

# Supporting Information

## Molecular Recognition with Microporous Multi-layer Films Prepared by Layer-by-Layer Assembly of Pillar[5]arenes

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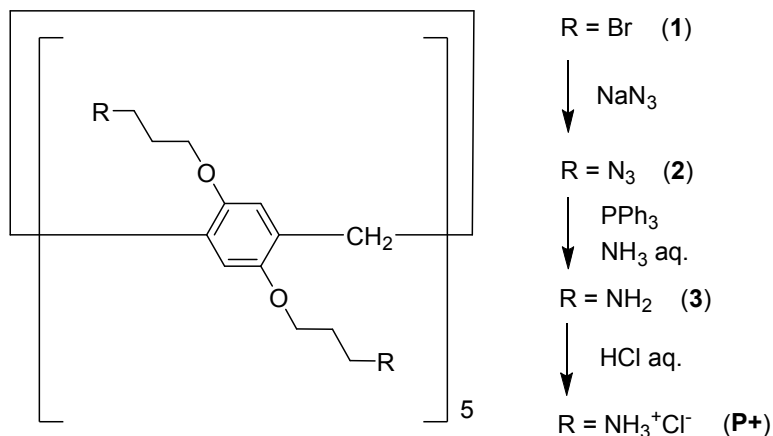
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## Experimental section

**Materials.** All solvents and reagents were used as supplied. Per-ethylated pillar[5]arene (**C2[5]**), anionic pillar[5]arene (**P-**) and unit models (**M+** and **M-**) were synthesized according to the previous papers.<sup>S1-S4</sup>

**Measurements.** The  $^1\text{H}$  NMR spectra were recorded at 500 MHz and  $^{13}\text{C}$  NMR spectra were recorded at 125 MHz with a JEOL-ECA500 spectrometer. UV-Vis absorption spectra were recorded with a JASCO V-670.

**Cationic Pillar[5]arene (**P+**).** To a solution of **1**<sup>S5</sup> (600 mg, 3.30 mmol) in *N,N*-dimethylformamide (50 mL), sodium azide (324 mg, 4.92 mmol) was added. The mixture was stirred at 50 °C for 12 h. Water was added to the resulting solution. The precipitate was isolated by filtration, and washing with water to yield **2** as a white solid (700mg, yield 68%). The obtained product **2** (450 mg, 0.31 mmol) and triphenylphosphine (1.63 g, 6.20 mmol) were dissolved in THF (20 mL). The reaction mixture was stirred at 25 °C for 2 h. After then, ammonia water (5 mL, 25-28wt%) was added to the mixture. The reaction mixture was stirred at 25 °C for 72 h. Water and 12 M aqueous HCl solution was added to the mixture until the mixture became acidic condition (pH = 1). The mixture was concentrated in *vacuo* to give a white solid. The resulting mixture was filtered, and ammonia water (25-28wt%) was added to the filtrate until the mixture became basic condition (pH = 14). The white solid was washed with methanol to produce compound **3** as a pure white solid (120 mg, yield 33%).  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 500 MHz, 25 °C, ppm):  $\delta$  6.83 (s, 10H, phenyl), 3.99 (t, 20H, methylene), 3.80 (s, 10H, methylene bridge), 3.21 (t, 20H, methylene), 2.20 (m, 20H, methylene).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 125 MHz, 25 °C, ppm):  $\delta$  149.9, 129.1, 115.3, 80.9, 66.3, 37.2, 27.6.



HRESIMS:  $m/z$  calcd for  $C_{65}H_{101}N_{10}O_{10}$   $[M+H]^+$ : 1181.7702, found 1181.7708. To the suspension of compound **3** (100 mg, 0.0880 mol) in aqueous solution (20 mL), 12 M aqueous HCl solution was added until the mixture became acidic condition (pH = 1). The heterogeneous suspension became a homogeneous solution by adding aqueous ammonia solution. The resulting solution was evaporated to give the salt **P+**, quantitatively.

