

Supporting Information

Autonomous macroscopic signal deciphering the geometric self-sorting of pillar[n]arenes

Mujeeb Alam,^a Rekha Sangwan,^a Chinmayee Agashe,^a Arshdeep Kaur Gill,^a and Debabrata Patra^{*a}

^aInstitute of Nano Science and Technology, Knowledge City, Sector 81, SAS Nagar, Mohali, Punjab, 140306, India. Email: patra@inst.ac.in.

Table of Content

- 1. Experimental Details**
- 2. Synthesis of Pillar[n]arenes**
 - 2.1 Synthesis of Cationic Pillar[5]arene ([⊕]P[5]A)
 - 2.2 Synthesis of Cationic Pillar[5]arene ([⊕]P[6]A)
 - 2.3 Synthesis of Anionic Pillar[5]arene ([⊖]P[5]A)
 - 2.4 Synthesis of Anionic Pillar[5]arene ([⊖]P[6]A)
- 3. Substrate**
- 4. Multilayer Film Pattern and Fluid Flow Tracking**
- 5. Fabrication of Dumbbell-Shaped Channel**
- 6. References**

1. Experimental Details

1.1 Reagents and Materials

Boron trifluoride diethyl etherate ($\text{BF}_3 \cdot (\text{OC}_2\text{H}_5)_2$), Branched polyethyleneimine (bPEI, 25kDa), methy viologen, ferrocene carboxylic acid and sulfate latex particles (5 μm in diameter) were purchased from Sigma-Aldrich. 1,4-bis(2-hydroxyethoxy)benzene, paraformaldehyde, trimethylamine, were obtained from TCI chemicals. Acetonitrile, 1,2-dichloroethane, hexane, dichloromethane, chloroform, tetrahydrofuran, potassium carbonate, methanol, ethanol, dimethyl sulfoxide (DMSO), hydrochloric acid and sodium hydroxide were purchased from Merck. DC/GEN/184 SYLGARD (PDMS Elastomer KIT) was supplied by from Kevin Electrochem. Millipore water (18.2 $\text{M}\Omega \cdot \text{cm}$ at 25 °C) was used in all experiments.

1.2 Characterization

The chemical structures of all synthesized compounds were characterized by ^1H nuclear magnetic resonance (^1H NMR) spectra on a 400 MHz Bruker AvanceII, and D_2O , DMSO-d_6 , CDCl_3 as the solvents. Isothermal Titration Calorimetric measurements were performed by Malvern MicroCal PEAQ-ITC. Videos were recorded using an inverted optical microscope (OLYMPUS IX73) with an X-Cite 120 LED Boost, via a 10X objective (CPLN10XPH), excitation light was focused on the sample. Emission light was captured by the objective, passed through interference filters and eventually recorded at 15 frames per second by a high resolution coloured cooled camera (DP74). Videos were recorded with DP74 camera connected to an optical microscope at 20X. To measure fluid-pumping velocity in each experiment, 20 tracer particles were tracked for a 30 second time interval using Tracker software (Motion Analysis Software).

2. Synthesis of Pillar[n]arenes

2.1 Synthesis of Cationic Pillar[5]arene ($^{\oplus}\text{P}[5]\text{A}$)

The cationic pillar[5]arene was synthesized according to the following reaction procedure.¹

2.1.1 Synthesis of 1

Carbon tetrabromide (39.8 g, 120 mmol) was gradually added in minute amounts to a 300 mL dry acetonitrile solution containing 1,4-bis(2-hydroxyethoxy)benzene (10.0 g, 50.4 mmol) and triphenylphosphine (31.5 g, 120 mmol) at 0 °C with stirring. The resulting solution was stirred for 4 hours under N_2 once the reaction mixture had cooled to room temperature. After 200 mL

of cold water was added to the reaction mixture, product 1 precipitated as a white solid. The product was collected using vacuum filtration and then thoroughly cleaned in a 60:40 methanol/water solution before being recrystallized from methanol. The white flake-like

