Electronic Supplementary Information

Liquid-Phase Epitaxy Growth of homochiral MOF thin film on Poly(L-DOPA) functionalized substrate improved enantiomer separation

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4.37 mL min−1, 76.2 cm s−1; oven: 90 °C,isotherm; injector: split, 9: 1 at 200 °C.
Figure S6. The gas chromatographic separation of a mixture of enantiomers carvone (R- carvone and S- carvone) in Cu_2(D-cam)$_2$dabco and Cu_2(D-cam)$_2$dabco@Poly(L-DOPA) grown in capillary column.
Figure S7. The gas chromatographic separation of a mixture of enantiomers ethyl lactate ((+)/(-)-ethyl lactate) in Cu_2(D-cam)$_2$dabco and Cu_2(D-cam)$_2$dabco@Poly(L-DOPA) grown in capillary column
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Materials and instrumentation

All the reagents and solvents employed were commercially available and were used as received without further purification. The samples grown on functionalized glass substrate were characterized with powder x-ray diffraction (PXRD) analysis. All GC separations were performed on a GC 9790II system (FULI, China) with capillary control unit, flame ionization detector and split injection port. Nitrogen (99.999 %) was used as the carrier gas with a linear velocity of 10 cm s^{-1} for –OH functionalized GC capillary column and MOF grown in the column. Oxygen (99.999 %) was used as the carrier gas with a linear velocity of 10 cm s^{-1} for Poly(L-DOPA) functionalized GC column. The injector was held at 250 °C and the injection split ratio was 100:1 in the GC experiments. Powder X-ray diffraction (PXRD) analysis was performed on a MiniFlex2 X-ray diffractometer using Cu-Kα radiation (λ = 0.1542 nm) in the 2θ range of 4–20° with a scanning rate of 0.5° min^{-1}. Scanning electron microscope (SEM) images for the morphology of thin films were measured by JSM6700.

Preparation of flat functionalized substrate

Commercially available glasses (SiO_2) were used for SURMOF preparation. After rinsing with water, the glass are subsequently immersed in a piranha solution consisting of sulfuric acid (H_2SO_4, 98%) and hydrogen peroxide (H_2O_2, 30%) with a volume ratio 3:1 at 80 °C for 30 minutes and then cleaned with deionized water and dried under nitrogen flux for the next preparation. Then the -OH functionalized glass substrate was obtained for next preparation.

Preparation of functionalized GC capillary column

A piranha solution with (H_2SO_4:H_2O_2 = 3:1) was forced through the GC column under nitrogen gas pressure at a rate of ~2 cm s^{-1} (see the setup in Figure 1a). After 40 min flowing, the treated GC column was cleaned with water, and then purged with N_2 for next step. For the preparation of poly(L-DOPA) functionalized GC column, the L-DOPA aqueous solution (pH=8.5) was forced through the column under oxygen gas pressure at a rate of ~2 cm s^{-1} for 2 h. the Poly(L-DOPA) can be assembled in the inner wall of the column via self-polymerize method (scheme 1). The modified GC column was cleaned with water, and then purged with N_2 for next step.

Preparation of Chiral MOF grown on functionalized substrates and GC capillary column

Cu_2(D-cam)$_2$P (P = dabco and bipy) thin films used in the present work were grown on OH-terminated glass substrate using the liquid-phase epitaxy (LPE) pump method at 50 °C. Here the composite of inner wall of capillary column is SiO_2, which is the same as flat glass. Therefore, flat glass was selected as a substrate for investigating the crystallinity and surface morphology structure of MOF thin film grown substrate. The chiral MOF Cu_2(D-cam)$_2$P (P= dabco and bipy) thin films were fabricated using the same following diluted ethanolic solutions: copper(II) acetate ($Cu(OAc)_2$; 1 mM) and D-cam/dabco (0.4 mM). The pump method is adopted in this work which is descripted in the earlier work. The immersion times were 15 min for the copper acetate solution and 30 min for the organic linkers solution. Each step was followed by a 3 min-rinsing step with pure ethanol to remove residual reactants. A total of 40 growth cycles were used for MOF grown on functionalized substrates in this work.

