)-(+)-hydrobenzoin, (*S*)-(-)-1,1'-bi-2-naphthol, (*R*)-(+)-1,1'-bi-2-naphthol, *D*-tyosine, benzenediamine, $NaClO_4{\cdot}H_2O$ are the products of J&K Scientific Ltd. 4-methoxyphenol, K_2CO_3, Na_2SO_4, succinic anhydride, $CuSO_4$, NaN_3 and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. DMSO-d_6, and chloroform-*d* were purchased from Sigma-Aldrich or Cambridge Isotope Laboratories, Inc. (CIL). All the commercially available products were used without further purification. All of the solvents were analytical grade and used as received except that 1, 2-dichloroethane (DCE) was dried with activated molecular sieves (4 Å) for several days and distilled just before use. Doubly distilled water was used throughout the experiments. Silica gel (100-400 mesh) was employed in column chromatography.

S2. Measurements

The UV-vis spectra were recorded on a spectrometer (Varian CARY 50 Probe) with a 1 cm quartz cell. ^{1}H NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer. FT-IR spectra (KBr pellet) were collected on a Bruker Vertex 80 V spectrometer (Germany) equipped with DTGS detector (32 scans) at a resolution of 4 cm^{-1}. Organic elemental analysis was carried out on an Elementar Vario micro cube. MALDI-TOF mass spectra were recorded on a matrix assisted laser desorption ionization (MALDI) time of flight (TOF) mass spectrometer (Bruker AutoflexTM speed TOF/TOF, Germany) equipped with a nitrogen laser (337 nm, 3 ns pulse). The matrix was trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB). The range of mass to charge ratio during datum acquisition was set from 700 to 2000

Da for reflection positive mode. TEM was conducted on a JEOL JEM-2100F under an accelerating voltage of 200 kV. AFM measurement was carried out on a Bruker FastScan atomic force microscope. Circular Dichroism spectra was recorded on a Biologic PMS 450 with a 1 cm quartz cell. The *ee* value was recorded by high performance liquid chromatography (HPLC) analysis using a SHIMADZU LC-20A equipped with a chiral OD-H column (4.6×250 mm) obtained from Daicel Chemical Industries Ltd. X-ray diffraction (XRD) data was recorded on a Rigaku SmartLab 3 (Japan) X-ray diffractometer using Cu Kα1 radiation at wavelength 1.542 Å.

S3. Synthesis of pillar[5]arene modified POMs and P4C

Synthesis of pillar[5]arene grafted POMs. The organic part and pillar[5]arene modified POM were prepared following the routes described in Fig. S1 and Fig. S2.

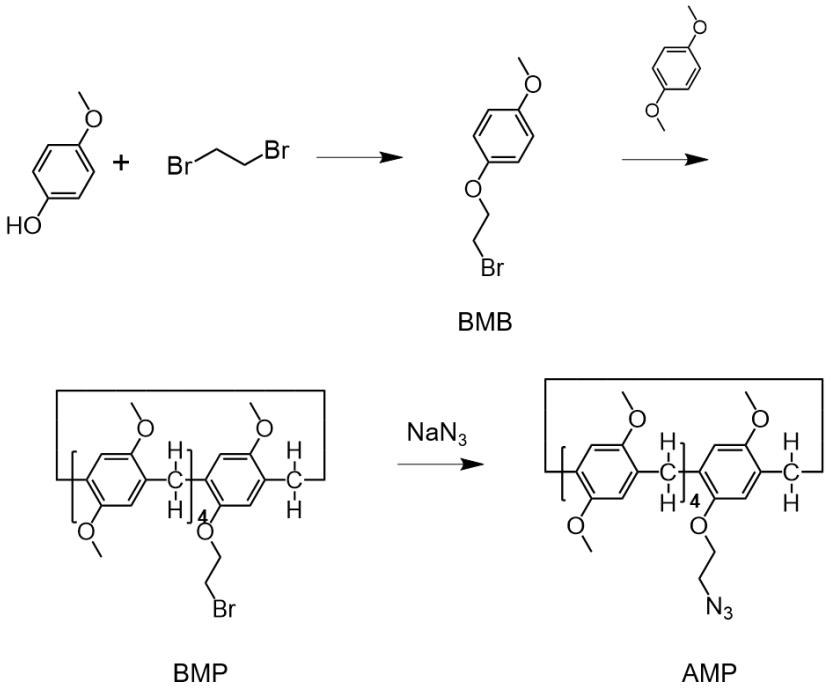
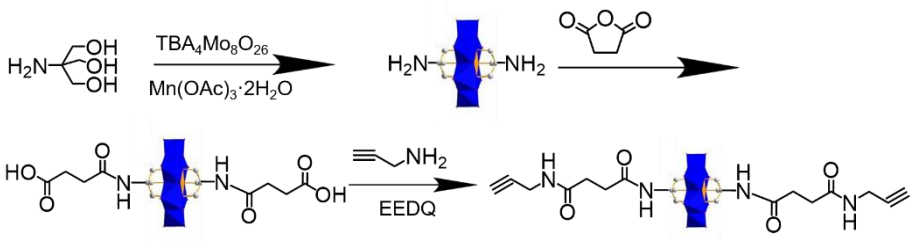


Fig. S1 Synthetic route of pillar[5]arene part that is used to graft on to POMs.



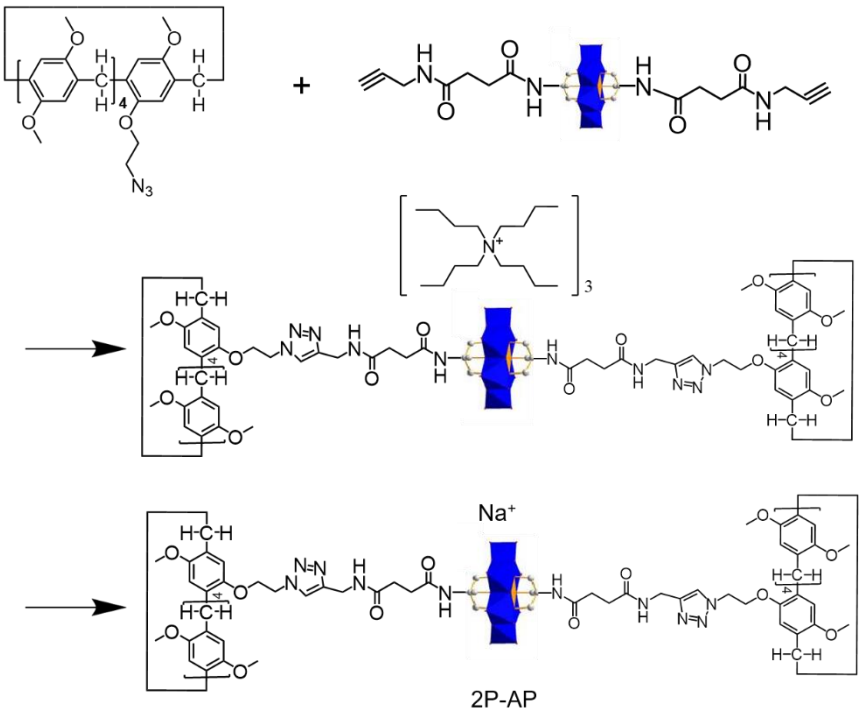


Fig. S2 Synthetic route of pillar[5]arene modified Mn-centered POM 2P-AP.

1-(2'-Bromoethoxyl)-4-methoxybenzene (BMB). To a solution of 1, 2-dibromoethane (11.27 g, 60 mmol) in acetone (300 mL), K_2CO_3 (8.28 g, 60 mmol) and 4-methoxyphenol (1.24 g, 10 mmol) were added. The mixture was refluxed while stirring overnight. After the reaction was completed, the solid residue was removed by filtration and the excess solvent was evaporated under a reduced pressure. Further purification was carried out on column chromatography over silica gel with CH_2Cl_2/*n*-hexane (4:1, in v/v) as eluent to give the product BMB (1.26 g, 5.45 mmol). Yield: 54.5%. ^{1}H NMR (DMSO-d_6, 500 MHz, 298 K) in δ (ppm): 6.92−6.84 (q, J = 9.0 Hz, 4H), 4.27−4.22 (t, J = 5.5 Hz, 2H), 3.79−3.74 (t, J = 5.5 Hz, 2H), 3.71 (s, 3H).

Mono-1-(2'-bromoethoxy) methoxylpillar[5]arene (BMP). To an anhydrous 1, 2-dichloroethane solution (100 mL) of BMB (1.28 g, 5.54 mmol) was added 1, 4-dimethoxybenzene (3.06 g, 22.16 mmol) and paraformaldehyde (0.84 g, 27.7 mmol), and then boron fluoride ethyl ether [$BF_3{\cdot}O(C_2H_5)_2$] (3.46 mL, 27.7 mmol) after bubbled over N_2 atmosphere for 10 minutes. The mixture was stirred under N_2 atmosphere for another 3.5 h at 25 °C. A mixture of water and methanol (200 mL, 1:1 in v/v) was added and stirred for another 2 h. After filtration, the product was extracted with CH_2Cl_2 and the collected organic phase was dried over Na_2SO_4. The excess solvent was evaporated under a reduced pressure. Further

purification was carried out via column chromatography on silica gel with CH_2Cl_2: *n*-hexane (5:1, v/v) as eluent to give the crude product BMP (4.38 g) for the reaction of next step directly. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K) in δ (ppm): 6.89−6.74 (m, 10H), 4.15−4.09 (t, J = 7.0 Hz, 2H), 3.84−3.65 (m, 37H), 3.58−3.50 (t, J = 6.5 Hz, 2H).

Mono-1-(2'-azidethoxy) methoxylpillar[5]arene (AMP). Sodium azide (65 mg, 1.0 mmol) was added to a solution of BMB (599.1 mg, 0.71 mmol) in *N, N*-dimethylformamide (50 mL). The reaction mixture was stirred at 80 °C for 24h. Then the solution was cooled to room temperature and added to CH_2Cl_2 (100 mL). The solution was washed by H_2O (2×50 mL) and NaCl solution (2×50 mL), and dried by Na_2SO_4. The organic layer was removed under a reduced pressure to give product AMP. Yield: 98.6%.^{1}H NMR (DMSO-d_6, 500 MHz, 298 K) in δ (ppm): 6.87−6.75 (m, 10H), 4.06−4.00 (t, J = 4.5 Hz, 2H), 3.80−3.53 (m, 39H).

$[N(C_4H_9)_4]_3MnMo_6O_{18}[(OH)_3(OCH_2)_3CNH_2]_2$ (TBA-NH_2-$MnMo_6$). $[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$[S1] and $Mn(CH_3COO)_3$[S2] were synthesized according the procedures in literatures. A mixture of $[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$ (223.0 mg, 0.104 mmol), $Mn(CH_3COO)_3$ (42.0 mg, 0.18 mmol) and tris(hydroxymethyl)aminoethane (43.6 mg, 0.36 mmol) in 30 mL acetonitrile was heated to reflux for 24 h. The resulted precipitate was removed by filtration. The resulted orange solution was cooled to room temperature, and filtered. Then, it was put in the atmosphere of diethyl ether for several days, generating orange crystals. Yield: 78.4%.^{1}H NMR (500 MHz, DMSO-d_6, 298 K) in δ (ppm): 60.89 (br, 12H), 3.21−3.12 (t, J = 8.0 Hz, 24H), 1.63−1.52 (s, 24H), 1.37−1.27 (m, 24H), 0.98−0.89 (t, J = 7.0 Hz, 36H).

$[N(C_4H_9)_4]_3MnMo_6O_{18}[(OH)_3(OCH_2)_3CNHCOCH_2CH_2COOH]_2$ (TBA-carboxyl-$MnMo_6$). Succinic anhydride (2 g, 20 mmol) and TBA-NH_2-$MnMo_6$ (1.97 g, 1.0 mmol) were dissolved in 50 mL DMF and stirred at 80 °C for 24 h. The mixture was cooled to room temperature and filtered. Then, it was put in the atmosphere of diethyl ether for several days, generating orange crystals. Yield: 95.3%. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K) in δ (ppm): 64.11 (br, 12H), 7.95 (s, 2H), 2.70 (s, 4H), 2.38 (s, 4H), 3.21−3.11 (t, J = 8.5 Hz, 24H), 1.57 (s, 24H), 1.36−1.19 (m, 24H), 1.00−0.78 (t, J = 7.0 Hz, 36H).