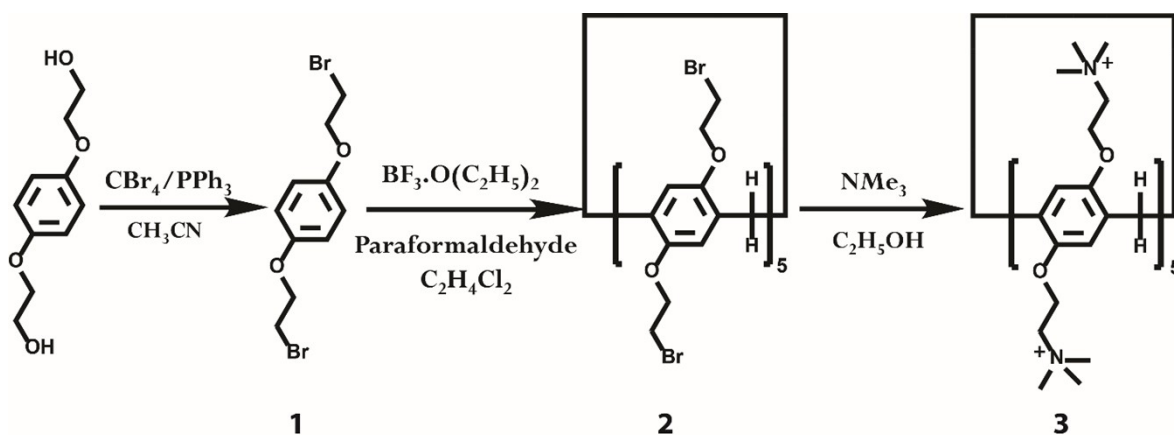


Figure S1. Synthesis of cationic pillar[5]arene ($^{\oplus}\text{P}[5]\text{A}$)

crystals were dried using a high vacuum.

2.1.2 Synthesis of 2

Paraformaldehyde (0.349 g, 11.5 mmol) was added to a solution of **1** (3.37 g, 11.5 mmol) in 1,2-dichloroethane (200 mL) under N_2 atmosphere. The solution was then stirred at room temperature for 3 hours with boron trifluoride diethyl etherate ($\text{BF}_3(\text{OC}_2\text{H}_5)_2$, 1.63 g, 11.5 mmol). A green product was prepared. After the solvent was removed, the solid was purified by column chromatography on silica gel with hexane/dichloromethane (1:2 v/v) as the eluent, obtaining a white powder.

2.1.3 Synthesis of 3

Compound **3** (1.00 g, 0.595 mmol) and trimethylamine (33% in ethanol, 6.43 mL, 23.8 mmol) were added to ethanol (50 mL). Overnight, the mixture was refluxed. The solvent was then evaporated, and 20 mL of deionized water was added. Following filtering, a clear solution was recovered. The water was then entirely evaporated, yielding **3** as a colourless solid (1.28 g, 95 percent). The ^1H NMR spectra of **3** is shown in Figure S2. Figure S7 depicts the ^1H NMR spectrum of **3**. ^1H NMR (400 MHz) δ (ppm): 6.94 (s, 10H), 4.44 (s, 20H), 3.93 (s, 10H), 3.80 (s, 20H), 3.22 (s, 90H).