MOF grown in functionalized capillary column was prepared by a liquid phase exptaxy layer by layer method. The solution of $Cu(OAc)_2$, organic linkers and pure ethanol were forced alternately through the column under gas pressure at a rate of 2 cms^{-1} via layer by layer approach. Firstly, 1 mM $Cu(OAc)_2$ ethanolic solution was forced through the functionalized capillary using a N_2 pressure for 10 min, then the column was injected with pure ethanol for 3 min for rinsing. Secondly, the capillary column was treated as the former procedure using 0.4 mM of ethanolic organic linkers solution for 15 min and then rinsed with pure ethanol for 3 min. All the preparation process is under 60°C. The studied MOF thin films grown in capillary column were obtained after repeating 40 cycles. The obtained column was purged with nitrogen and solidified with nitrogen for 3 h at 70 °C.

Characterization of samples

X-ray diffraction (XRD)

XRD was carried out on MiniFlex2 advance in θ-θ geometry equipped with a Si-strip detector (PSD Lynxeye (C)) using Cu K_alpha1,2 radiation. On the tube side a variable divergence slit set to V12 (fixed slit with 12 mm opening) and on the receiving side a 2.5° Soller slit was used.
Scans ran from 5° to 20° (2θ with a step width of 0.025° and 0.5 min/degree). Evaluation of data was done with Rigaku evaluation software JADE 5.0.

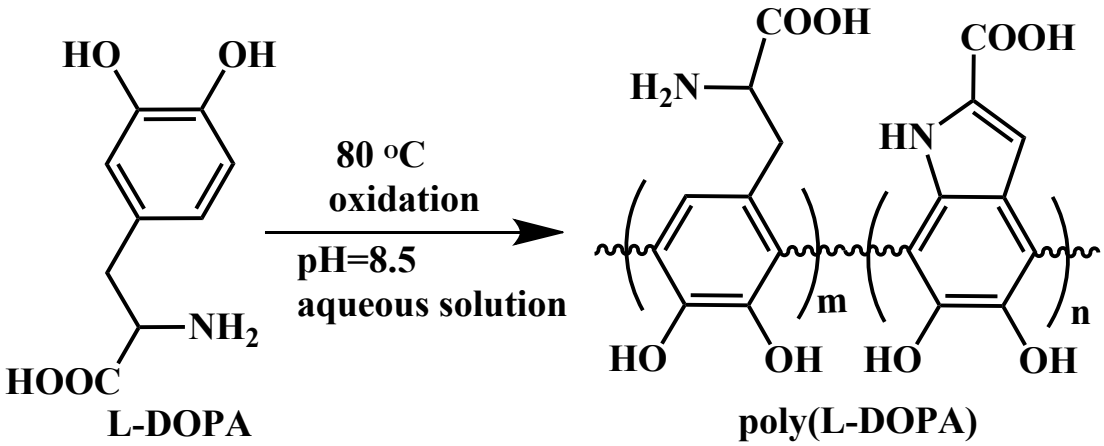
Infrared Reflection-Absorption Spectroscopy (IRRAS)

The SURMOFs were characterized with IRRAS. IRRAS data were recorded using a FTIR spectrometer (Bruker VERTEX 70) in this thesis. With a resolution of 2 cm^{-1} at an incidence angle of 80° relative to the surface normal is used. Liquid nitrogen is used for cooling the mercury cadmium telluride (MCT) narrow band (4000-400cm^{-1}) detector. Perdeuterated hexadecanethiol SAMs on Au substrate was used as reference for SURMOF grown on SAMs Au substrate. The quartz glass was used for the background of SURMOF grown on functionalized quartz glass. In both case 1024 scans were accumulated for the reference measurement. Dry air was purged continuously through the spectrometer and the sample compartment, which reduces the possibility of atmospheric water or CO_2 contamination of the spectra and samples. Samples were measured as long as the water absorption bands from ambient air disappeared (900-1300 scans). The data were processed using Bruker OPUS® software version 5.5.

Scanning electron microscopy (SEM)

In this work, the morphology measurements are carried out in a JSM6700 Field Emission Gun Environmental Scanning Electron Microscope (FEG-ESEM). To avoid charging, insulating materials have to be coated with a thin Gold/Palladium film. Then the specimen can be imaged under high vacuum conditions (10-5 Pa) using acceleration voltages between 5 and 20 kV.

All GC separations were performed on a GC 9790II system (FULI, China) with capillary control unit, flame ionization detector, and split injection port. Nitrogen (99.999 %) was used as the carrier gas with a linear velocity of 10 cm s^{-1} for –OH functionalized GC capillary column, MOF grown in column.



Scheme S1. Schematic illustration of the formation of poly(L-DOPA) via self-polymerization of L-Dopa under pH 8.5 aqueous solution at 80 °C.

