Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Porous aromatic cage-based electrochemical sensor for enantioselective recognition of DOPA

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Experimental Procedures

General information

All reagents and solvents were obtained from commercial sources and used without further purification. Fourier transform infrared (FT-IR) spectra (KBr pellets) were recorded in the range 4000–400 cm^{-1} on Nicolet 6700 using the KBr pellet method. UVVis spectra were recorded at a UV-Vis-NIR spectrophotometer (Hitachi U-3900).

Synthesis of C_{60}@R/S-PAC-2.

R/S-Br-BINAM (0.066 g, 0.15 mmol), TFP (0.021 g, 0.1 mmol) , fullerene C_{60} (0.01mmol), O-Xylene (5 mL) , n-butanol (1 mL) and 6M acetic acid (0.6 mL) were combined in a 20 mL Teflon reactor, sealed, and heated to 120°C for 84 h. After cooling in air to room temperature, the resulting crystals were filtered and repeatedly washed with Ethyl ether.

Electrochemical experiments

A bare glass carbon electrode (GCE) with a radius of 3 mm was polished continuously on a chamois for 60 s and then rinsed with deionised water. A total of 1 mg of samples, 200 μL ethanol and 100 μL of Nafion solution (5 wt%) were first dispersed in 200 μL of water to produce a suspension. Following a 30-minute sonication-assisted treatment, the homogeneous sample suspensions were loaded onto GCE. The experiments electrochemical tests were conducted on a CHI-760E electrochemical workstation and a Biologic VMP3 electrochemical workstation with a three-electrode configuration. An Ag/AgCl (saturated KCl) electrode and a Pt were used as a reference electrode and counter-electrode respectively; GCE loaded with samples were used as working electrodes.

Electrochemical Chiral Recognition of Analyte Enantiomers.

Electrochemical chiral recognition of analyte enantiomers was investigated by differential pulse voltammetry (DPV). The as-prepared chiral electrodes were placed into 5mL test fluid. Then, DPVs were recorded from 0.0 to 0.7 V, with a step potential of 4 mV and an amplitude of 50 mV. Finally, the peak current ratio was calculated to evaluate the recognition efficiency.

Results and Discussion

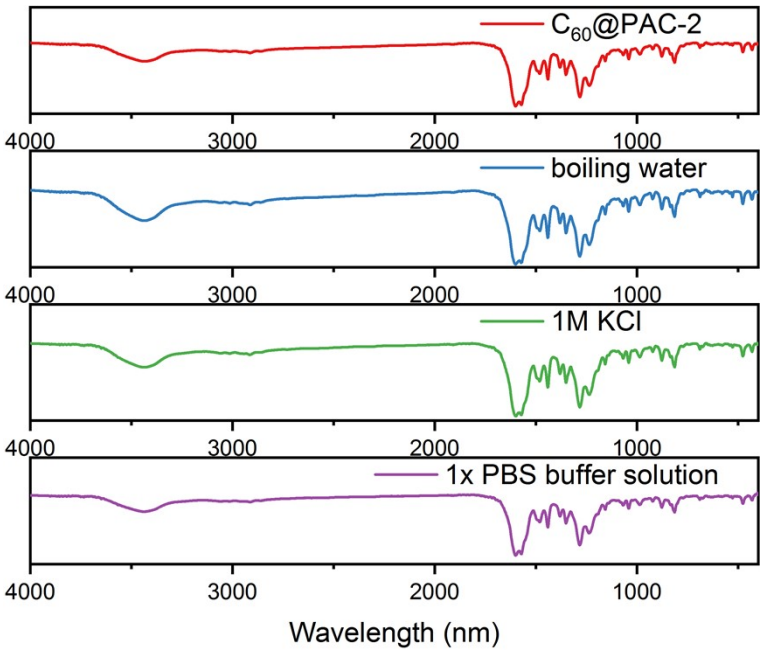

Fig. S1. FTIR spectrum (KBr pellets) of C_{60}@*R*-PAC-2 after soaking under different conditions. FTIR spectrum of the pristine C_{60}@*R*-PAC-2 (Red), under boiling water (blue), 1M KCl (green) and 1 X PBS buffer solution (purple).