$[N(C_4H_9)_4]_3MnMo_6O_{18}[(OH)_3(OCH_2)_3CNHCOCH_2CH_2CONHCH_2CCH]_2$ (TBA-alkynyl-$MnMo_6$). Propargylamine (33 mg, 0.6 mmol), TBA-carboxyl-$MnMo_6$ (416.5 mg, 0.2 mmol) and EEDQ (247.29 mg, 1 mmol) were dissolved in 15 mL acetonitrile and refluxed for 48 h. The mixture was cooled and filtered. Then, it was put in the atmosphere of diethyl ether for several days, Orange crystals were collected. Yield: 57.5%. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K) in δ (ppm): 64.27 (br, 12H), 8.29 (s, 2H), 7.54 (s, 2H), 3.86 (s, 4H), 3.07 (s, 2H), 2.69 (s, 4H), 2.27 (s, 4H), 3.21−3.03 (t, J = 8.5 Hz, 24H), 1.58 (s, 24H), 1.36−1.19 (m, 24H), 1.00−0.78 (t, J = 7.5 Hz, 36H).

$[N(C_4H_9)_4]_3\{MnMo_6O_{18}[(OH)_3(OCH_2)_3CNHCOCH_2CH_2CONHCH_2CCHN_3CH_2CH_2OC_6H_2OCH_3CH_2(C_9H_{10}O_2)_4]_2\}$ (TBA-AMP-$MnMo_6$). TBA-alkynyl-$MnMo_6$ (179 mg, 0.083 mmol), and AMP (1.08 g, 1.34 mmol) were dissolved in 5 mL DMF to get transparent orange solution. Then, $CuSO_4$ (46.25 mg, 0.185 mmol) in 0.5 mL H_2O was added to the above-obtained orange solution, and the mixture turned green. In this solution, NaAsc (69 mg, 0.355 mmol) in 0.5 mL H_2O was added, getting a muddy mixture after 3 days. Proper resin amberlyst 15 hydrogen form was soaked into tetrabutylammonium bromide water solution for 24 h in advance to obtain TBA modified amberlysts. Excessive amberlysts were added to the mixture and the solution turned orange. Most of DMF was removed by reduced pressure distillation. The solid was precipitated with ethyl acetate and centrifugalized to get pure TBA-AMP-$MnMo_6$. Yield: 73.7%. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K) in δ (ppm): 64.02 (br, 12H), 8.38 (s, 2H), 7.95 (s, 2H), 6.88−6.61 (m, 20H), 4.43 (s, 4H), 4.38−4.00 (m, 8H), 3.93−3.49 (m, 74H), 3.17 (s, 24H), 2.65 (s, 2H), 2.38 (s, 2H), 1.58 (s, 24H), 1.41−1.25 (m, 24H), 1.03−0.86 (t, J = 7.0 Hz, 36H).

$Na_3\{MnMo_6O_{18}[(OH)_3(OCH_2)_3CNHCOCH_2CH_2CONHCH_2CCHN_3CH_2CH_2OC_6H_2OCH_3CH_2(C_9H_{10}O_2)_4]_2\}$ (2P-AP). TBA-AMP-$MnMo_6$ (376.8 mg, 0.1 mmol) was dissolved in 10 mL acetonitrile to obtain orange solution, following with the dropwise addition of $NaClO_4 \cdot H_2O$ (840 mg, 6 mmol) in 10 mL acetonitrile. The resulted solution was centrifugalized to get pure 2P-AP. Yield: 97.2%. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K) in δ (ppm): 64.01 (br, 12H), 8.36 (s, 1H), 8.08 (s, 1H), 6.96−6.60 (m, 10H), 4.75 (s, 2H), 4.34−4.19 (d, J = 34.0 Hz, 4H), 3.98−3.43 (m, 37H), 2.71 (s, 2H), 2.29 (s, 2H), as shown in Fig. S3.

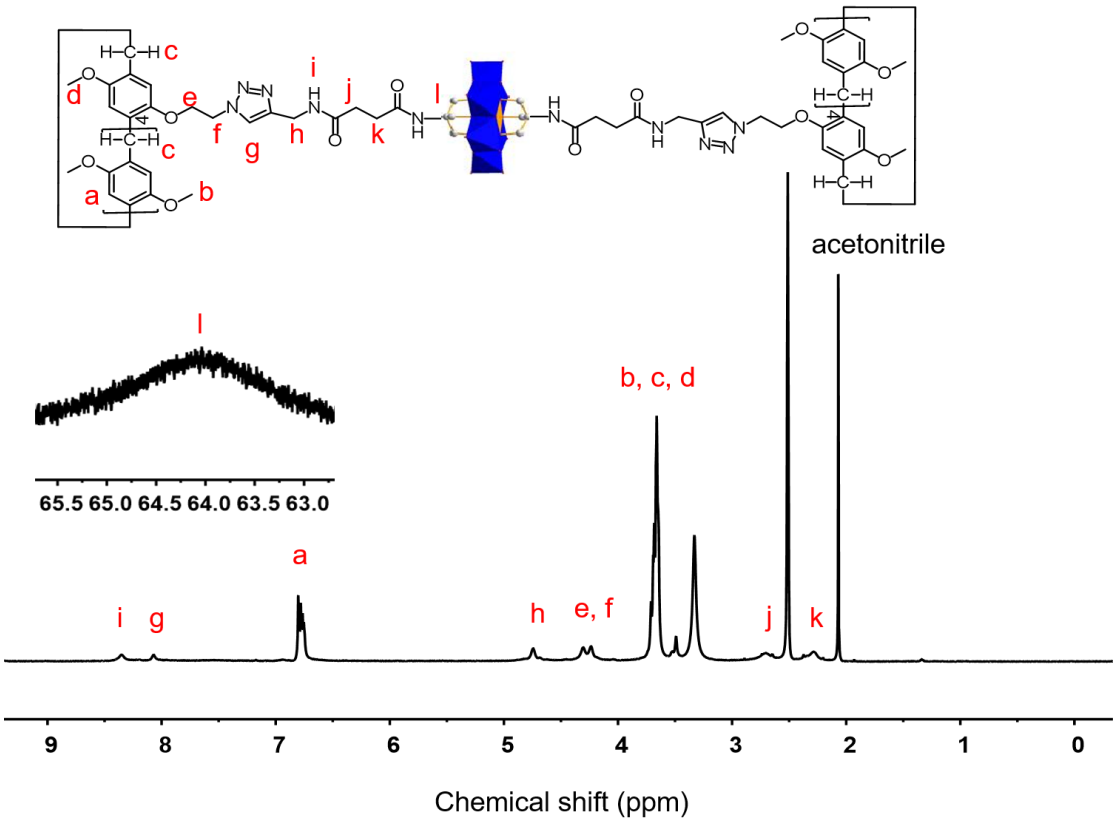


Fig. S3 ^{1}H NMR spectrum (500 MHz, DMSO-d_6, 298 K) of 2P-AP.

$Na(C_{26}H_{29}N_2O)_2\{MnMo_6O_{18}[(OH)_3(OCH_2)_3CNHCOCH_2CH_2CONHCH_2CCHN_3CH_2CH_2OC_6H_2OCH_3CH_2(C_9H_{10}O_2)_4]_2\}$ (2P-AP·BC). 2P-AP (268 mg, 0.086 mmol) was dissolved in 40 mL mixed solvent acetone/water (4:1, v/v), and then *N*-benzylcinchonidinium chloride (108.8 mg, 0.259 mmol) in 15 mL mixed solvent acetone/water (4:1, v/v) was added, generating precipitation slowly. The solution was centrifugalized to get pure 2P-AP·BC. Yield: 67.8%. ^{1}H NMR (500 MHz, DMSO-d_6, 298 K) in δ (ppm): 63.98 (br, 12H), 9.00 (s, 2H), 8.36 (s, 1H), 8.32−8.26 (d, J = 8.0 Hz, 2H), 8.16−8.10 (d, J = 9.0 Hz, 2H), 8.08 (s, 1H), 7.90−7.84 (t, J = 7.5 Hz, 2H), 7.84−7.81 (d, J = 4.0 Hz, 2H), 7.80−7.74 (t, J = 7.5 Hz, 2H), 7.70 (s, 4H), 7.60 (s, 6H), 6.84−6.70 (m, 11H), 6.56 (s, 2H), 5.74−5.64 (m, 2H), 5.18−5.04 (dd, J = 17.0, 27.5 Hz, 4H), 5.00−4.92 (t, J = 9.5 Hz, 3H), 4.74 (s, 2H), 4.38−4.17 (d, J = 34.0 Hz, 6H), 3.94−3.88 (t, J = 10.0 Hz, 2H), 3.77−3.46 (m, 39H), 2.78−2.63 (d, J = 24.5 Hz, 4H), 2.18−2.13 (t, J = 10.5 Hz, 2H), 2.08−1.98 (m, 4H), 1.87−1.78 (t, J = 11.0 Hz, 2H), 1.35−1.26 (t, J = 11.0 Hz, 2H), as shown in Fig. S4.

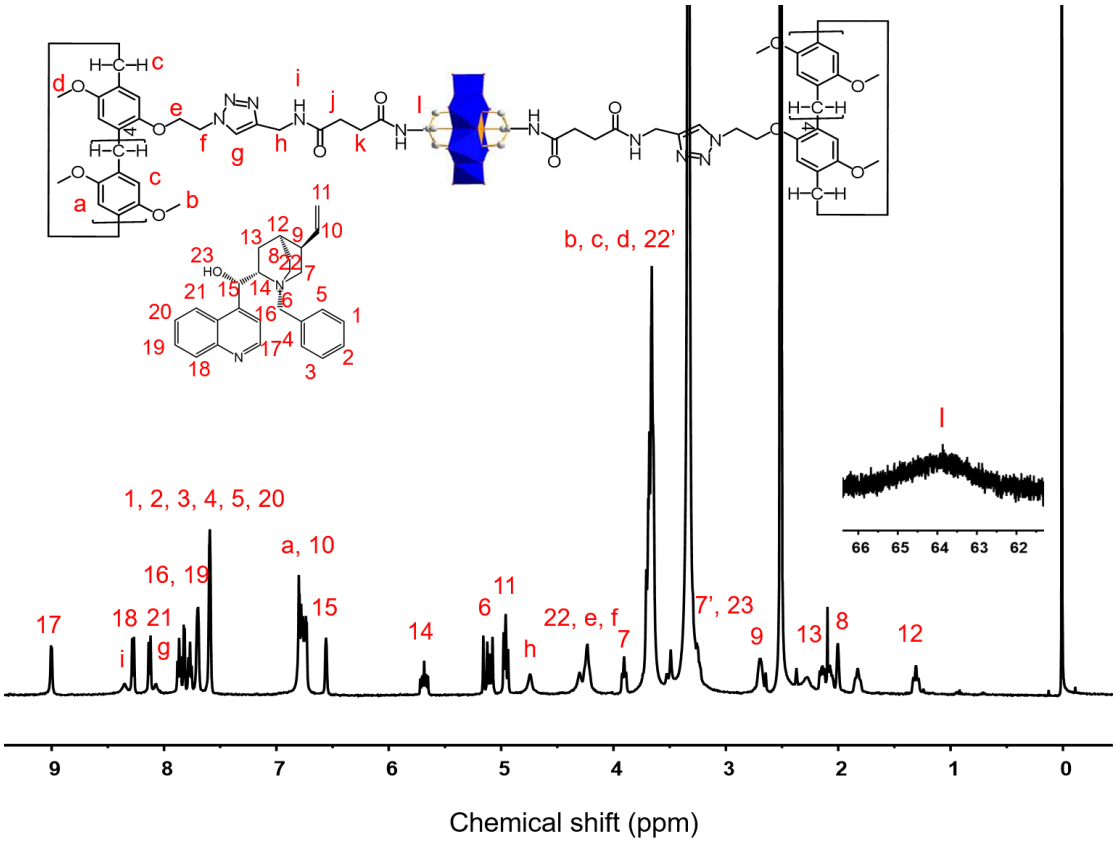


Fig. S4 ^{1}H NMR spectrum (500 MHz, DMSO-d_6, 298 K) of 2P-AP·BC.

Table S1 Elemental analysis result of 2P-AP·BC.

Chemical formula: $Na(C_{26}H_{29}N_2O)_2(C_{114}H_{132}N_{10}O_{48}MnMo_6)\cdot 8H_2O$

2P-AP·BC	C (%)	H (%)	N (%)
Found	49.90	5.08	5.16
Calculated	50.11	5.22	4.93
Error	0.21	0.14	0.23

Synthesis of branched guest (P4C). The preparation route follows Fig. S5.