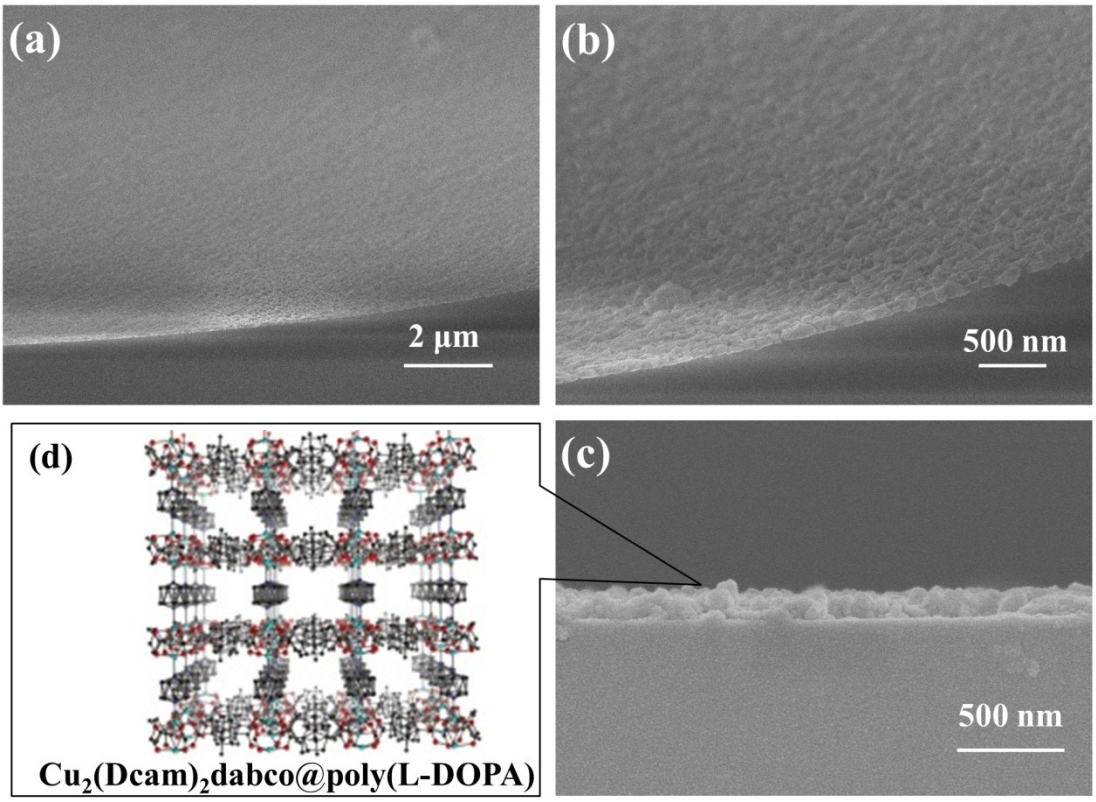


Figure S1. SEM images (a-c) of Cu_2(D-cam)$_2$dabco@Poly(L-DOPA) thin film grown in capillary column using layer by layer approach; (d) the structure of chiral MOF Cu_2(D-cam)$_2$dabco.

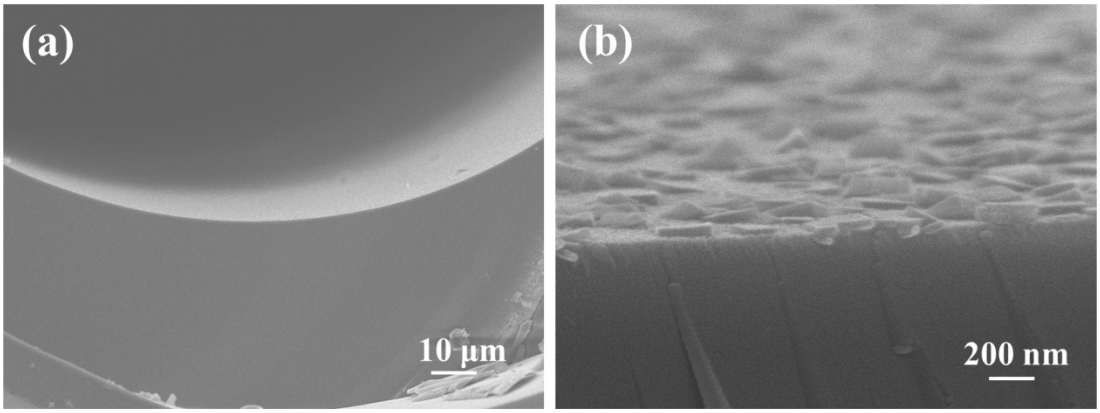


Figure S2. SEM images (a,b) of of Cu_2(L-cam)$_2$dabco@Poly(L-DOPA) thin film grown in capillary column using layer by layer approach