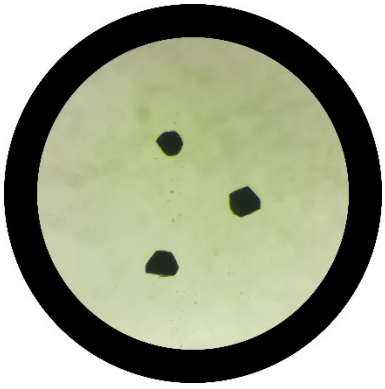

Fig. S2. Photograph of the prepared crystals of C_{60}@*R*-PAC-2.

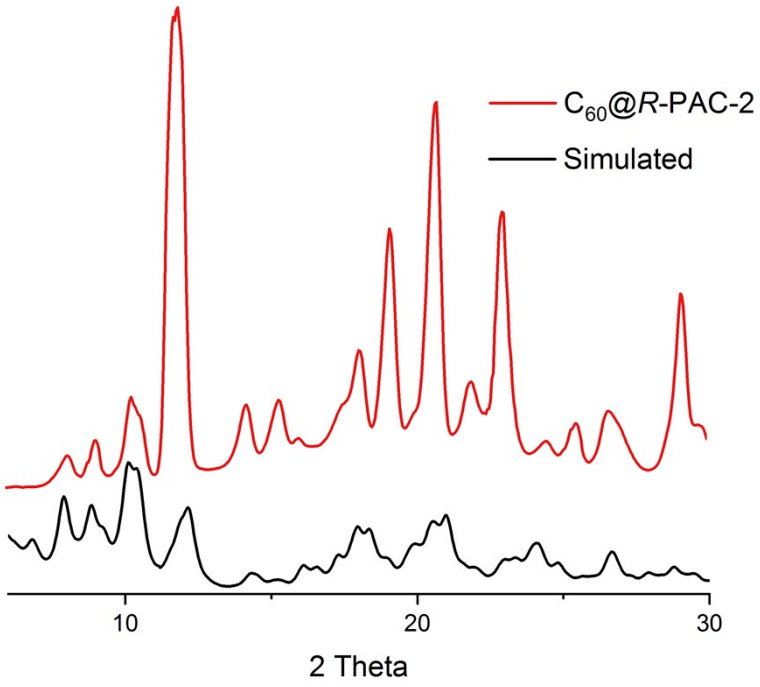

Fig. S3. PXRD patterns of cages. The synthesized (red line) and simulated one of C_{60}@*R*-PAC-2(black line).

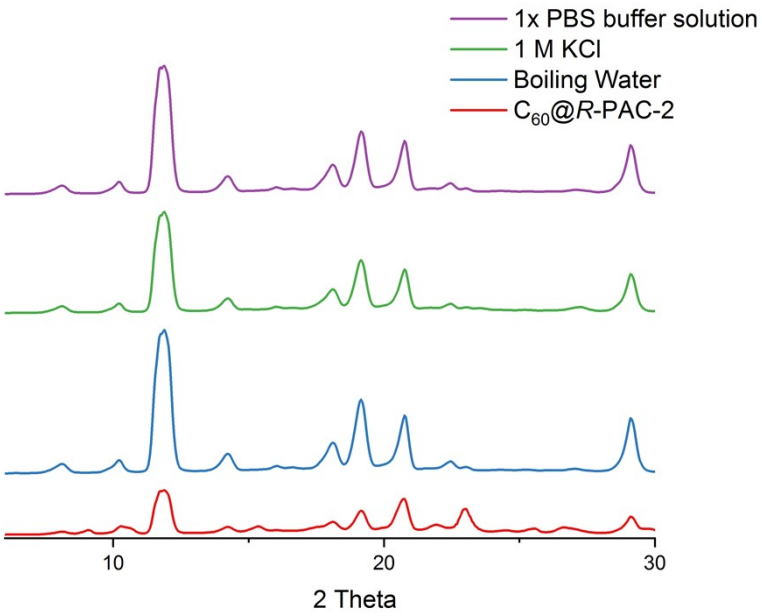

Fig. S4. PXRD patterns of C_{60}@*R*-PAC-2 under different harsh conditions. The the C_{60}@*R*-PAC-2 (red), C_{60}@*R*-PAC-2 under boiling water (blue), 1M KCl (green) and 1 X PBS buffer solution (purple).