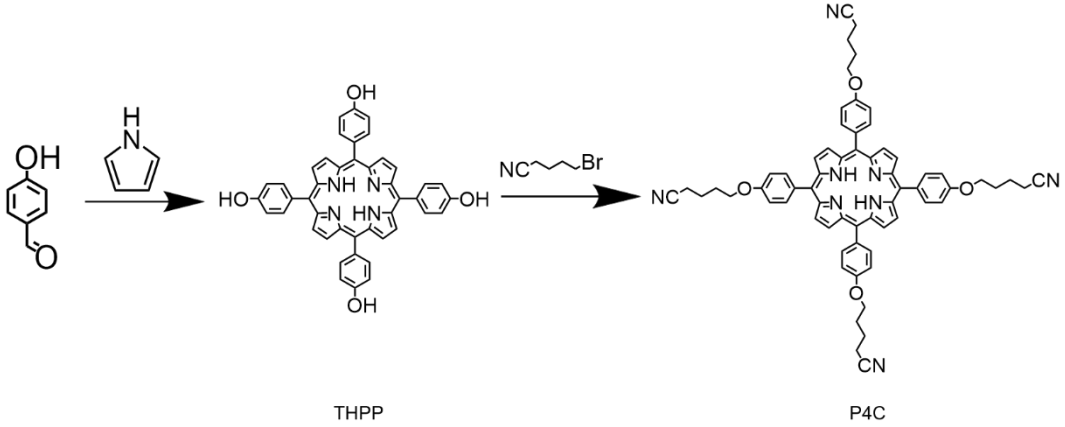


Fig. S5 Synthetic route of P4C.

5, 10, 15, 20-Tetra(4-hydroxyphenyl) porphyrin (THPP). 4-hydroxybenzaldehyde (10.00 g, 81.89 mmol) was dissolved in propionic acid (250 mL) under N_2 atmosphere and the solution was heated to 140 °C, following by dropwise addition of pyrrole (5.50 mL, 81.89 mmol) in propionic acid (50 mL) within 30 minutes through a constant pressure drop funnel under protection of lucifuge treatment. The reaction mixture was stirred vigorously under N_2 for another 1 h and then filtrated after cooling down to room temperature. The residue was collected and washed with DCM for several times until the solution turned colorless. Further purification was carried out by column chromatography of silica gel using CH_2Cl_2: acetone (20:1, v/v) as eluent to give the product THPP (7.01 g, 10.33 mmol). Yield: 49.2%. ^{1}H NMR (DMSO-d_6, 500 MHz, 298 K) in δ (ppm): 9.95 (s, 4H), 8.89 (s, 8H), 8.07−7.94 (d, J = 8.5 Hz, 8H), 7.25−7.18 (d, J = 8.5 Hz, 8H), −2.87 (s, 2H).

5,10,15,20-Tetra[4-(4'-cyano)butoxyphenyl] porphyrin (P4C). THPP (1.00 g, 1.47 mmol), K_2CO_3 (4.88 g, 35.28 mmol) and 4-bromobutyl cyanide (1.91 g, 11.79 mmol) were added into dried acetone (150 mL) and then the mixture solution was heated to reflux overnight. After the reaction cooling down, the solid was filtered off and the filtrate was evaporated under a reduced pressure to remove excess solvent. The residue was purified by column chromatography on a silica gel using CH_2Cl_2:ethyl acetate (50:1, in v/v) as eluent, giving a pure product P4C (0.77 g, 0.77 mmol). Yield: 52.3%. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K) in δ (ppm): 8.88 (s, 8H), 8.22−8.10 (d, J = 8.5 Hz, 8H), 7.30 (s, 8H), 4.42−4.26 (t, J = 5.5 Hz, 8H), 2.67−2.56 (t, J = 7.0 Hz, 8H), 2.23−2.07 (m, 16H), −2.74 (s, 2H), as shown in Fig. S6.

MALDI-TOF (m/z) calculated for C64H58O4N8: 1003.22, found: 1003.32. Elemental analysis calculated for $C_{64}H_{58}O_4N_8$ (1003.22 g/mol): C, 76.62%; H, 5.83%; N, 11.17%, found: C, 76.67%; H, 5.90%; N, 11.14%.

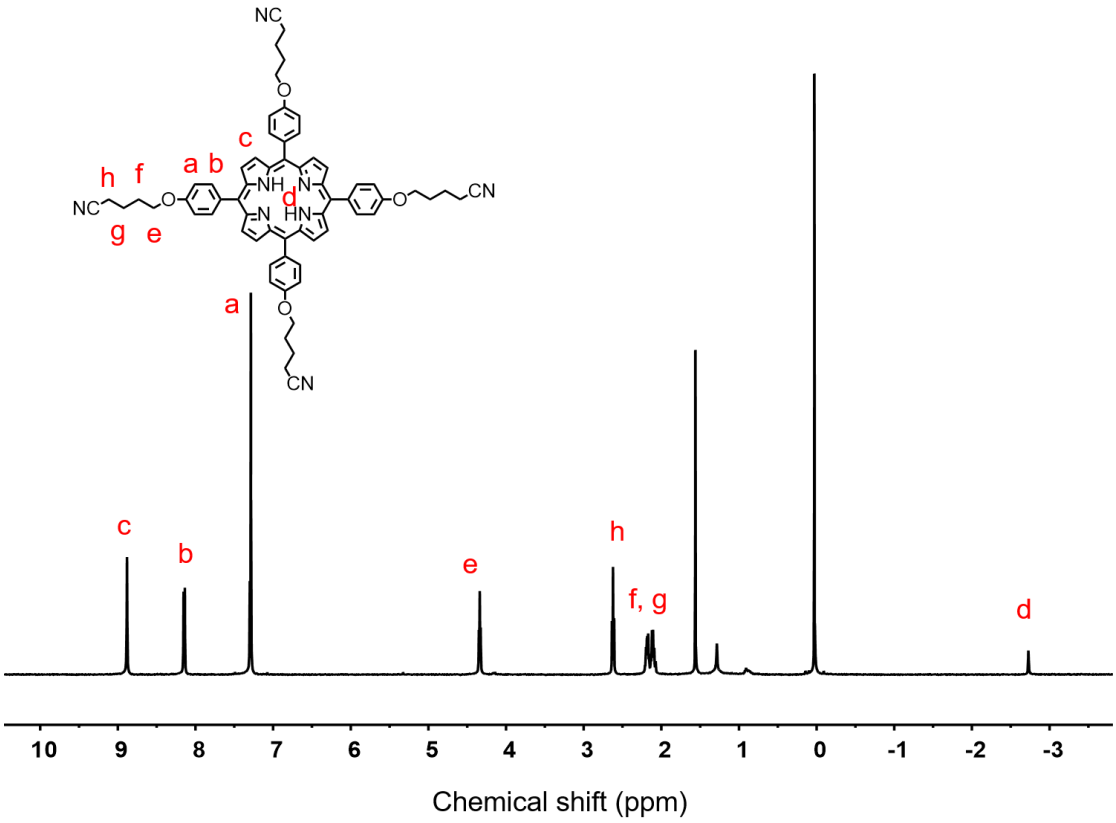


Fig. S6 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of P4C.

P4C@2P-AP·BC. To a solution of 2P-AP·BC (23.4 mg, 6 μmol) in 10 mL $CHCl_3$ was added P4C (3 mg, 3 μmol) in $CHCl_3$ (5 mL) dropwise. After 1 day, the formed precipitate was filtered off and washed with $CHCl_3$ (30 mL×3), and then dried in vacuum, giving the framework (23.2 mg, 4.9 μmol). Yield: 81.67%. ^{1}H NMR ($CDCl_3$:DMSO-d_6 = 14:1, 500 MHz, 298 K) in δ (ppm): 64.15 (br, 12H), 9.00 (s, 2H), 8.88 (s, 1H), 8.35 (s, 1H), 8.31−8.25 (d, J = 8.5 Hz, 2H), 8.19−8.10 (d, J = 8.0 Hz, 4H), 8.08 (s, 1H), 7.93−7.52 (m, 10H), 7.45−7.34 (d, J = 7.0 Hz, 2H), 6.90−6.68 (m, 11H), 6.56 (s, 1H), 5.75−5.62 (m, 1H), 5.20−5.04 (m, 4H), 5.02−4.90 (m, 4H), 4.75 (s, 4H), 4.42−4.15 (m, 6H), 3.97−3.87 (t, J = 6.5 Hz, 2H), 3.67 (s, 39H), 3.26 (s, 2H), 2.70 (s, 4H), 2.11−1.97 (m, 4H), 1.83 (s, 2H), 1.37−1.22 (m, 2H), −0.55 (s, 4H), −1.89 (s, 2H), −2.87 (s, 1H). FT-IR (KBr pellet) in v (cm^{-1}): 3661−3127, 3032−2783, 1673, 1506, 1463, 1401, 1210, 1044, 948, 925 and 672.

Table S2 Elemental analysis result of P4C@2P-AP·BC.

Chemical formula: $(C_{32}H_{29}O_2N_4)Na(C_{26}H_{29}N_2O)_2(C_{114}H_{132}N_{10}O_{48}MnMo_6)$

P4C@2P-AP·BC	C (%)	H (%)	N (%)
Found	54.25	4.95	5.91
Calculated	53.84	5.09	5.81
Error	0.41	0.14	0.10

Preparation of carbon quantum dots (CQDs) solution. 0.156 g of D-tyosine and 0.124 g of benzenediamine were mixed with 10 mL of water for hydrothermal synthesis at 140°C.

S4. Characterization on host-guest inclusion of 2P-AP·BC and P4C

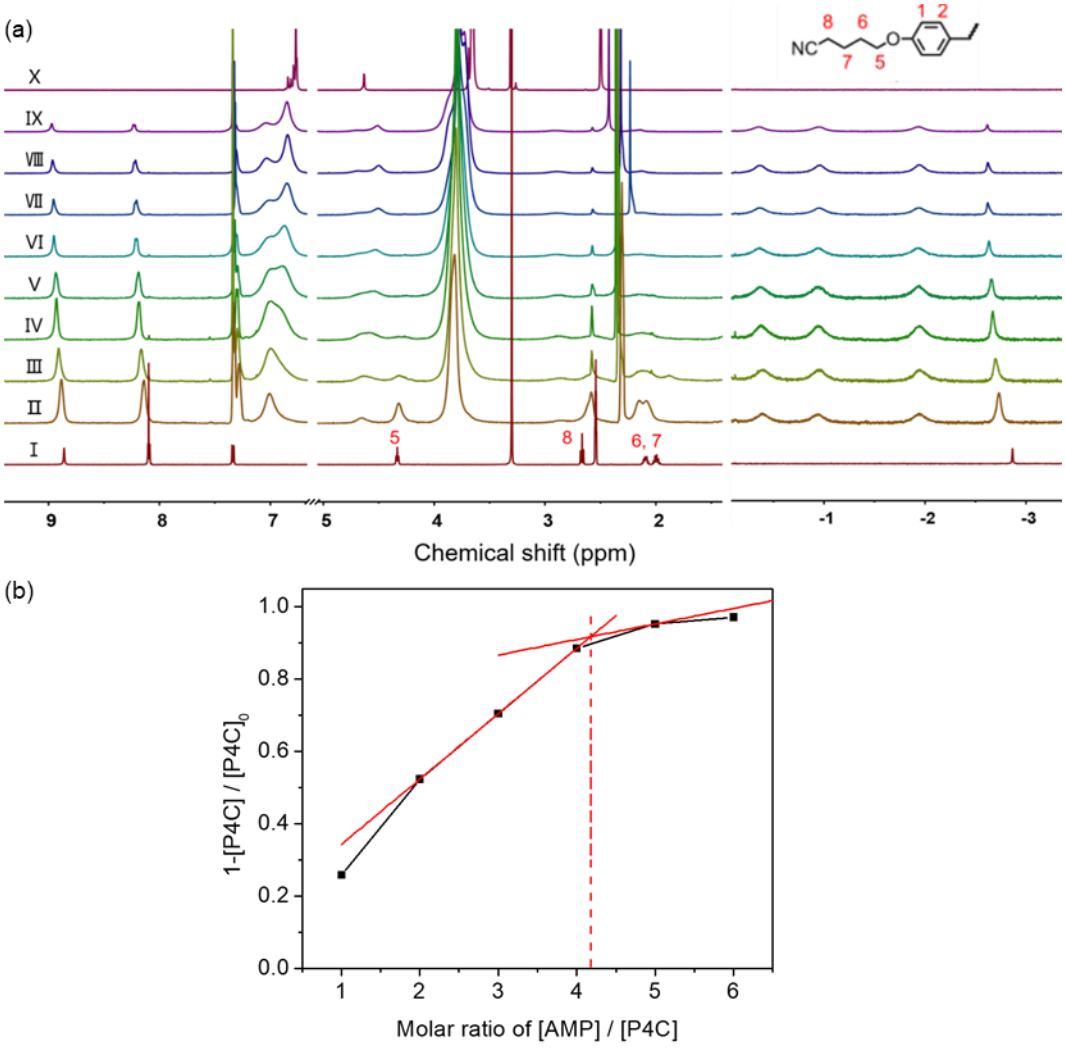


Fig. S7 (a) Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of P4C (2 mM) upon addition of (I) 0, (II) 1, (III) 2, (IV) 3, (V) 4, (VI) 5, (VII) 6, (VIII) 7, (IX) 8 eq. AMP, and (X) 10 mM AMP. (b) The plot of relative content of inclusion complexes calculated from integral area H(5) versus the molar ratio of AMP to P4C.