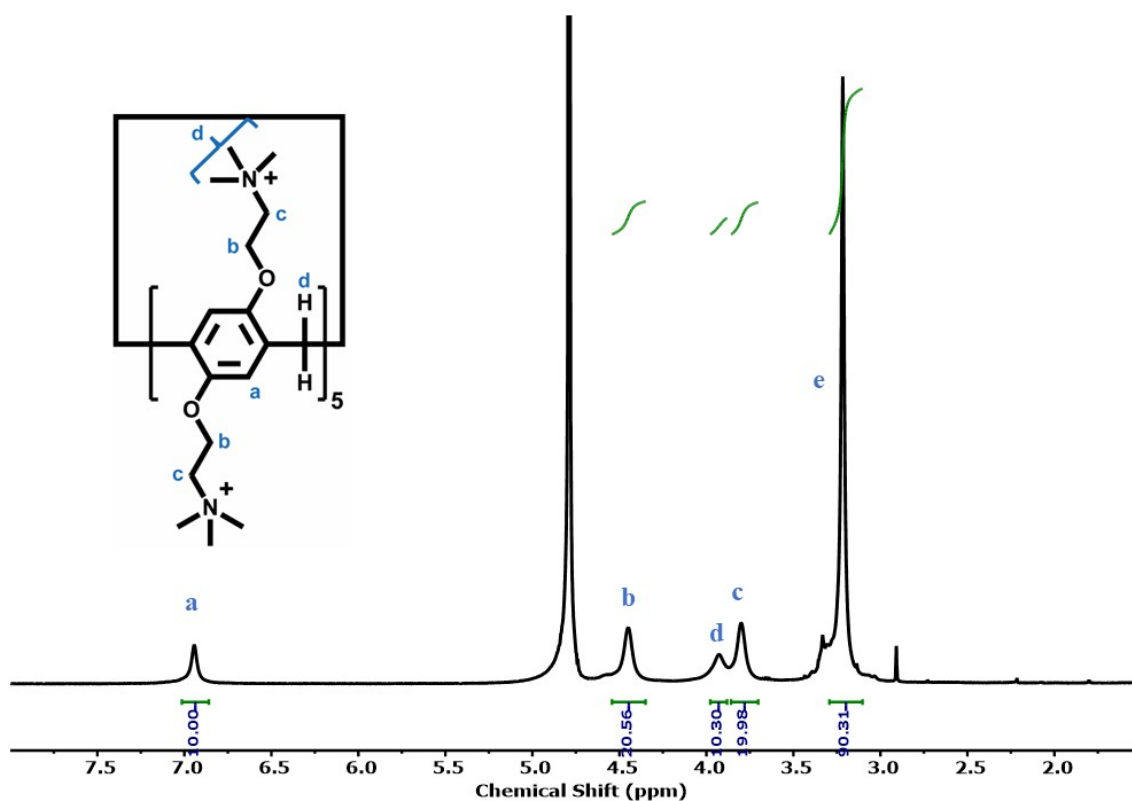


Figure S2. 400 MHz ¹H NMR spectra of 3 in D₂O

2.2 Synthesis of Cationic Pillar[6]arene (⁺P[6]A)

The cationic pillar[6]arene was synthesized according to the following reaction procedure.²

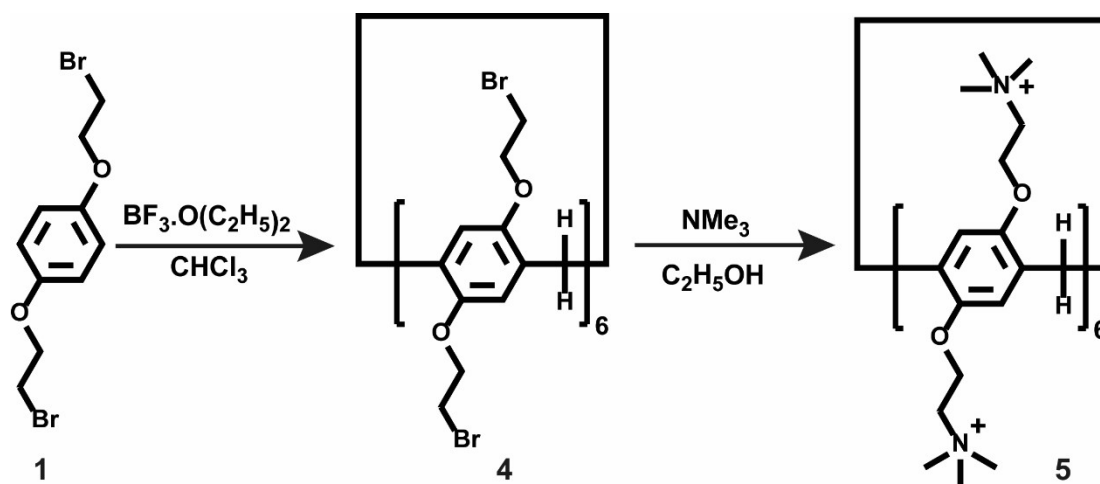


Figure S3. Synthesis of cationic Pillar[6]arene (⁺P[6]A)

2.2.1 Synthesis of 4

Paraformaldehyde (0.349 g, 11.5 mmol) was added to a solution of 1 (3.37 g, 11.5 mmol) in 1, chloroform (200 mL) under N₂ atmosphere. The solution was then stirred at room temperature for 3 hours with boron trifluoride diethyl etherate (BF₃(OC₂H₅)₂, 1.63 g, 11.5 mmol). A green product was prepared. After the solvent was removed, the solid was purified by column chromatography on silica gel with hexane/dichloromethane (1:2 v/v) as the eluent, obtaining a white powder.

2.2.2 Synthesis of 5

Compound 4 (1.00 g, 0.595 mmol) and trimethylamine (33% in ethanol, 6.43 mL, 23.8 mmol) were added to ethanol (50 mL). Overnight, the mixture was refluxed. The solvent was then evaporated, and 20 mL of deionized water was added. Following filtering, a clear solution was recovered. The water was then entirely evaporated, yielding 3 as a colourless solid (1.28 g, 95 %). The ¹H NMR spectra of 5 is shown in Figure S4.