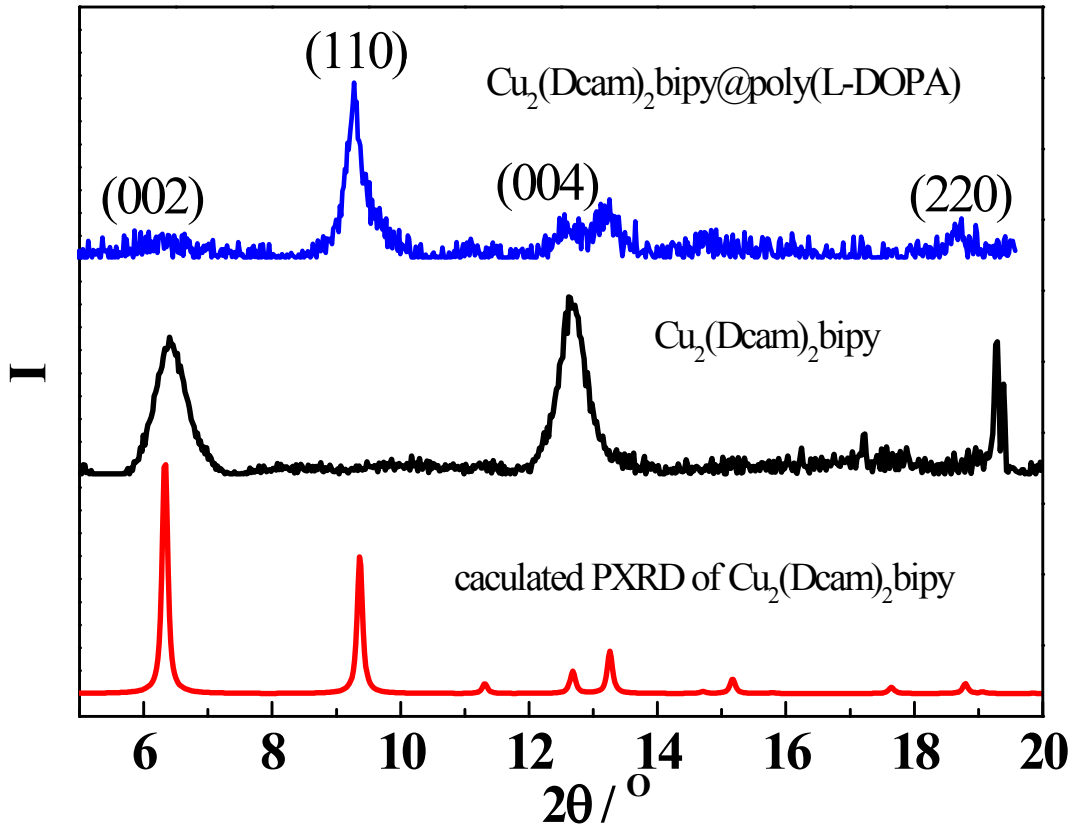


Figure S3. Calculated and experimental XRD of Cu_2(D-cam)$_2$bipy and Cu_2(D-cam)$_2$bipy@Poly(L-DOPA) thin film grown on flat Si substrate using LPE layer by layer approach.