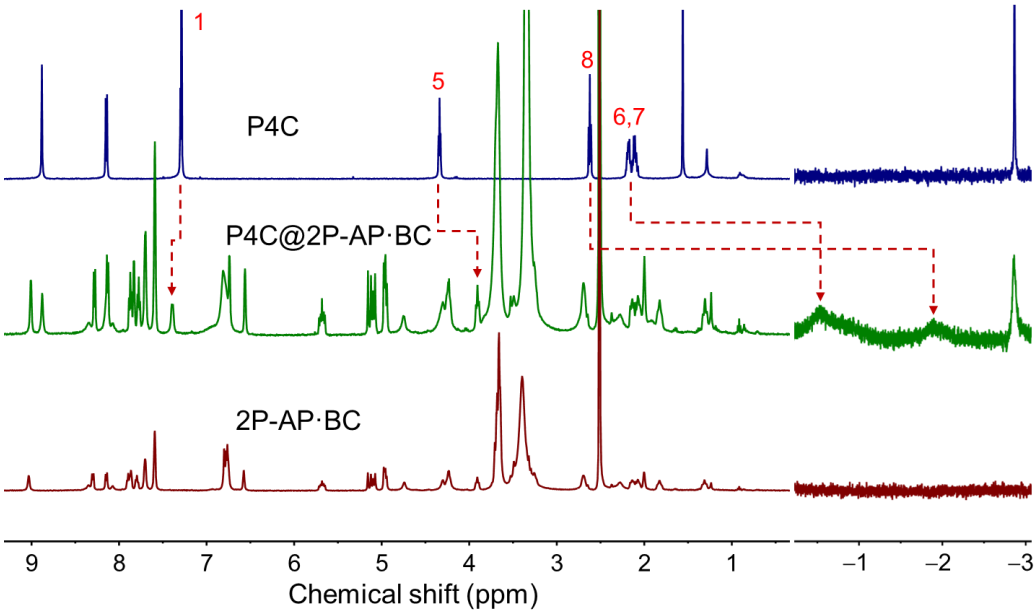


Fig. S8 ^{1}H NMR spectra of 2P-AP·BC, P4C, and their inclusion complex P4C@2P-AP·BC in $CDCl_3$/DMSO-d_6 (14/1 in v/v).

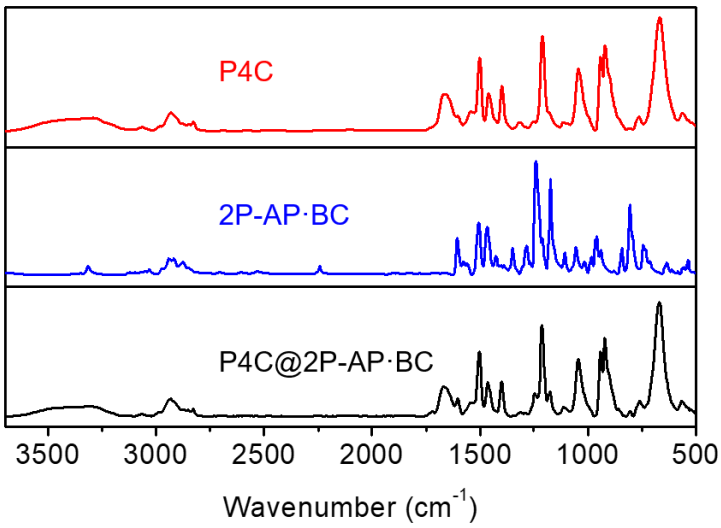


Fig. S9 IR spectra of 2P-AP·BC, P4C and their combination complex P4C@2P-AP·BC.

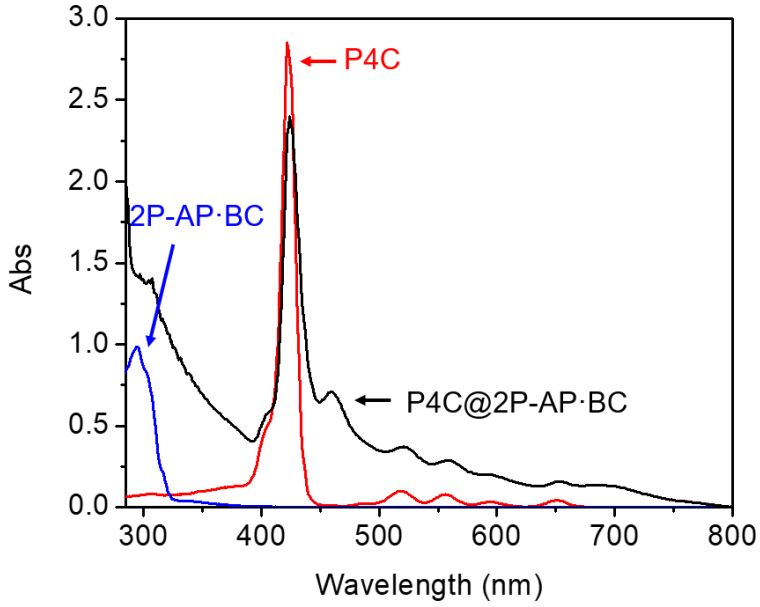


Fig. S10 UV-vis spectra of 2P-AP·BC, P4C and their combination complex P4C@2P-AP·BC in $CHCl_3$.

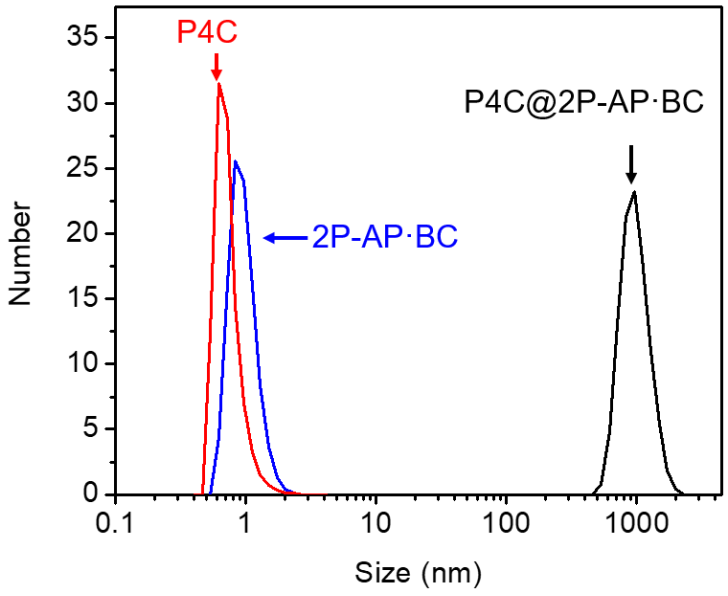


Fig. S11 DLS plots of 2P-AP·BC, P4C and their combination complex P4C@2P-AP·BC in $CHCl_3$.

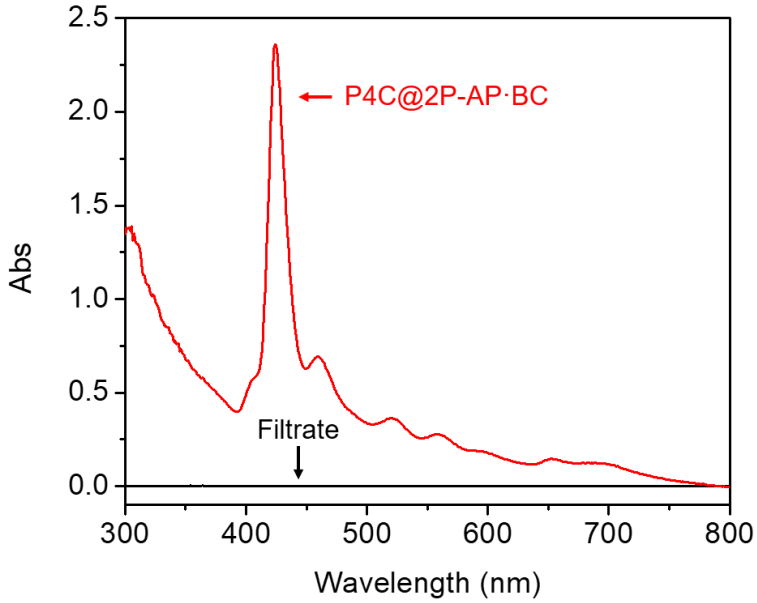


Fig. S12 UV-vis spectra of filtrate solution through the membrane which consists of P4C@2P-AP·BC.

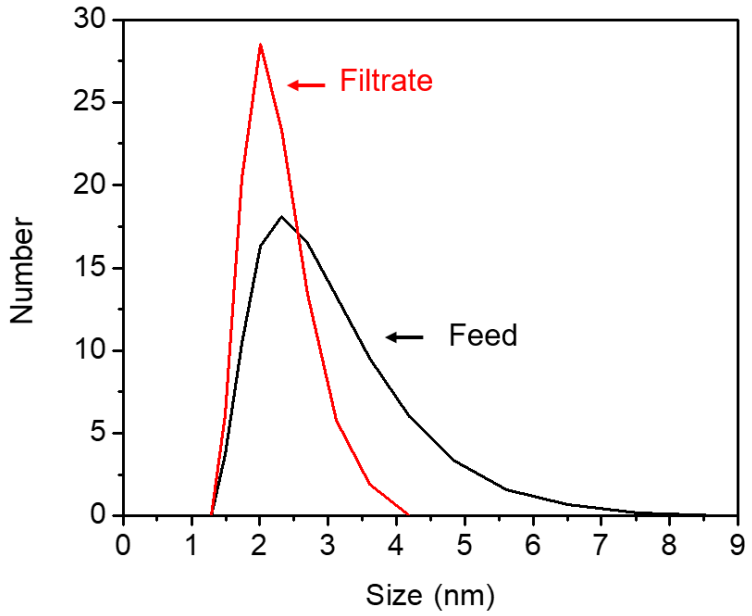


Fig. S13 DLS plots of CQDs in feed solution and filtrate solutions.

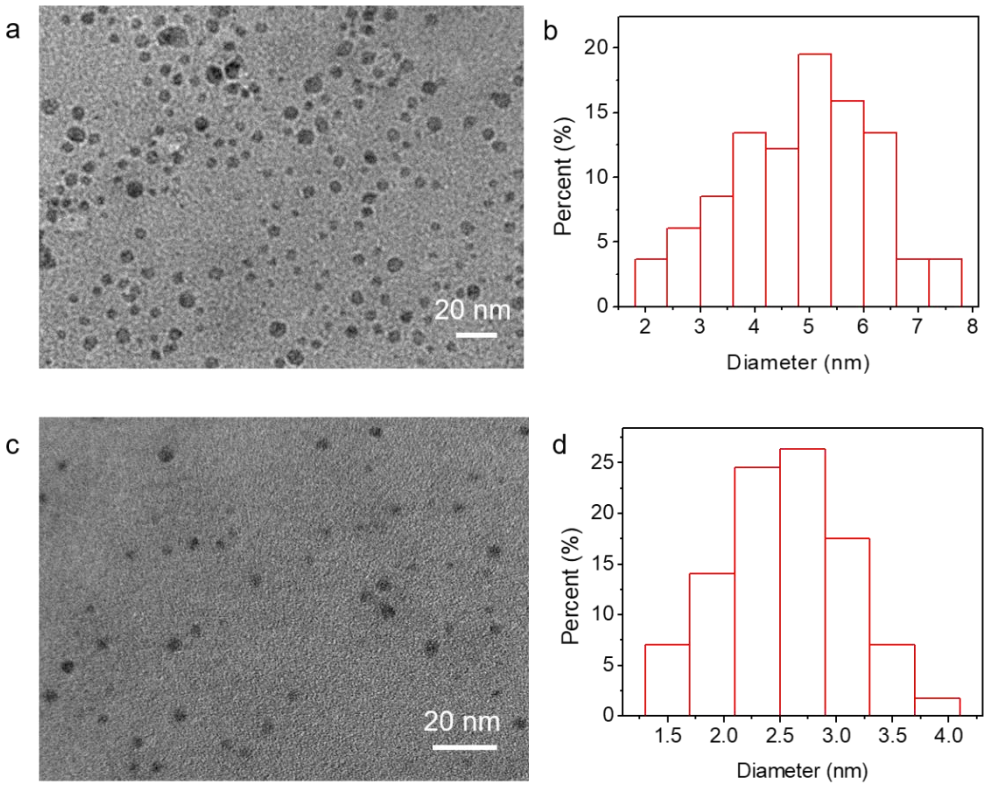


Fig. S14 TEM images of CQDs and the corresponding statistic histograms of particle size (a, b) from feed solution, (c, d) from filtrate solution after the separation of the membrane via filtration.