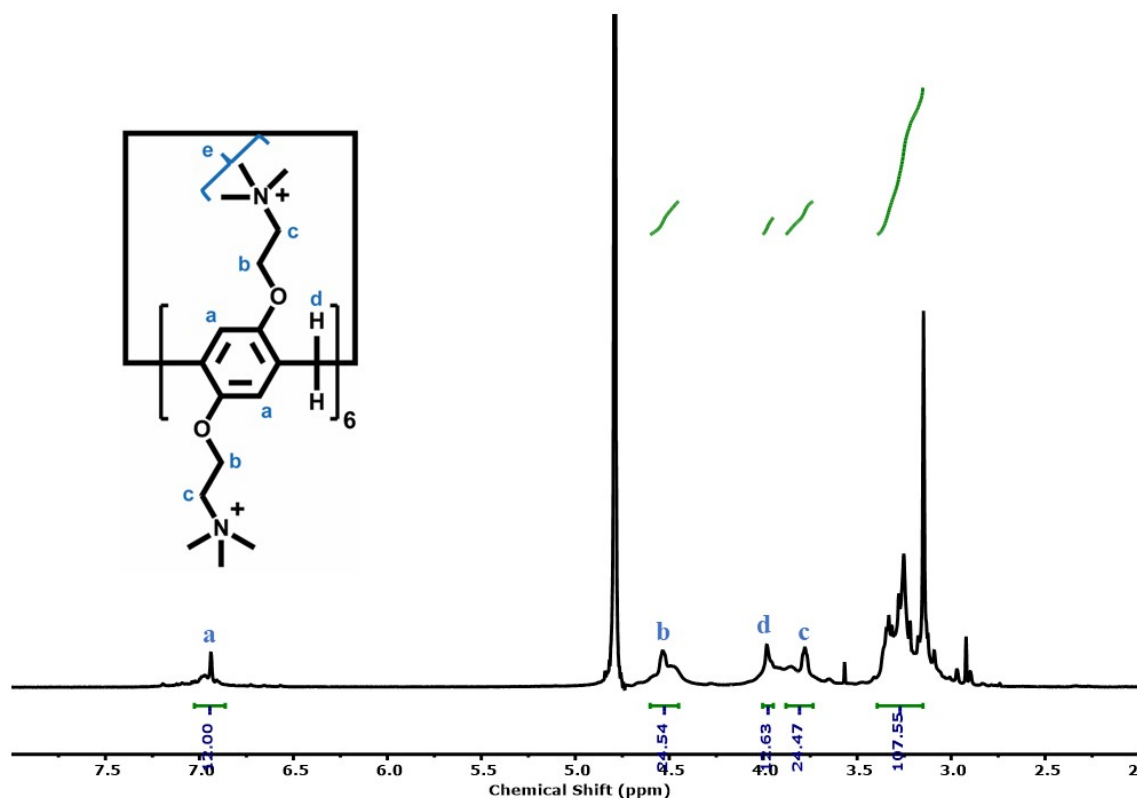


Figure S4. 400 MHz ¹H NMR spectra of 5 in D₂O.

2.3 Synthesis of Anionic Pillar[5]arene (°P[5]A)

The anionic pillar[6]arene was synthesized according to the following reaction procedure.³

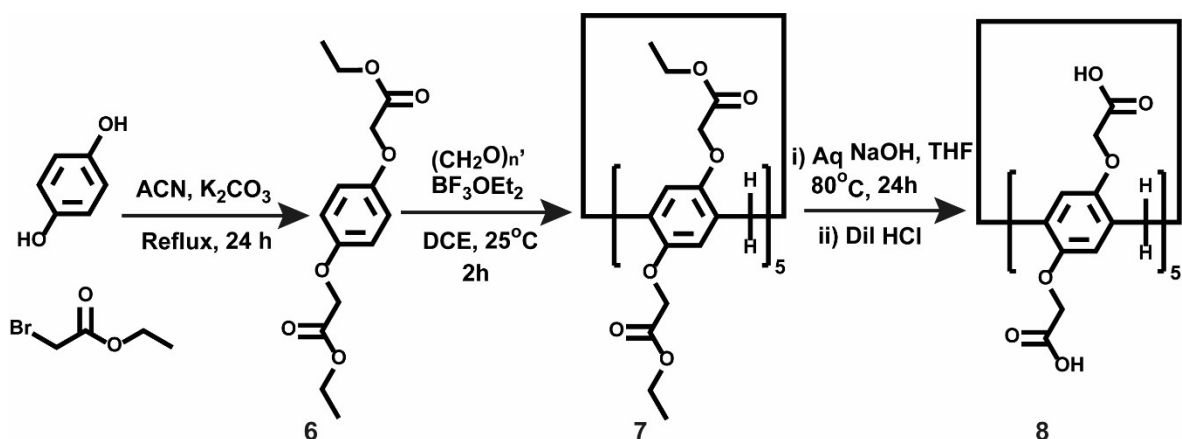


Figure S5. Synthesis of anionic Pillar[5]arene (${}^{\ominus}P[5]A$)

2.3.1 Synthesis of 6

Hydroquinone (5.5 g, 50 mmol) and ethyl bromoacetate (300 mmol) were dissolved in acetone (300 ml) under a nitrogen atmosphere, followed by the addition of K_2CO_3 . The reaction mixture was refluxed for one day. The cooled reaction mixture was then filtered and washed with DCM. To get a white powder, the residue was purified using column chromatography on silica gel (hexane/ethyl acetate, 4:1).