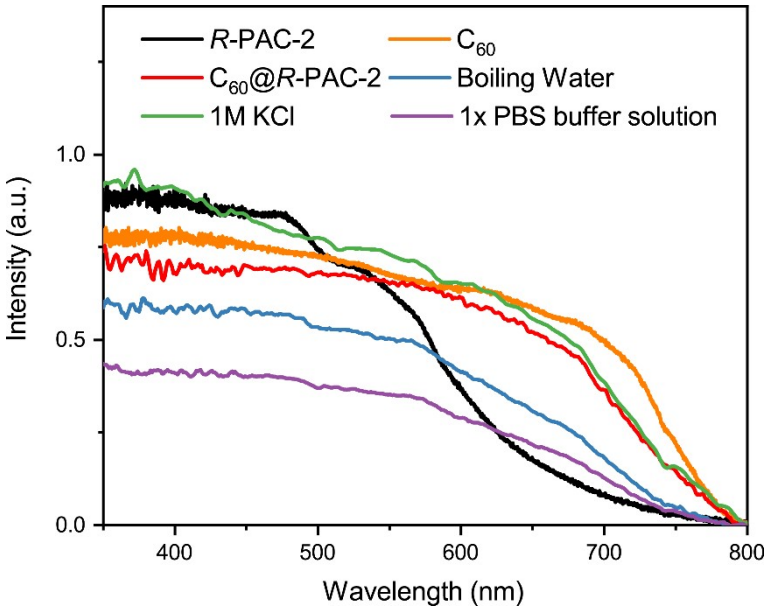

Fig. S5. UV-vis diffuse reflectance spectra of *R*-PAC-2 (black) and C_{60}@*R*-PAC-2 (red). UV-vis diffuse reflectance spectra of the pristine C_{60}@*R*-PAC-2 under boiling water (blue), 1M KCl (green) and 1 X PBS buffer solution (purple).

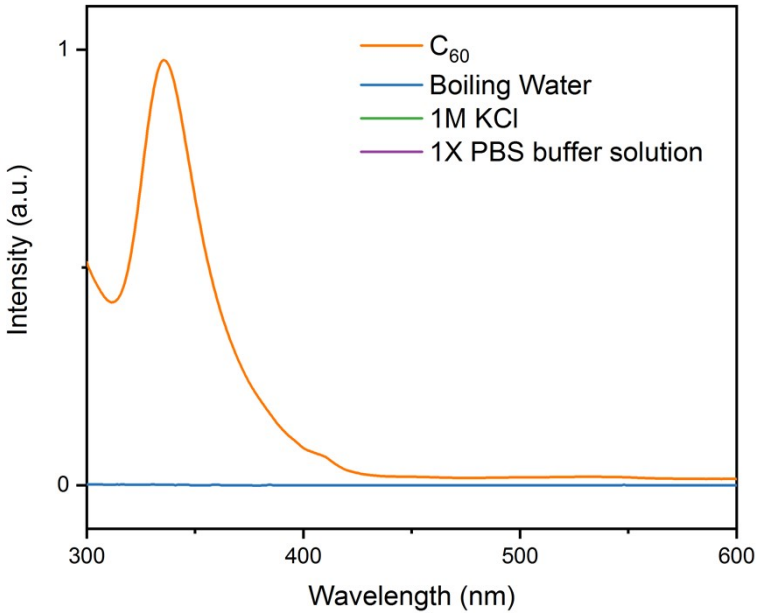

Fig. S6. UV absorption spectra of C_{60} in toluene (orange). UV absorption spectra of different solution after immersing C_{60}@*R*-PAC-2.