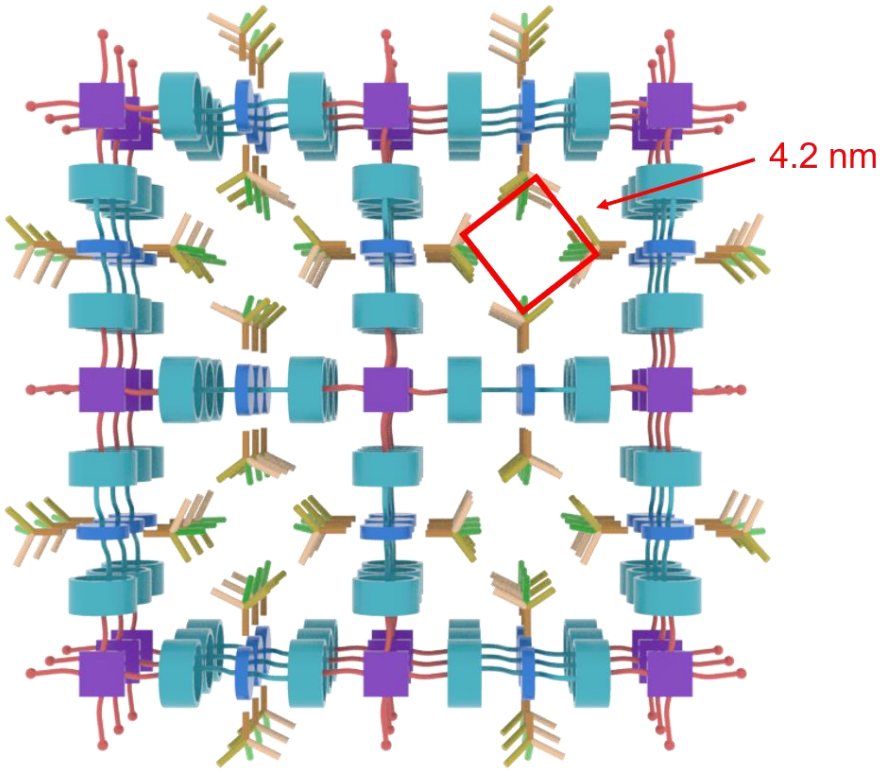


Fig. S15 Experimental size of pores in membrane consisted of P4C@2P-AP·BC via filtration.

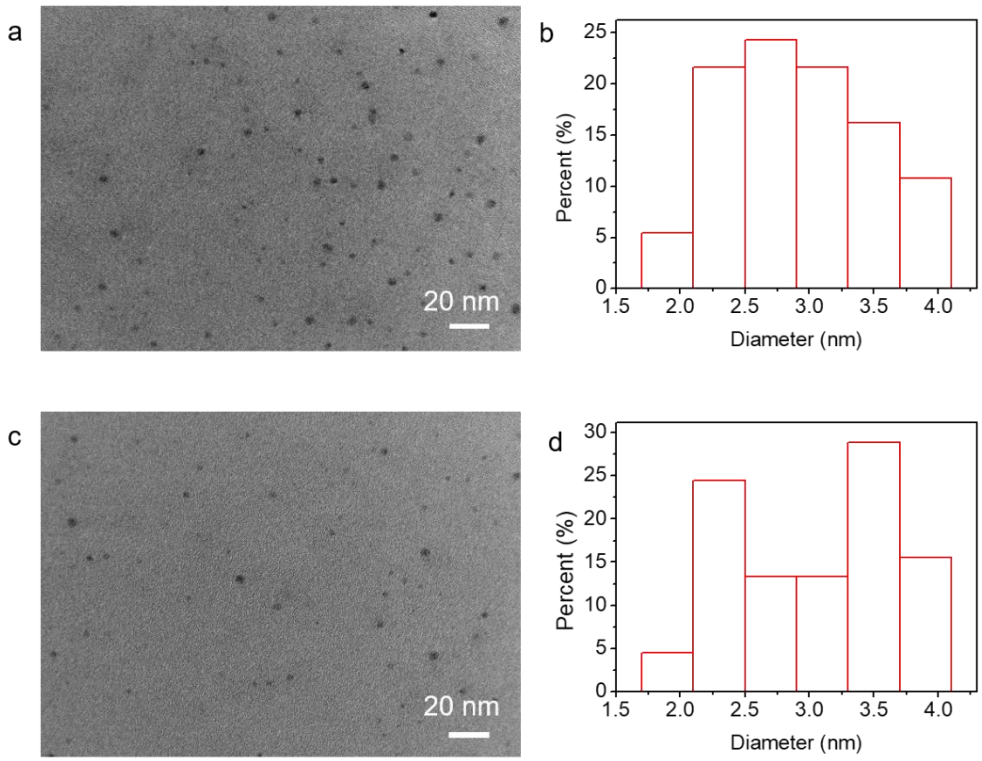


Fig. S16 TEM images of CQDs and the corresponding statistic histograms of particle size (a, b) when the mass of membrane was 2.0 mg, (c, d) the filtration was under a pressure of −0.02MPa.

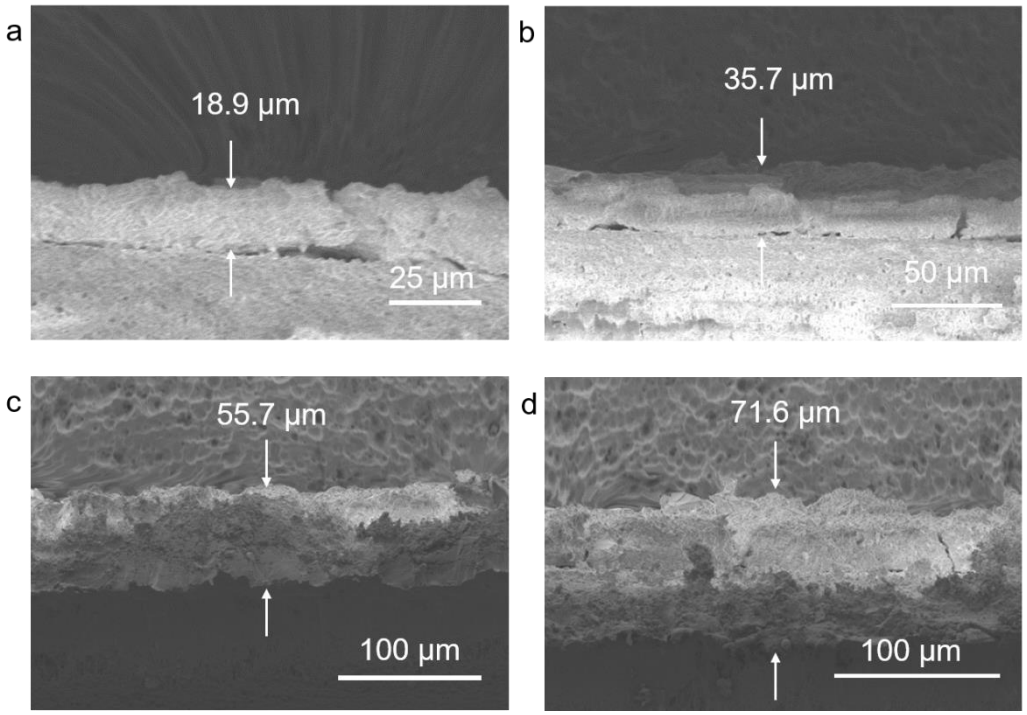


Fig. S17 SEM cross-sectional images of membranes with the mass of (a) 2.0 mg, (b) 4.0 mg, (c) 6.0 mg, and (d) 8.0 mg.

S5. Chiral separation performance of supramolecular framework membranes

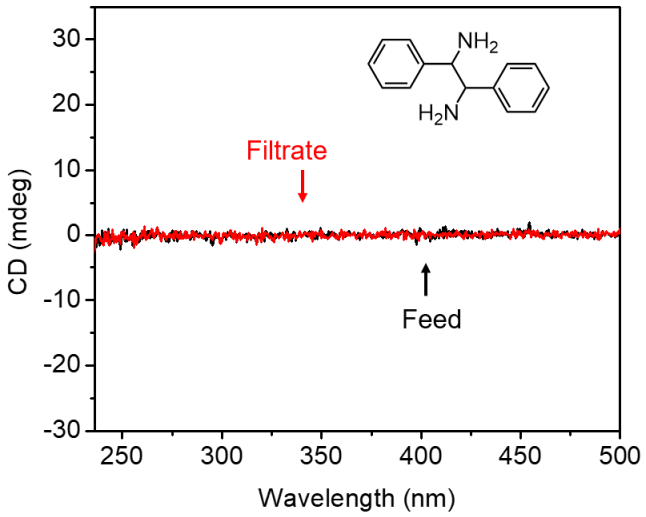


Fig. S18 CD spectra of the feed solution and filtrate solution under a pressure of −0.02 MPa using racemic 1, 2-diphenylenediamine as substrate.

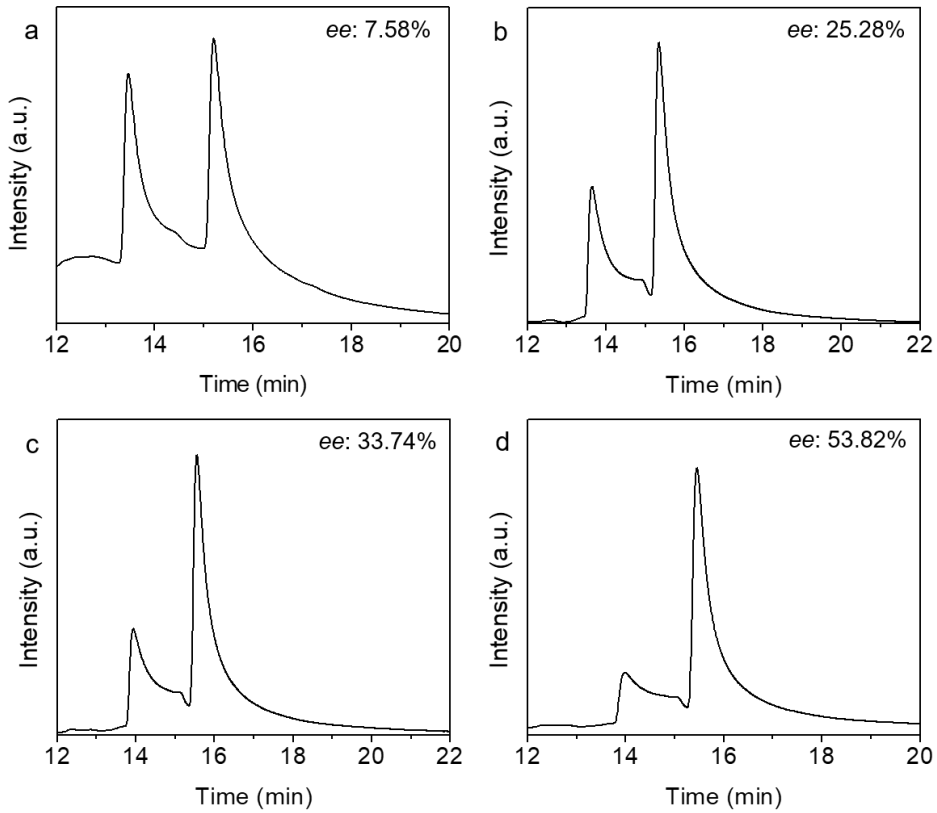


Fig. S19 HPLC results of 1,2-diphenylethylenediamine filtrate via membranes using (a) 2.0, (b) 4.0, (c) 6.0, and (d) 8.0 mg of SF assembly. Experimental conditions: mobile phase, *n*-hexane:isopropanol = 60:40, 1.0 mL min^{-1}. The UV monitor wavelength is 225 nm. Feed concentration is 1.0 mg mL^{-1}.