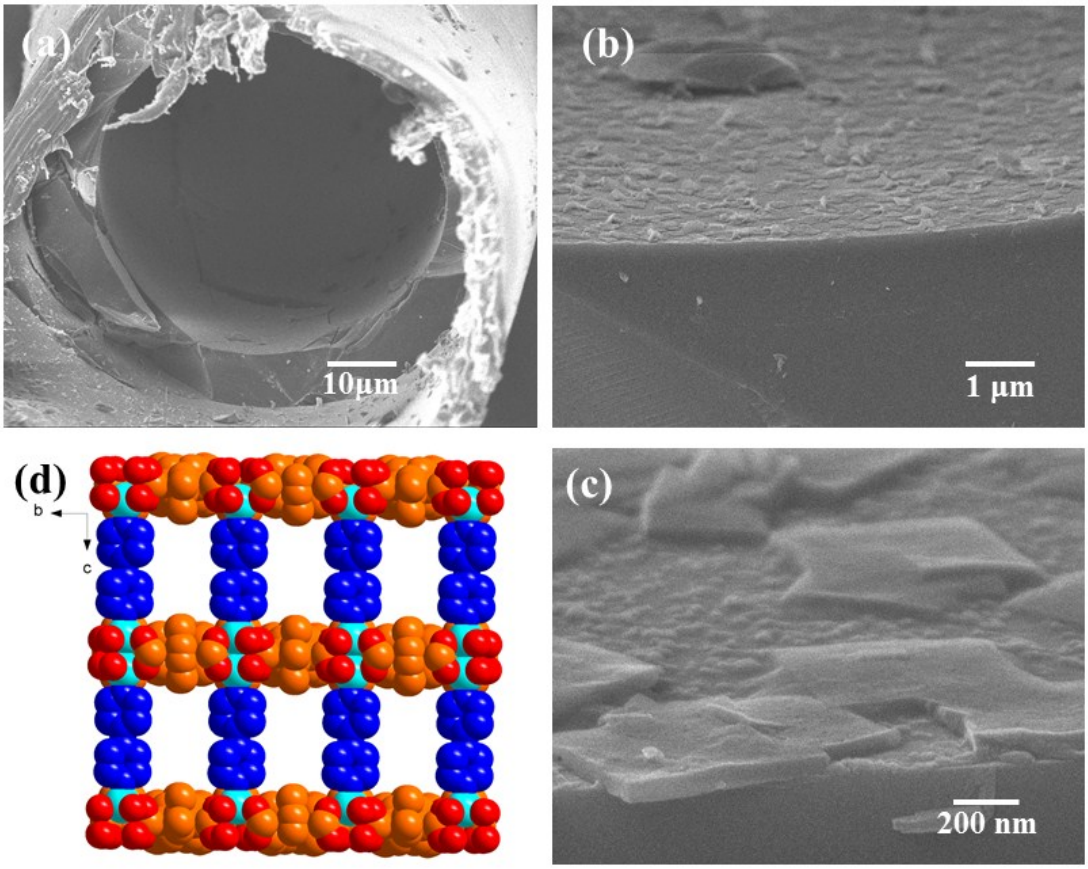


Figure S4. SEM images (a-c) of Cu_2(D-cam)$_2$bipy@Poly(L-DOPA) thin film grown in capillary column using layer by layer approach; (d) the structure of chiral MOF Cu_2(D-cam)$_2$bipy.