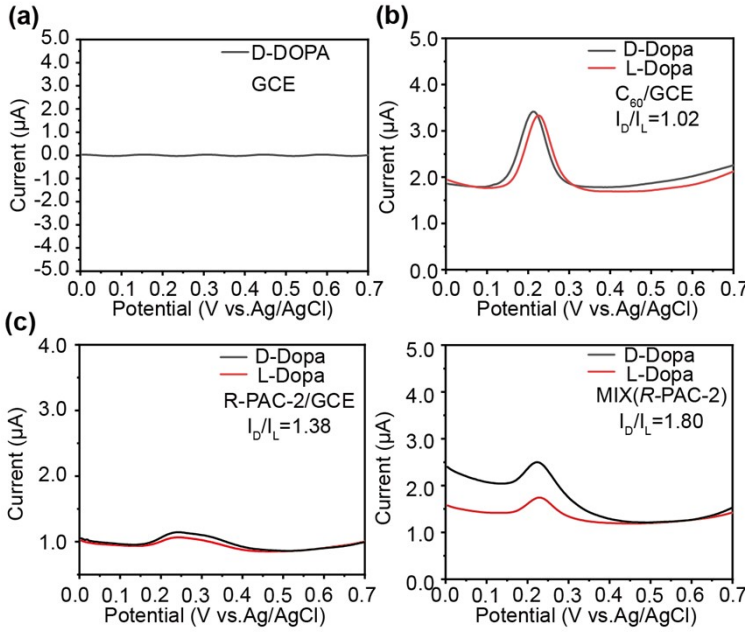

Fig. S7. DPV of (a) GCE, (b) C_{60}/GCE, (c) PAC-2/GCE and (d) MIX in 0.01 M PBS solution containing 0.1 mM D-Dopa or L-Dopa.

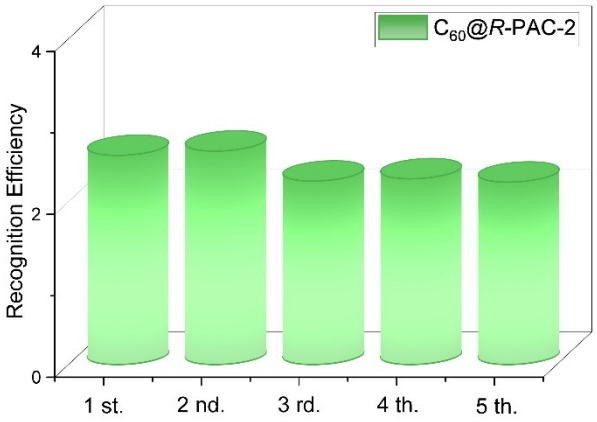

Fig. S8. Repeated electrochemical recognition of DOPA enantiomers by using C_{60}@*R*-PAC-2/GCE electrode.

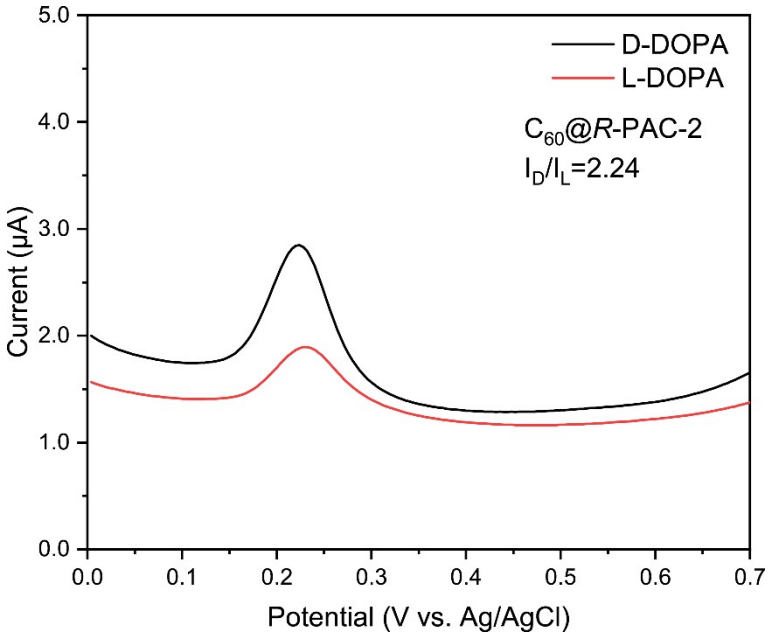

Fig. S9. The stability of the C_{60}@R-PAC-2/GCE sensor was studied after storing for 1 week.