Table S3 The summary of thickness, flux and separation efficiency of membranes with different masses.

Mass of membrane (mg)	2.0	4.0	6.0	8.0
Thickness (μm)	18.9	35.7	55.7	71.6
Flux (L m^{-2} h^{-1} bar^{-1})	47.7	25.5	13.7	8.9
ee (%)	7.58	25.28	33.74	53.82

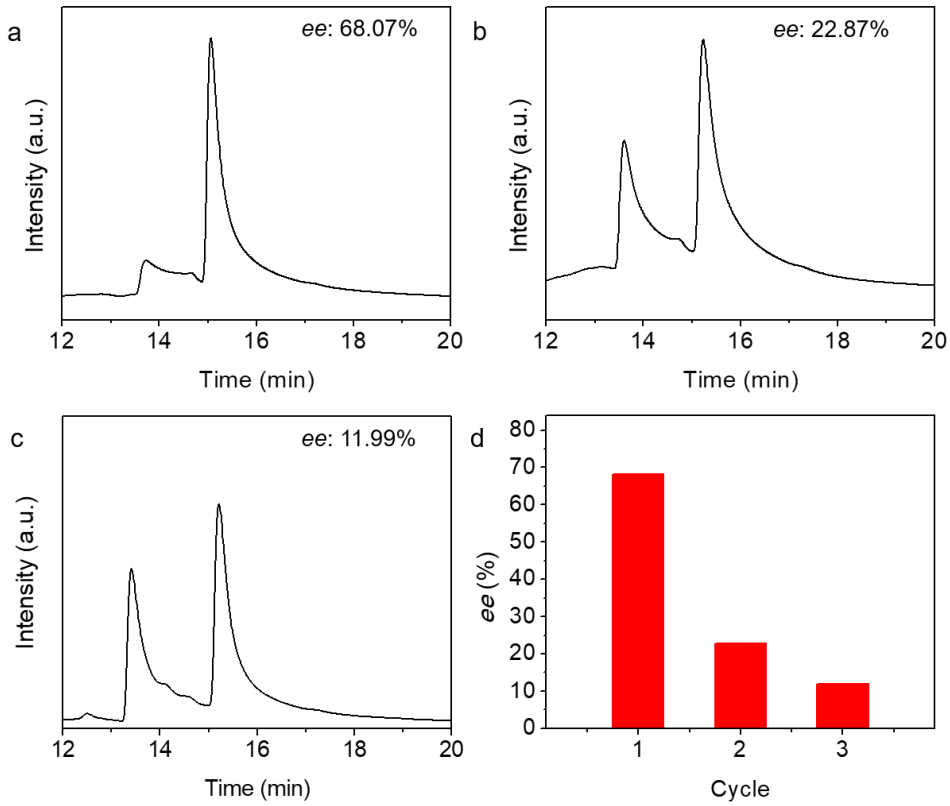


Fig. S20 HPLC results of the filtrate when 8.0 mg membrane was used to separate 5 mL 1,2-diphenylethylenediamine for the (a) first time, (b) second time, (c) third time, and (d) summary statistics of *ee* values of (a, b, c). Experimental conditions: mobile phase, *n*-hexane:isopropanol = 60:40, 1.0 mL min^{-1}. The UV monitor wavelength is 225 nm. Feed concentration is 0.5 mg mL^{-1}.

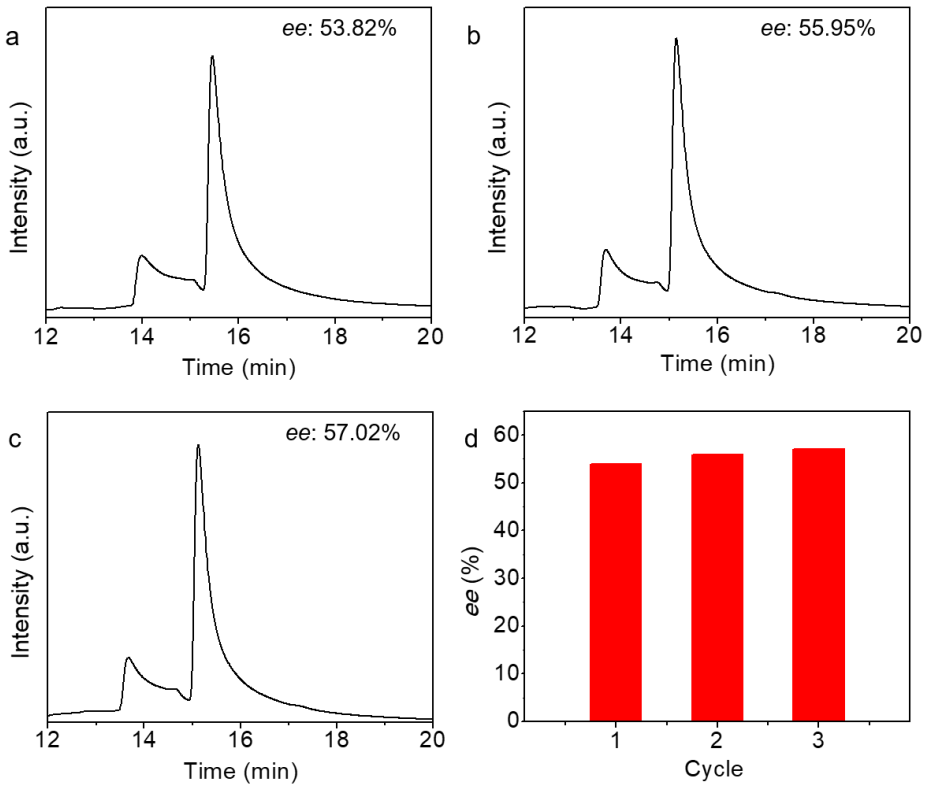


Fig. S21 HPLC results of the same filtrate (5 mL 1,2-diphenylethylenediamine) repeating separation with the same membrane for the (a) first time, (b) second time, (c) third time, (d) *ee* values of each cycle. Experimental conditions: mobile phase, *n*-hexane:isopropanol = 60:40, 1.0 mL min^{-1}. The UV monitor wavelength is 225 nm. Feed concentration is 1.0 mg mL^{-1}.

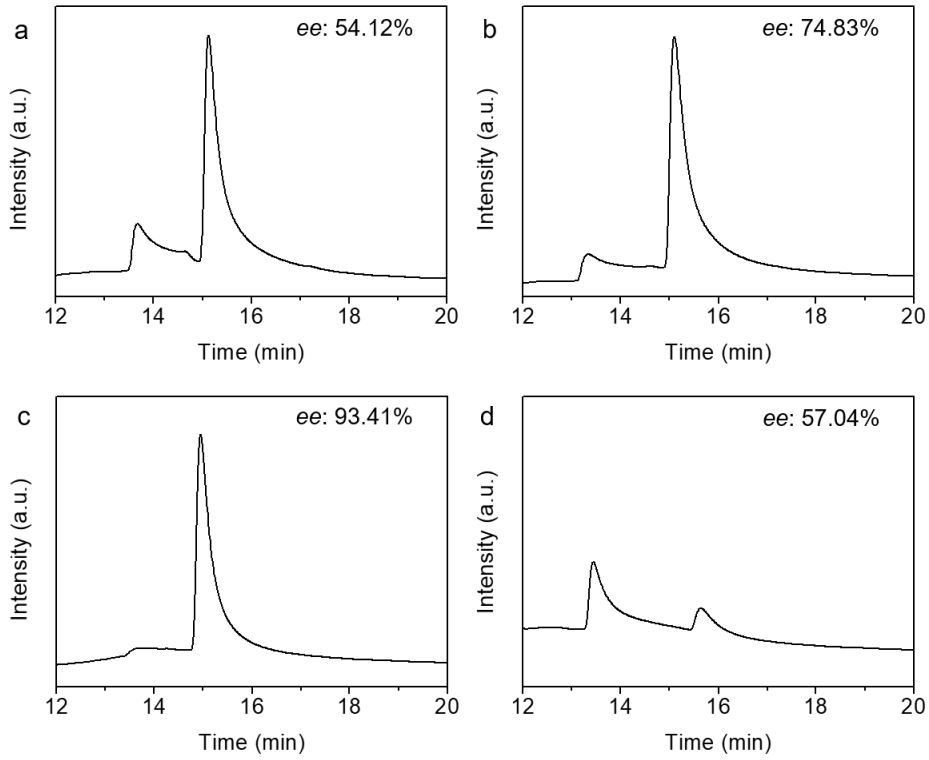


Fig. S22 HPLC results of the same filtrate (5 mL 1,2-diphenylethylenediamine) repeating separation with different membranes (8.0 mg) for the (a) first run, (b) second run, (c) third run, (d) retentate solution. Experimental conditions: mobile phase, *n*-hexane:isopropanol = 60:40, 1.0 mL min^{-1}. The UV monitor wavelength is 225 nm. Feed concentration is 1.0 mg mL^{-1}.

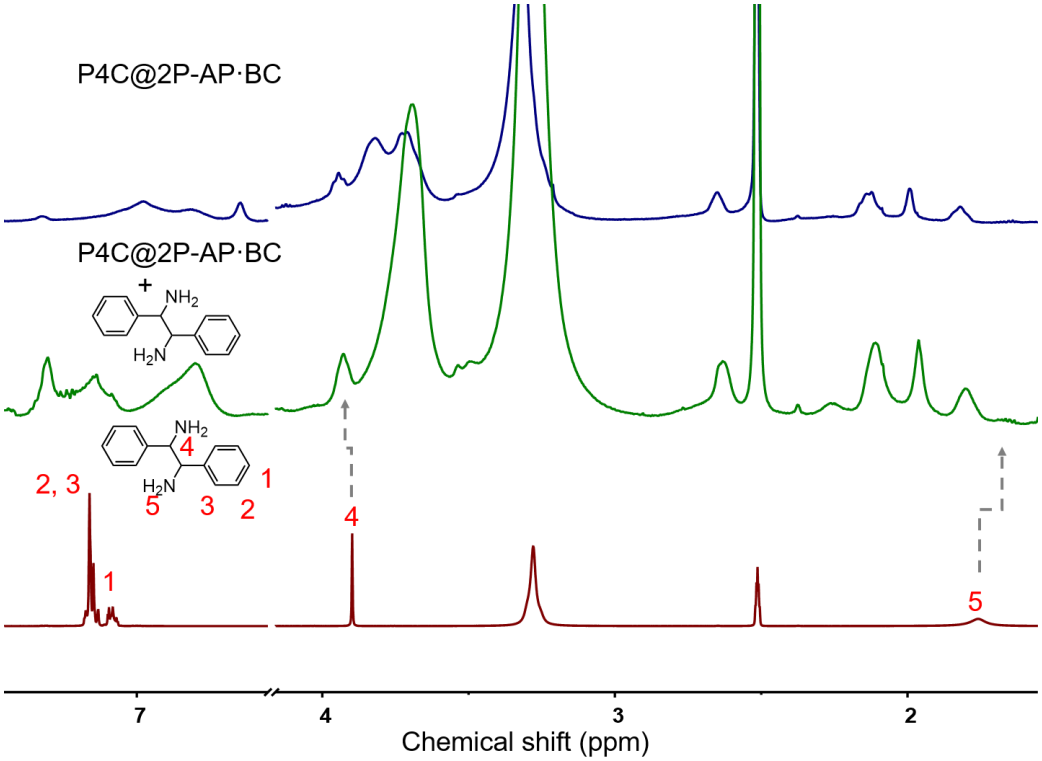


Fig. S23 ^{1}H NMR spectra (500 MHz, $CDCl_3$/DMSO-d_6 = 14:1, 298 K) of P4C@2P-AP·BC, 1,2-diphenylethylenediamine and their combination complex at a molar ratio of 1:1.