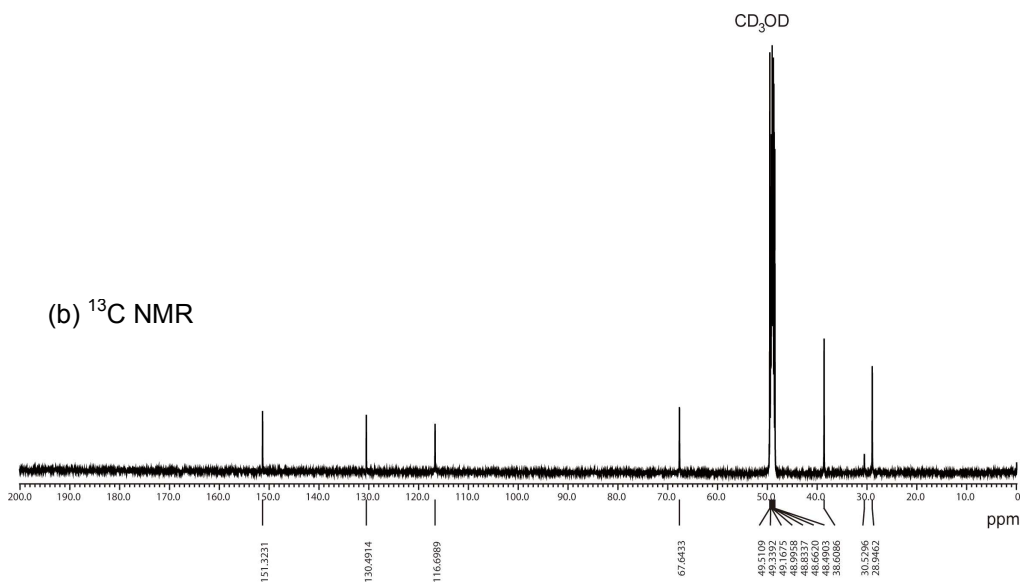
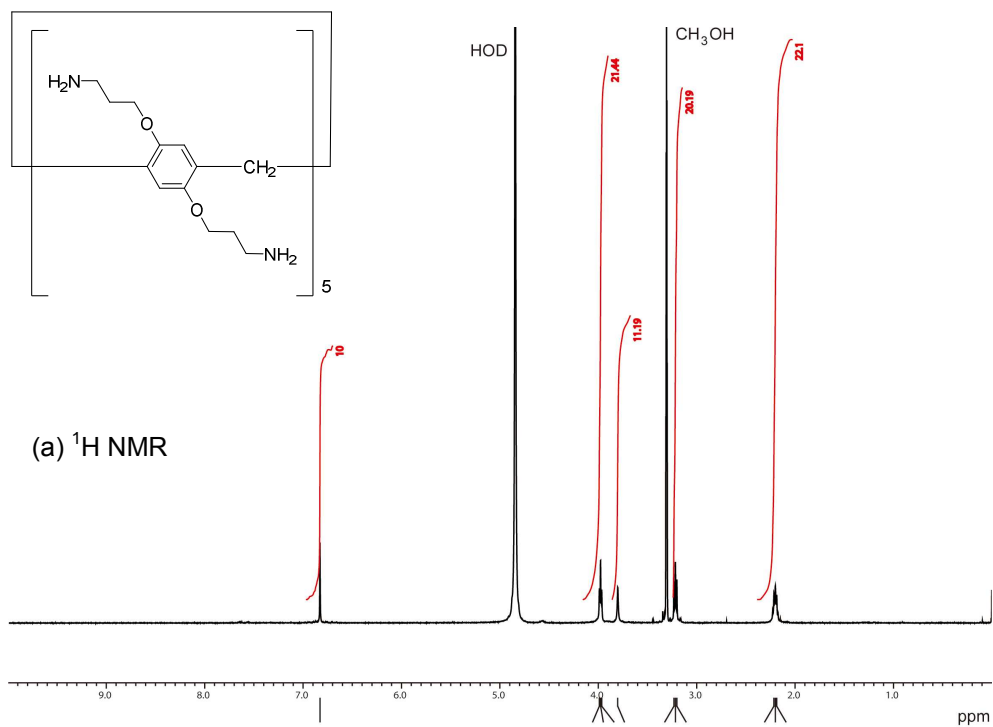
**LbL Film Assembly.** Substrates were sonicated in concentrated nitric acid for 30 min and finally washed with methanol for three times, and dried for 12 h at 100 °C to generate anionic silanol moieties on the surface. First, the substrate was immersed in **P+** in aqueous solution for 2 h to introduce **P+** molecules onto the anionic substrate surface. The immersing time (2 h) was enough to reach equilibrium state. The sample was washed with a large amount of water to remove excessive un-modified **P+** molecules and dried for 2 h at 25 °C under reduced pressure to obtain the cationic monolayer (**1L**). Then, **1L** was immersed into **P-** in aqueous solution for 2 h to introduce **P-** molecules onto **1L** of **P-** molecules, and washed with a large amount of water and dried in a vacuum for 2 h at 25 °C to give the bilayer with anionic surface (**2L**). Multi-layer films (**nL**, **n** is numbers of deposited times) were obtained by repeating the alternating immersion steps in **P+** and **P-** solutions.