2.3.2 Synthesis of 7

Paraformaldehyde was added to a solution of compound 6 (676 mg, 2 mmol) in 1,2 dichloroethane (10 mL) (186 mg, 6 mmol). The solution was then treated with 0.25 mL (2 mmol) boron trifluoride diethyletherate $BF_3 \cdot Et_2O$ and stirred at room temperature for 2 hours. After quenching with water, the organic layer was washed with water, saturated aqueous $NaHCO_3$ solution, and brine, dried over Na_2SO_4 , and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1 \rightarrow 2:1) to yield a white powder.

2.3.3 Synthesis of 8

Compound 7 (0.150 g, 0.102 mmol), NaOH (0.300 g), ethanol (15 mL), water (15 mL), and THF (15 mL) were refluxed for 24 hours. Diluted aqueous HCl was added to the solution. Filtration was used to collect the precipitated solid. The solid was washed repeatedly with water and dried under reduced pressure. The 1H NMR spectra of 8 is shown in Figure S6.

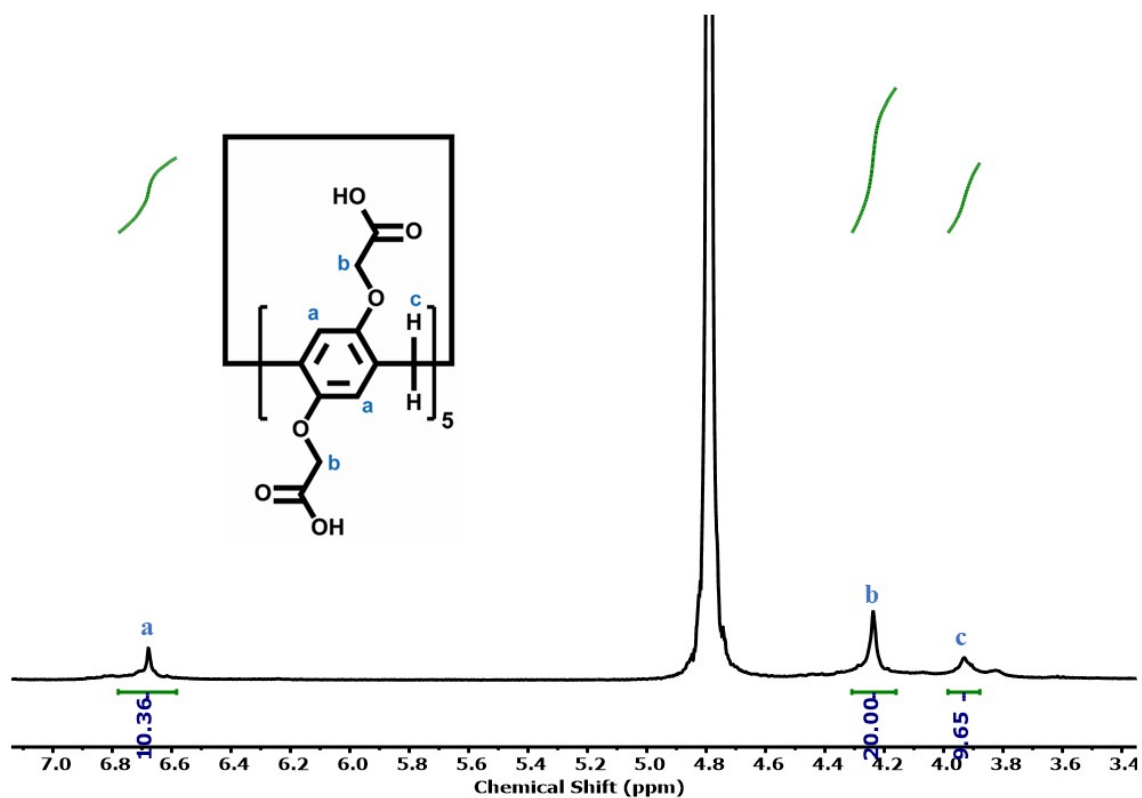


Figure S6. 400 MHz ^1H NMR spectra of 8 in DMSO-d_6 .