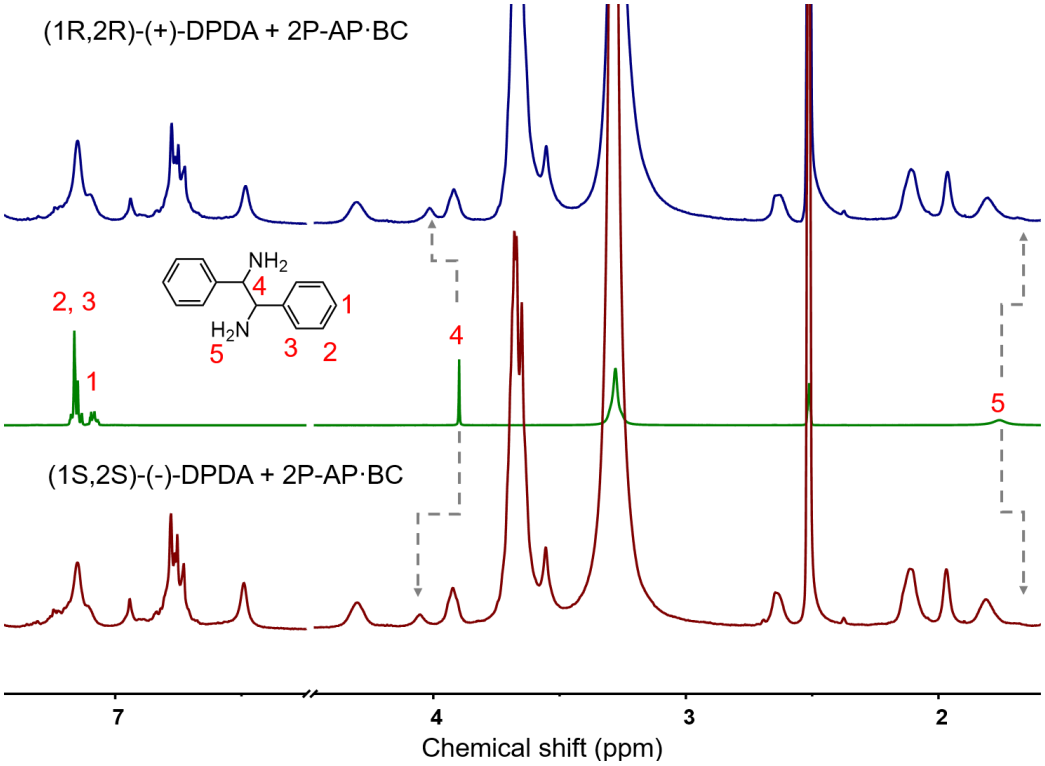


Fig. S24 ^{1}H NMR spectra (500 MHz, $CDCl_3$/DMSO-d_6 = 14:1, 298 K) of DPDA, combination complexes of 2P-AP·BC and (1S,2S)-(-)-DPDA, 2P-AP·BC and (1R,2R)-(+)-DPDA at a molar ratio of 1:1.

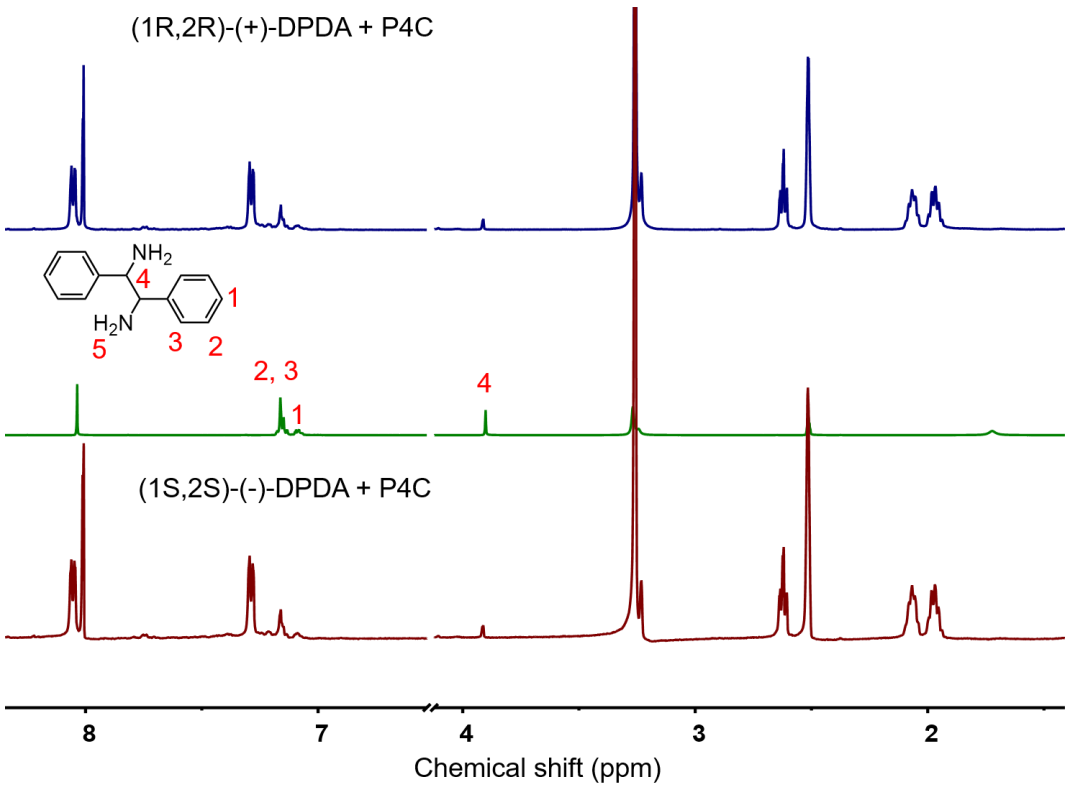


Fig. S25 ^{1}H NMR spectra (500 MHz, $CDCl_3$/DMSO-d_6 = 14:1, 298 K) of DPDA, combination complexes of P4C and (1S,2S)-(-)-DPDA, P4C and (1R,2R)-(+)-DPDA at a molar ratio of 1:1.

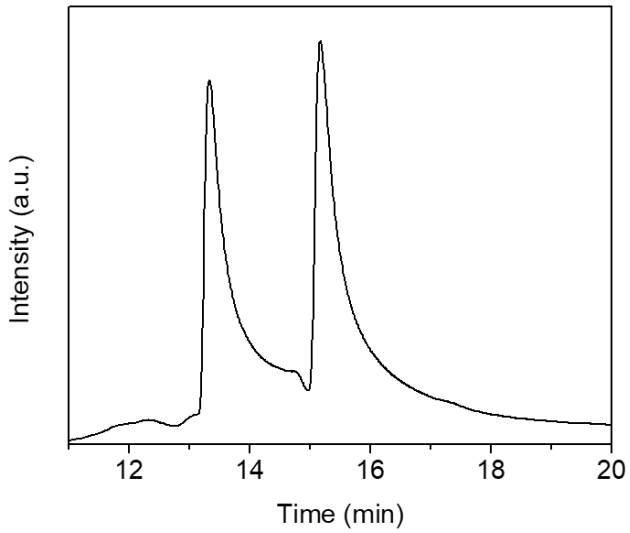


Fig. S26 HPLC result of the filtrate using 2P-AP·BC membrane to separate 10 mL DPDA solution under natural gravity. 8.0 mg 2P-AP·BC is dispersed in methanol and spread on a polymer-supported matrix by filtration under a pressure of −0.08 MPa. Experimental conditions: mobile phase, *n*-hexane:isopropanol = 60:40, 1.0 mL min^{-1}. The UV monitor wavelength is 225 nm. Feed concentration is 1.0 mg mL^{-1}.

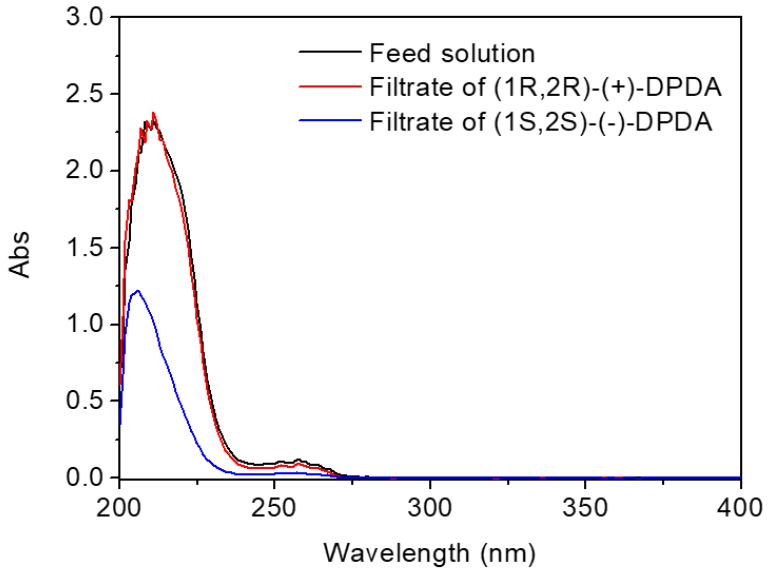


Fig. S27 UV-vis spectra of the filtrate when separating 10 mL (1S,2S)-(-)-DPDA and (1R,2R)-(+)-DPDA respectively.

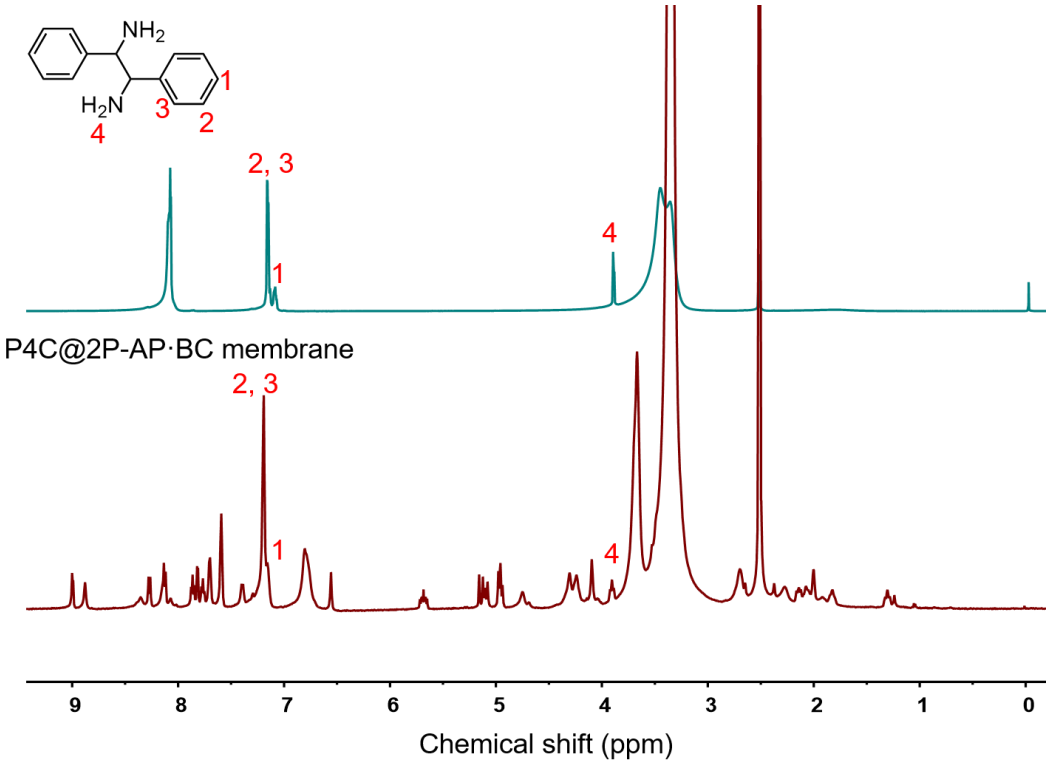


Fig. S28 ^{1}H NMR spectra (500 MHz, DMSO-d_6, 298 K) of 1,2-diphenylethylenediamine and P4C@2P-AP·BC membrane (2 mM) after separation.