**Determination of Association Constant.** In **C2[5]**  $\supset$  *p*-**DNB** complex in  $CDCl_3$ , chemical exchange between free and complexed species was fast on an NMR timescale. Thus, NMR titrations were done with solutions which had a constant concentration of **C2[5]** (5 mM) and varying concentrations of *p*-**DNB**. By the non-linear curve-fitting methods, the association constant for **C2[5]**-*p*-**DNB** complex in  $CDCl_3$  was estimated to be  $220 \pm 50 \text{ M}^{-1}$  for 1:1 stoichiometry. The non-linear curve-fitting was based on the equation:<sup>S3</sup>

$$\Delta\delta_{\text{obs}} = \frac{\Delta\delta_{11}}{2K[H]_0} [1 + K[G]_0 + K[H]_0 - \{(1 + K[G]_0 + K[H]_0)^2 - 4K^2[G]_0[H]_0\}^{1/2}]$$

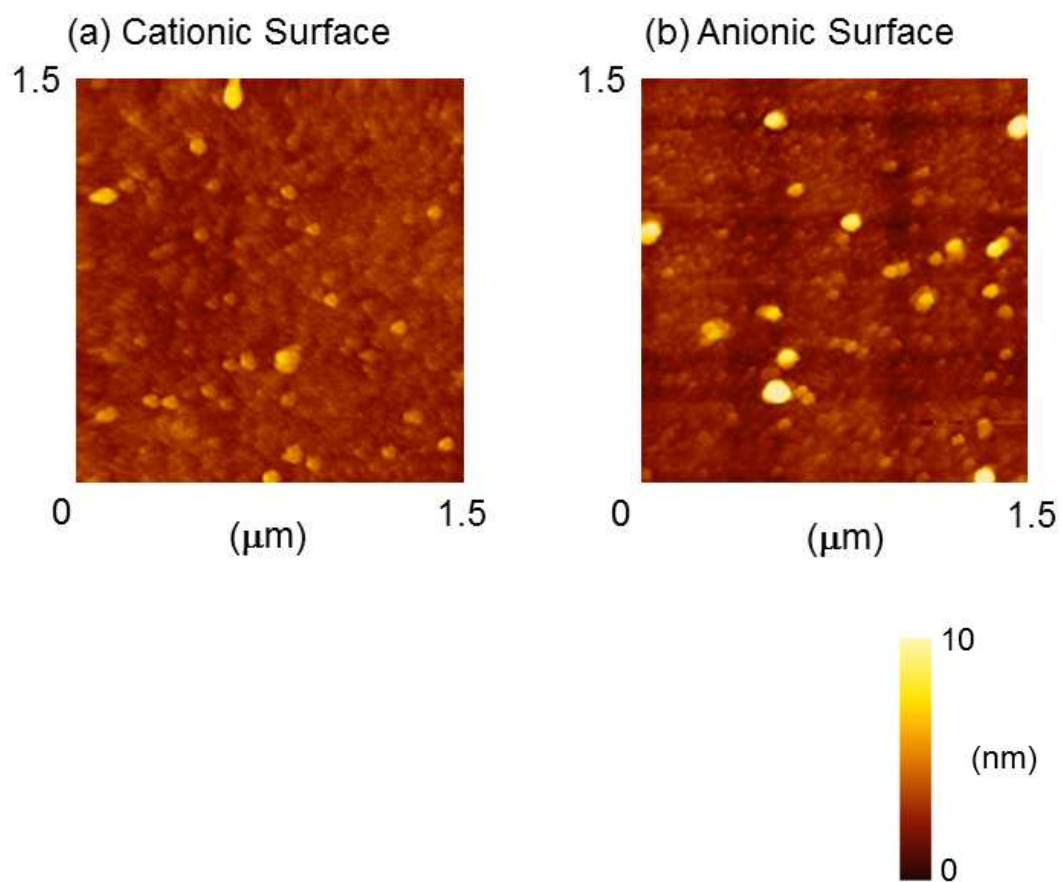
Where  $\Delta\delta_{\text{obs}}$  is the chemical shift change of proton signal of methyl moiety of **C2[5]** (Figure S7, peak d) at  $[G]_0$ ,  $\Delta\delta_{11}$  is the chemical shift change of the proton resonance when **C2[5]** is completely complexed,  $[G]_0$  is the fixed initial concentration of *p*-**DNB**, and  $[H]_0$  is the initial concentration of the host **C2[5]**.