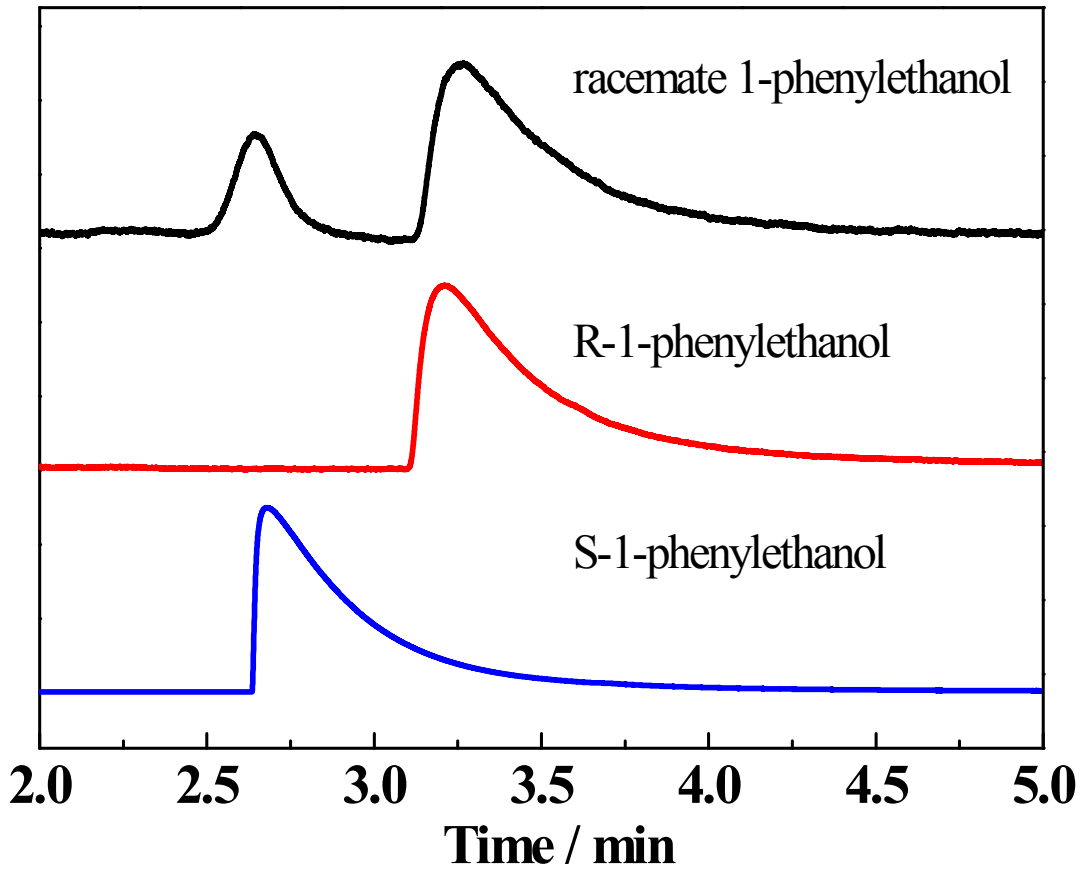


Figure S5. The gas chromatographic separation of a mixture of enantiomers phenylethanol (R- phenylethanol and S-phenethanol) in Cu_2(D-cam)$_2$bipy@Poly(L-DOPA) grown in capillary column; (b) Experimental setup: column: Cu_2(D-cam)$_2$bipy@Poly(L-DOPA) (30 m × 0.25 mm ×0.15 μm); carrier: N_2, flow: 4.37 mL min−1, 76.2 cm s^{-1}; oven: 90 °C,isotherm; injector: split, 9: 1 at 200 °C.

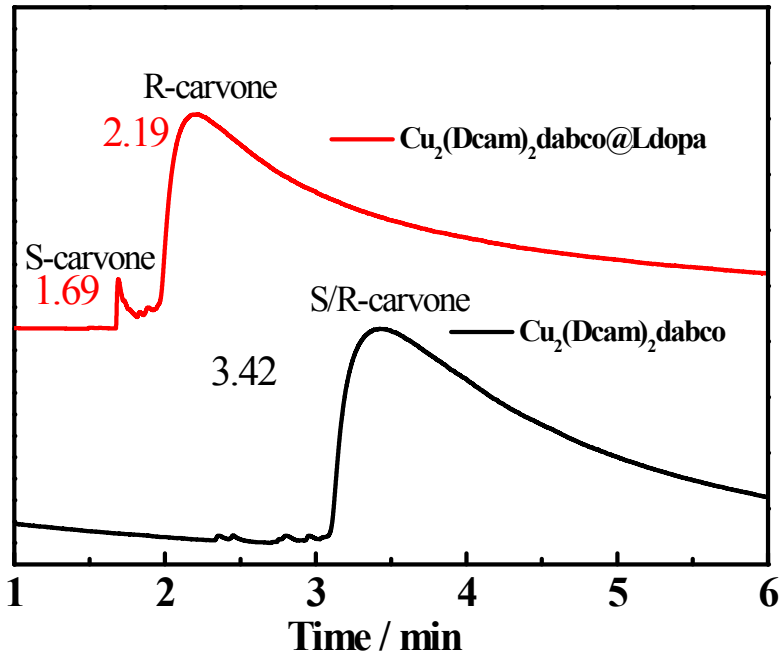
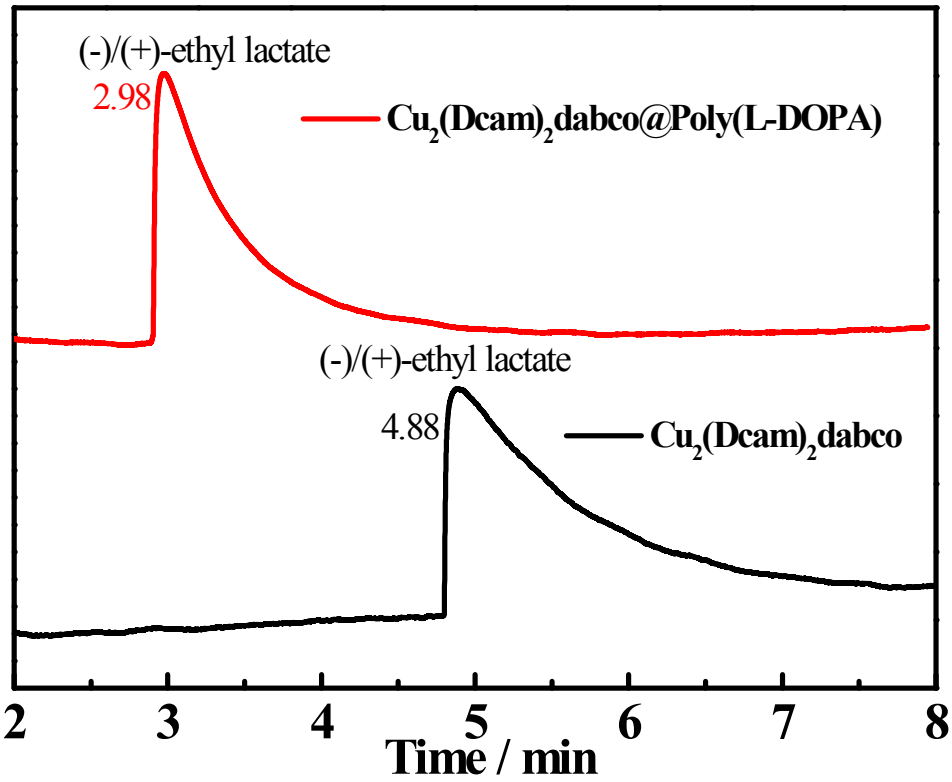