2.4 Synthesis of Anionic Pillar[6]arene ($^{\ominus}\text{P}[6]\text{A}$)

The anionic pillar[6]arene was synthesized according to the following reaction procedure.⁴

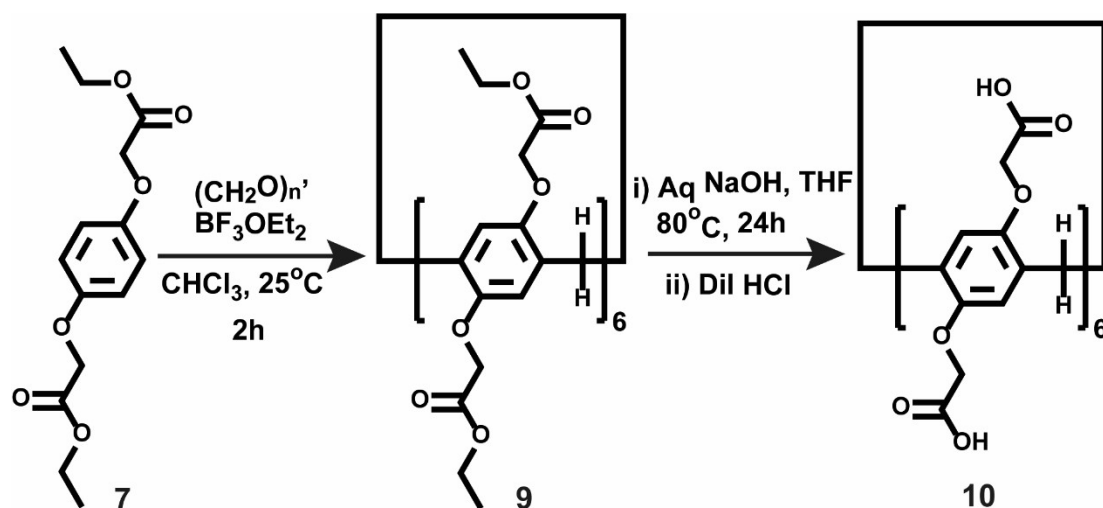


Figure S7. Synthesis of anionic Pillar[6]arene ($^{\ominus}\text{P}[6]\text{A}$)

2.4.1 Synthesis of 9

Paraformaldehyde was added to a solution of compound 6 (676 mg, 2 mmol) in chloroform (10 mL) (186 mg, 6 mmol). The solution was then treated with 0.25 mL (2 mmol) boron trifluoride

diethyletherate $\text{BF}_3\text{Et}_2\text{O}$ and stirred at room temperature for 2 hours. After quenching with water, the organic layer was washed with water, saturated aqueous NaHCO_3 solution, and brine, dried over Na_2SO_4 , and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1 \rightarrow 2:1) to yield a white powder.

2.4.2 Synthesis of 10

Compound 7 (0.150 g, 0.102 mmol), NaOH (0.300 g), ethanol (15 mL), water (15 mL), and THF (15 mL) were refluxed for 24 hours. Diluted aqueous HCl was added to the solution. Filtration was used to collect the precipitated solid. The solid was washed repeatedly with water and dried under reduced pressure. The ^1H NMR spectra of 10 is shown in Figure S8.