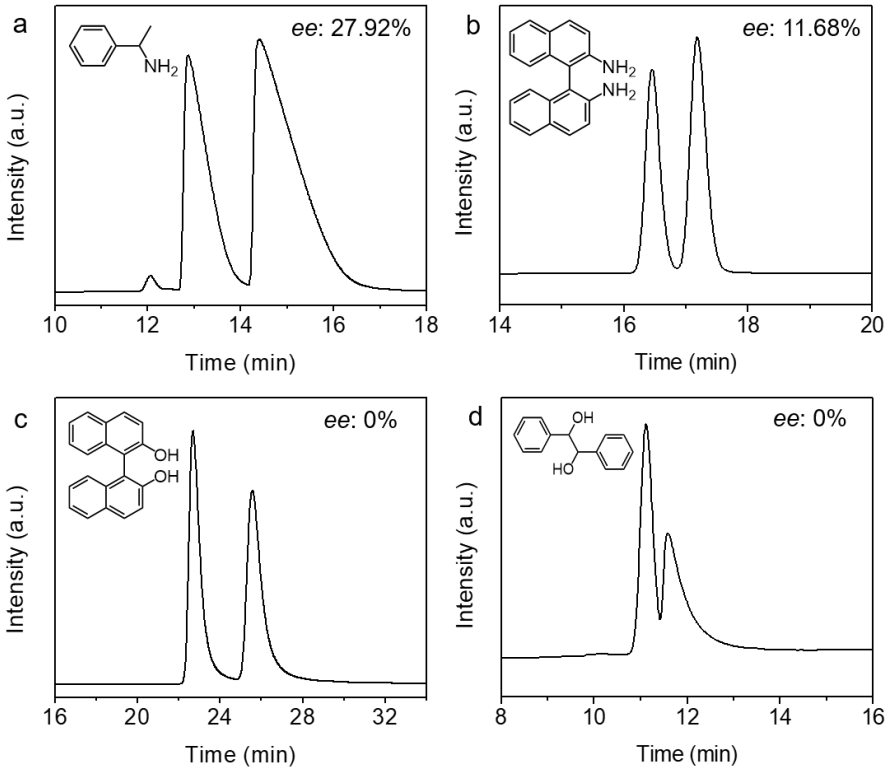


Fig. S29 HPLC results of the filtrate with (a) *α*-methylbenzylamine, (b) 1,1′-binaphthyl-2,2′-diamine, (c) 1, 1'-bi-2-naphthol, (d) bydrobenzoin as substrate when the mass of the membrane is 8.0 mg. (a) Experimental conditions: mobile phase, *n*-hexane:isopropanol = 90:10, 0.5 mL min^{-1}. The UV monitor wavelength is 210 nm. Feed concentration is 1.0 mg mL^{-1}. (b) Experimental conditions: mobile phase, *n*-hexane:isopropanol = 60:40, 1.0 mL min^{-1}. The UV monitor wavelength is 210 nm. Feed concentration is 1.0 mg mL^{-1}. (c) Experimental conditions: mobile phase, *n*-hexane:isopropanol = 80:20, 0.5 mL min^{-1}. The UV monitor wavelength is 335 nm. Feed concentration is 1.0 mg mL^{-1}. (d) Experimental conditions: mobile phase, *n*-hexane:isopropanol = 60:40, 1.0 mL min^{-1}. The UV monitor wavelength is 280 nm. Feed concentration is 1.0 mg mL^{-1}.

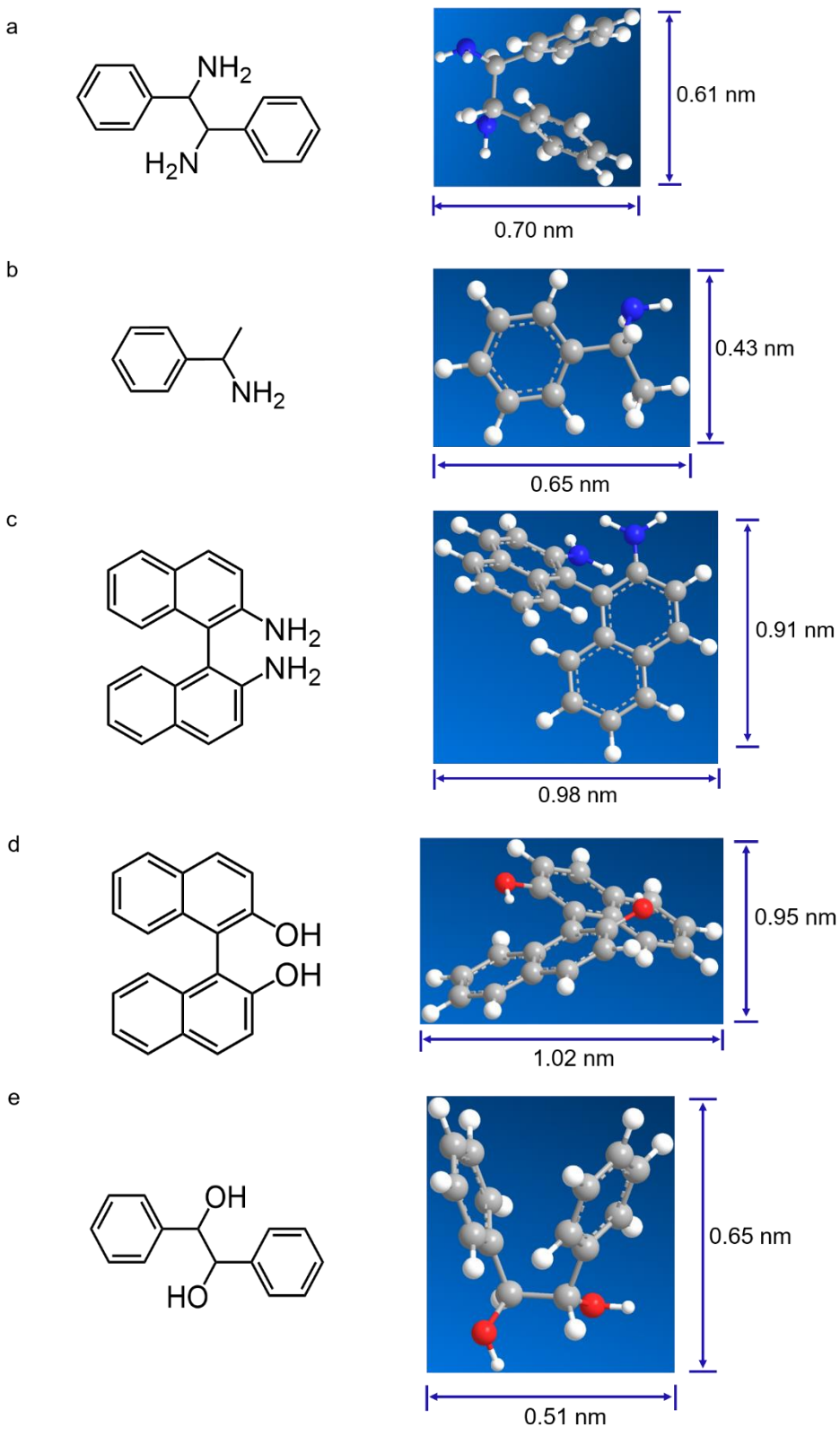


Fig. S30 Molecular sizes calculated by ChemBio3D of (a) 1,2-diphenylethylenediamine, (b) *α*-methylbenzylamine, (c) 1,1′-binaphthyl-2,2′-diamine, (d) 1, 1'-bi-2-naphthol, (e) hydrobenzoin.

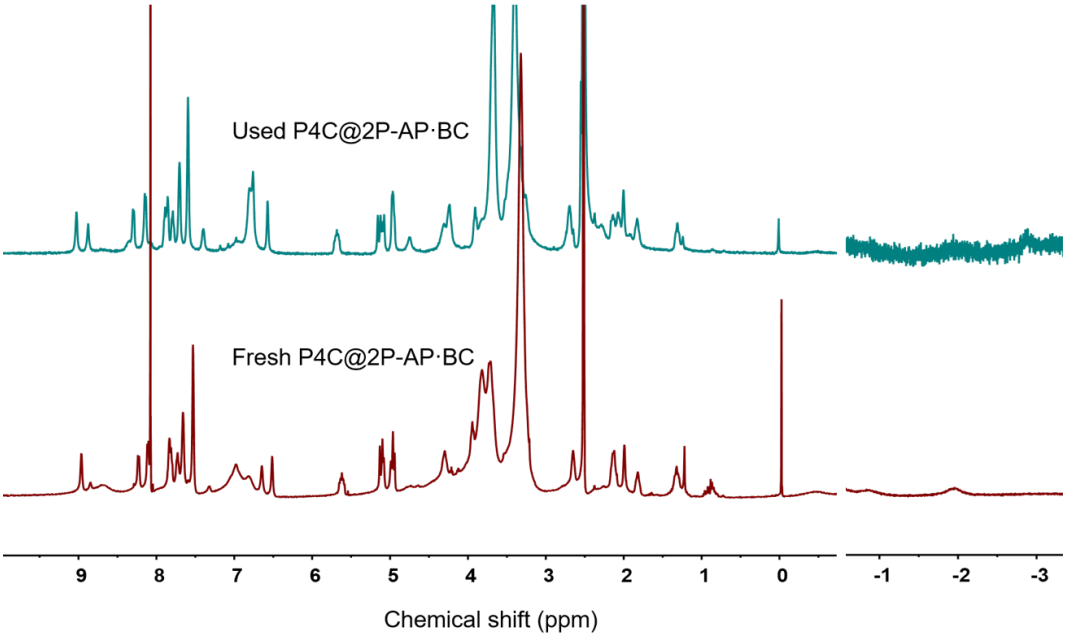


Fig. S31 ^{1}H NMR spectra (500 MHz, $CDCl_3$/DMSO-d_6 = 14/1, 298 K) of P4C@2P-AP·BC before and after chiral separation.

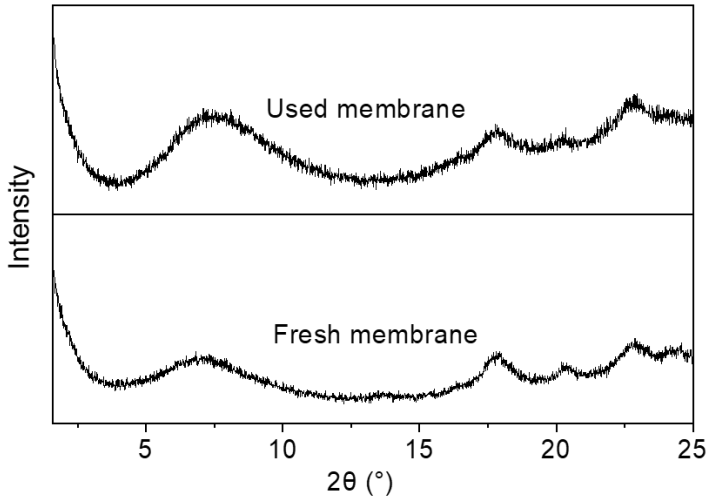


Fig. S32 XRD patterns of P4C@2P-AP·BC before and after chiral separation.

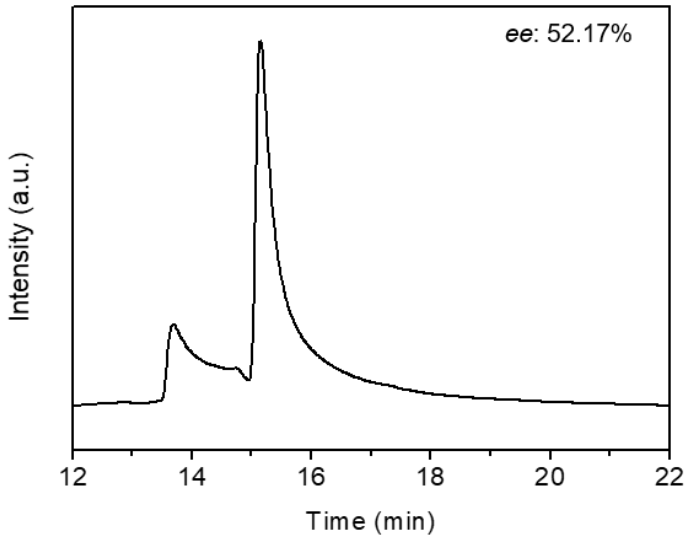


Fig. S33 HPLC result of the 1,2-diphenylethylenediamine filtrate through a re-constructed membrane by using a P4C@2P-AP·BC assembly sourcing from the used membrane following the same method described above. The used membrane is washed with methanol. Then the membrane is dispersed in chloroform and spread on a polymer-supported matrix by filtration under a pressure of −0.08 MPa to construct a new membrane. The separation experiment is under natural gravity. Experimental conditions: mobile phase, *n*-hexane:isopropanol = 60:40, 1.0 mL min^{-1}. The UV monitor wavelength is 225 nm. Feed concentration is 1.0 mg mL^{-1}.

S6. References

[1] W. G. Klemperer, *Inorg. Syn.*, 1990, **27**, 74−85.

[2] X. Li, J. Xu, Y. Gao, H. Fang, G. Tang and Y. Zhao, *J. Org. Chem.*, 2015, **80**, 2621−2626.