Figure S6. The gas chromatographic separation of a mixture of enantiomers carvone (R- carvone and S- carvone) in Cu_2(D-cam)$_2$dabco and Cu_2(D-cam)$_2$dabco@Poly(L-DOPA) grown in capillary column.



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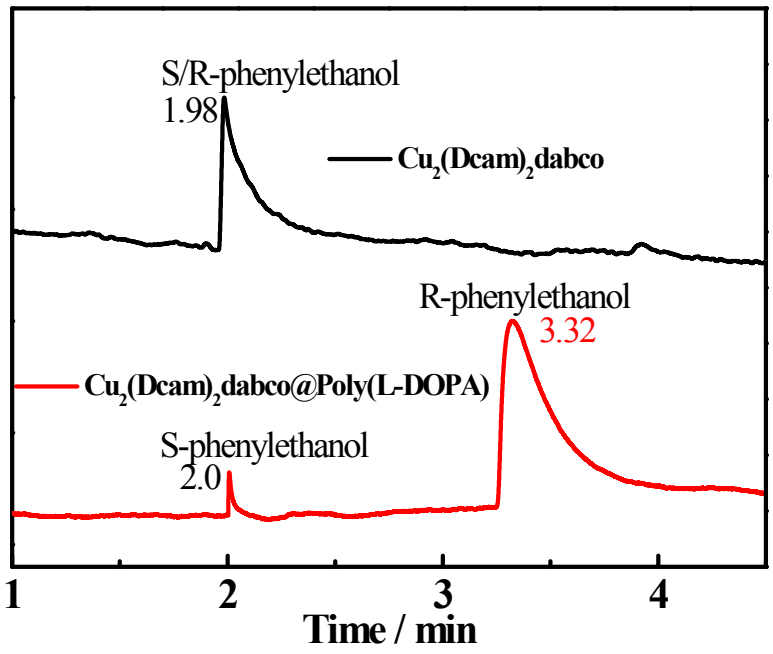