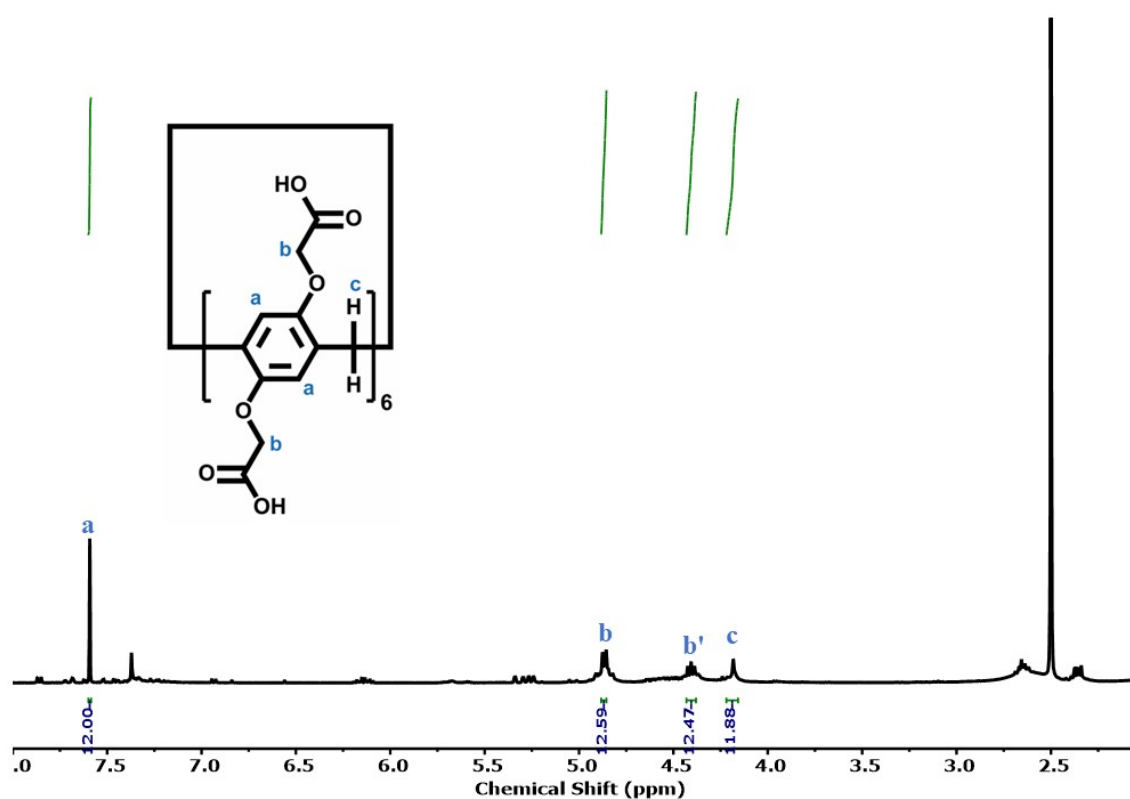


Figure S8. 400 MHz ^1H NMR spectra of 10 in DMSO-d_6 .

3. Substrate

The multilayer films were constructed using glass slides as a substrate. PDMS elastomer was made by blending Sylgard 184 in a 10:1 oligomeric base to curing agent weight ratio and casting onto a plastic Petri plate. Allow the prepolymer PDMS to settle for 2 hours in a convection oven set to $70\text{ }^\circ\text{C}$. Before deposition, all glass slides were cleaned with piranha solution for 45 minutes and then washed with DI water. *Beware! Piranha solution reacts severely to organic materials and must be handled with caution.*

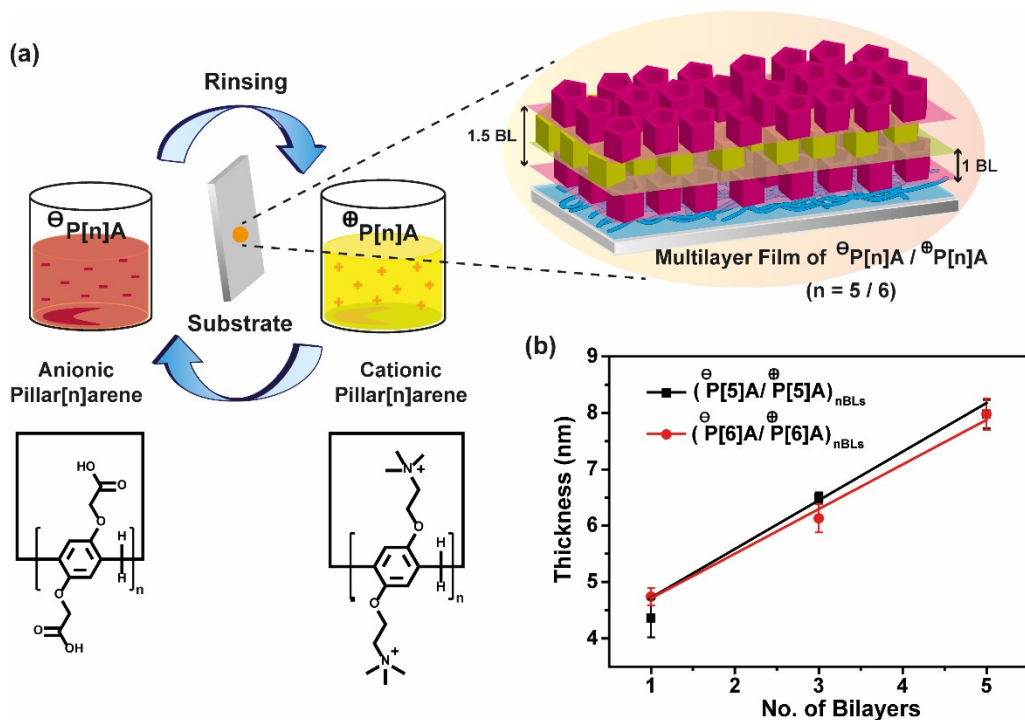


Figure S9. (a) Schematic of layer-by-layer (LbL) assembly using cationic and anionic pillar[n]arenes. (b) Thickness profile of multilayer films measured by ellipsometer.