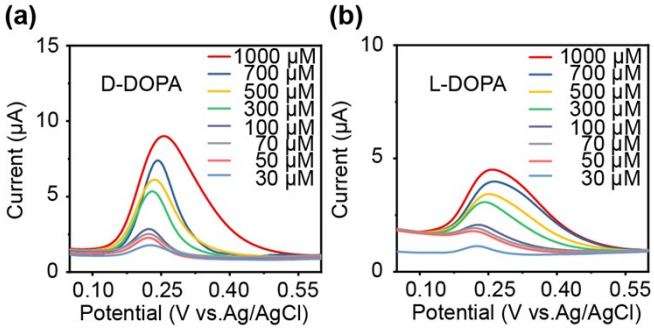

Fig. S10. DPV curves of increased concentrations (30 - 1000 μM) of enantiomers D-DOPA(a) and L-DOPA(b) at the C_{60}@*R*-PAC-2/GCE electrode.

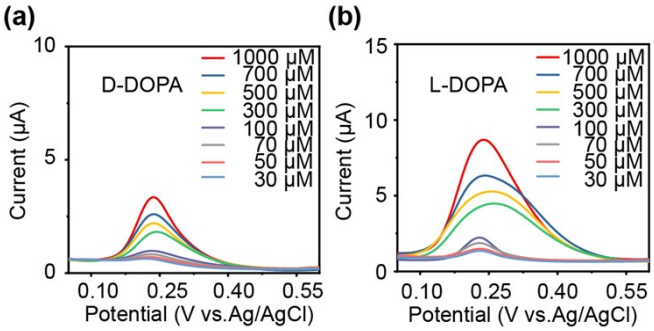

Fig. S11. DPV curves of increased concentrations (30 - 1000 μM) of enantiomers D-DOPA(a) and L-DOPA(b) at the C_{60}@*S*-PAC-2/GCE electrode.

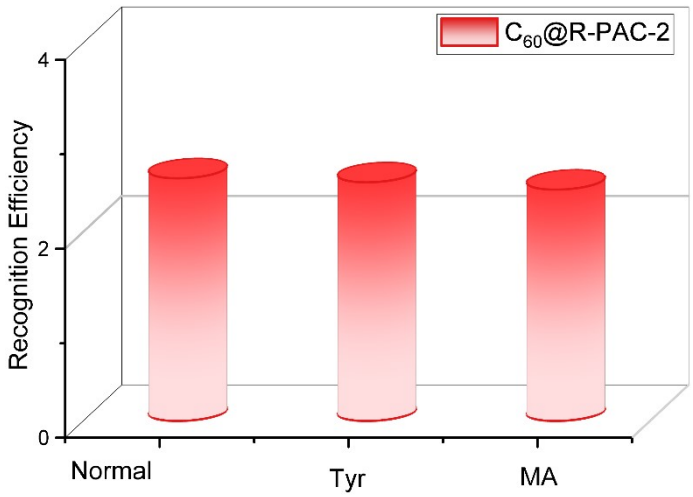

Fig. S12. The detection performance of chiral sensor C_{60}@*R*-PAC-2 for interfering organic molecules.

Supplementary Table 1. Summary of DOPA Chiral Sensors

Modifier	Method	Recognition difference	LOD	Ref.
AuND/GCE	DPV	2.33	2.5 μM	[1]
SWCNTs-EDA	CV	2.55	-	[2]
M-(6,5)-SWCNT	DPV	2.05	-	[3]
P-(6,5)-SWCNT	DPV	1.90	-	[3]
β-CD/MWCNTs-IL	DPV	1.51	1.2 nM	[4]
Poly-lysine	CV/DPV	1.56	0.17 μM	[5]
L-tryptophan / Graphene / Pt NPs	DPV	1.60	$1.7\ 10^{-8}$ M	[6]
cSWCNTs	SWV	1.4	-	[7]
GNPs/cSWCNTs	SWV	2.1	-	[8]
PLL/GCE	DPV	1.60	0.33 μM	[5]
P-SWCNTs/CFE	DPV	1.4	-	[9]
CdSe/ZnS QDs-PADP	Fluorescence	2.49	-	[10]
C_{60}@R-PAC-2	DPV	2.6	0.2μM	This work

Supplementary References

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