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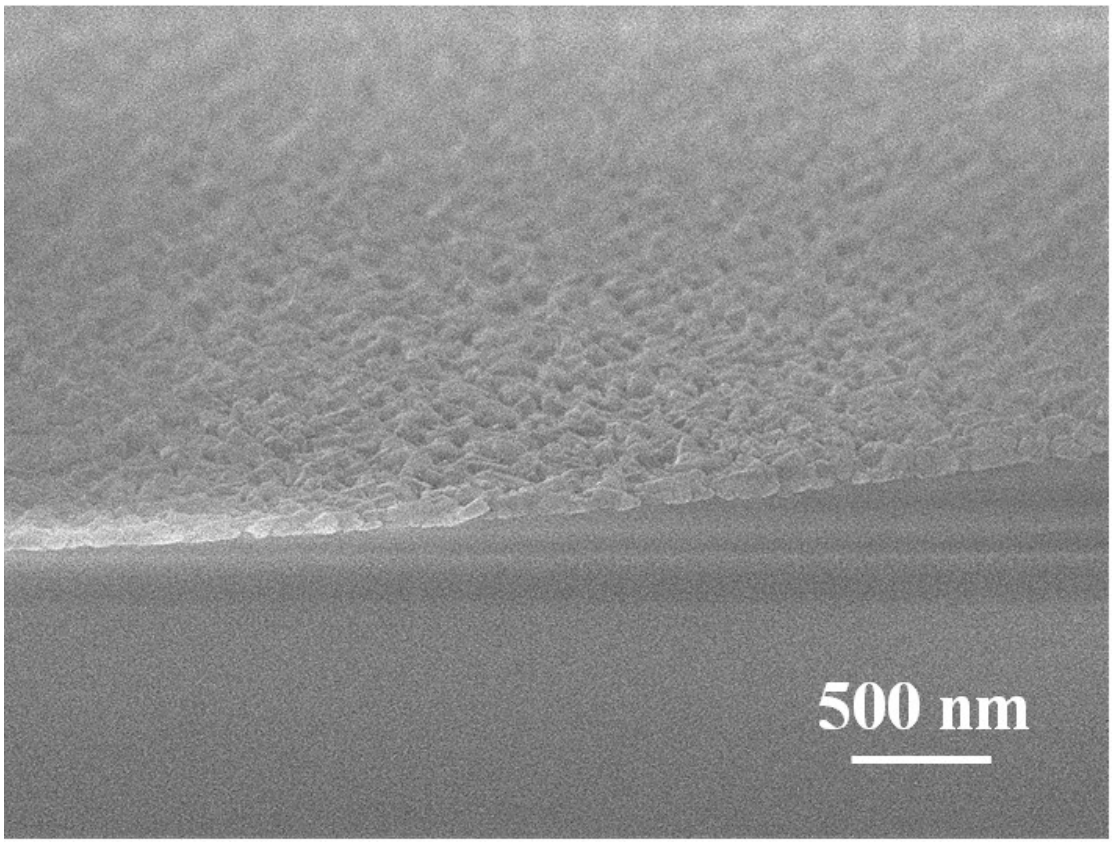

Figure S9. SEM images of Cu_2(D-cam)$_2$dabco@Poly(L-DOPA) thin film grown in capillary column using layer by layer approach after the GC experiment.

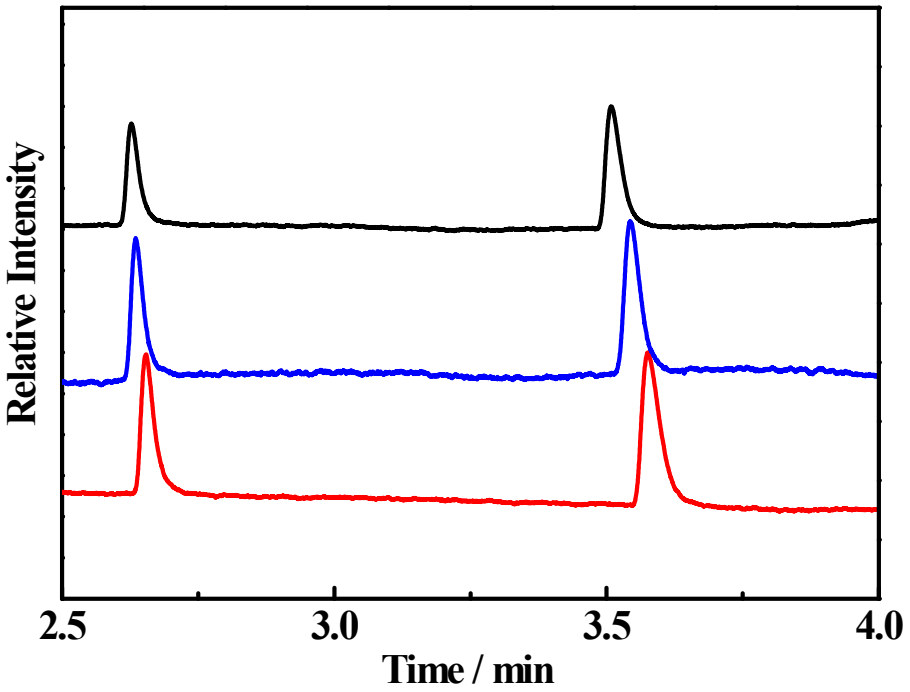

Figure S10. The repeated retention time of a mixture of enantiomers (L- and D-methyl lactate) in $Cu_2(Dcam)_2dabco$@Poly(L-DOPA) thin film grown in capillary column in GC experiment, showing the sample is very stable for improved enantiomer separation.