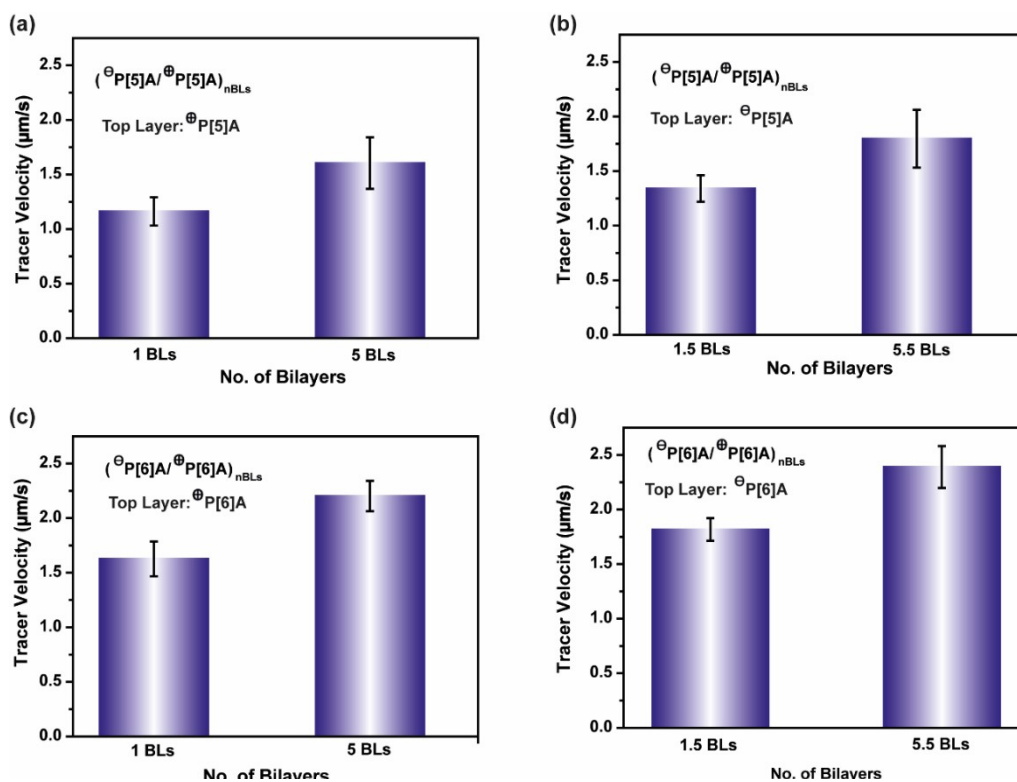


Figure S10. Tracer velocity with varying number of BLs for (a) (P[5]A[⊖]/P[5]A[⊕])_{1BL}, (b) (P[5]A[⊖]/P[5]A[⊕])_{1.5BL}, (c) (P[6]A[⊖]/P[6]A[⊕])_{1BL}, and (d) (P[6]A[⊖]/P[6]A[⊕])_{1.5BLs} in the presence of their corresponding substrates (P[5]A[⊖], P[5]A[⊕], P[6]A[⊖], and P[6]A[⊕]).

4. Multilayer Film Pattern and Fluid Flow Tracking

Initially, a thin layer of PDMS sheet with a 4.6 mm diameter circular aperture in the centre was manufactured and deposited on the glass surface such that the circular opening remained in the middle of the slide. The same slide was utilised as a substrate for the desired number of cycles of LbL deposition. As LbL deposition resulted in conformal coating, the layer was applied to the whole slide. Following the formation of the desired bilayers, the PDMS sheet was peeled away to expose the film pattern, leaving the covered portion uncoated. The surface was properly cleansed with water before being blown with nitrogen gas. After that, an air tight imaging chamber ($l = 1$ cm, $b = 1$ cm, $h = 1.8$ mm) was placed over the pattern, and an aqueous solution of substrates together with 5 μ m diameter neutral charged non-interacting polystyrene particles (tracer particles) was introduced into the chamber. The complete setup was observed using an optical microscope, and videos were recorded for later analysis in Tracker software. The flow velocity was determined by analysing the motion of tracer particles captured using digital cameras, which is the usual measuring approach in fluid dynamics research. In each experiment, 20 tracer particles were monitored for 30 seconds using Tracker software to measure fluid pumping velocity.

5. Fabrication of Dumbbell-Shaped Channel

Soft lithography was used to construct microfluidic channels.⁵ The master framework was made first using the CleWin software. Following that, the SU-8 2100 photoresist was spin-coated on a 4×4 silicon wafer, and the pattern was transferred to the wafers via maskless photolithography (Durham Magneto Optics Maskless MicroWriter ML3). The surface was then dipped into the developer and rinsed with 2-propanol. The patterned surface was then baked for 2 minutes to stabilise the structure. The wafer was poured with PDMS 184 SYLGARD and a curing agent at a 10: 1 (w/w) ratio and degassed using a vacuum desiccator until the trapped air bubbles were released. The device was placed in a 60 °C oven for 1 hour. The microchannels formed on the PDMS mould were removed from the wafer after drying, and the device was punctured with a 1 cm diameter biopsy punch.

6. References

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