### <sup>1</sup>H and <sup>13</sup>C NMR spectra of amino pillar[5]arene (3)



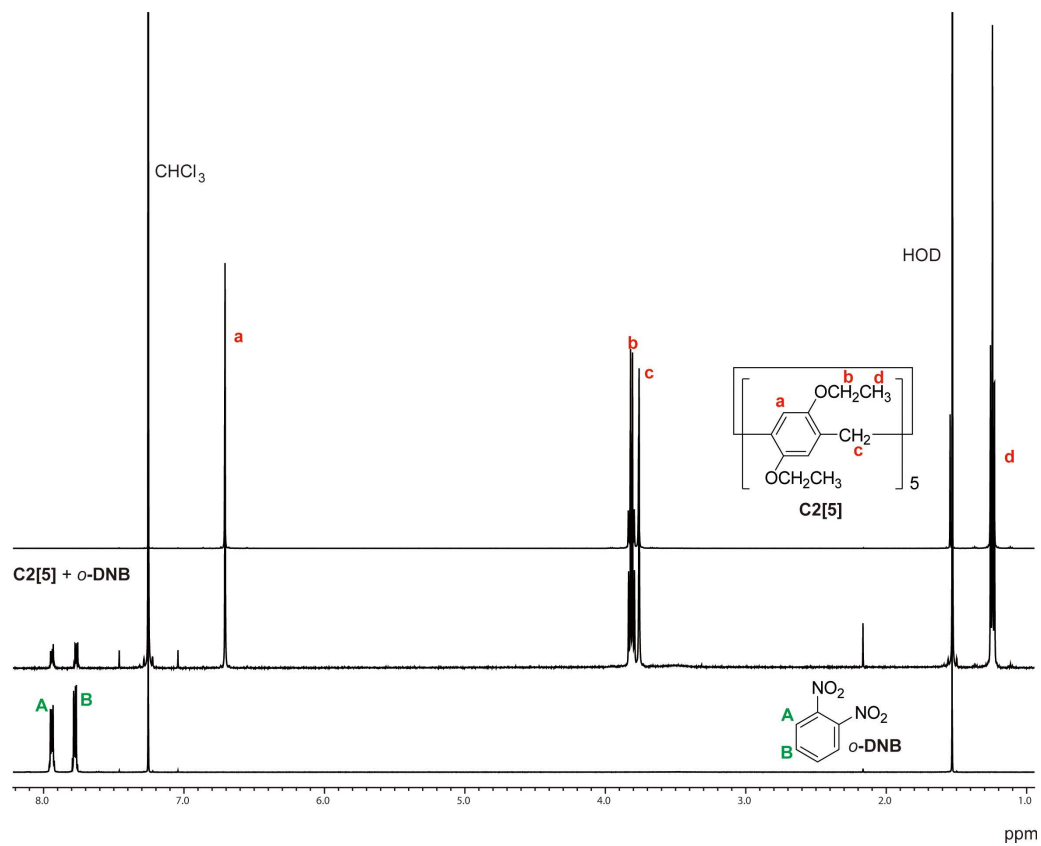
**Figure S1** (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$  NMR spectra of amino pillar[5]arene (**3**) in  $\text{CD}_3\text{OD}$  at  $25^\circ\text{C}$ .

**AFM images of the monolayer with cationic surface and bilayer with anionic surface**



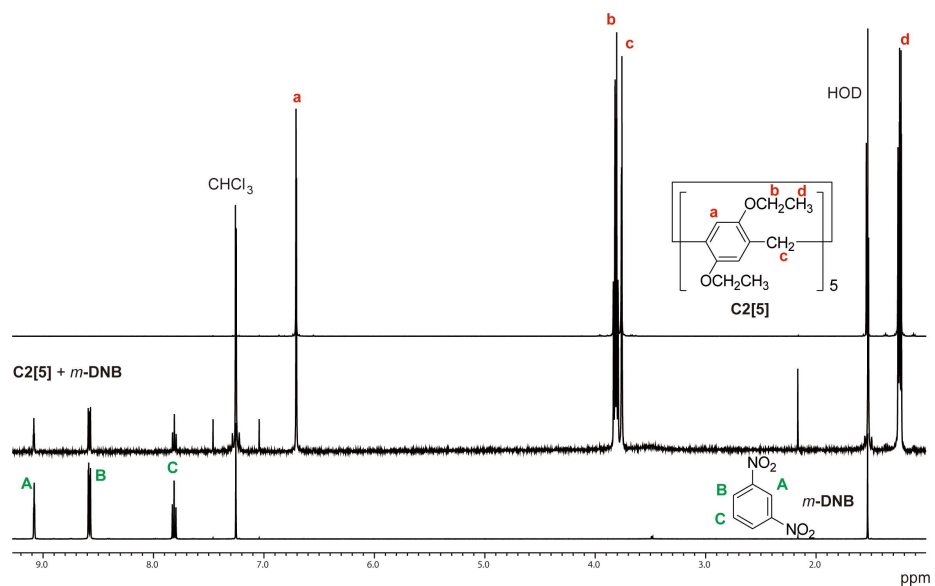
**Figure S2** AFM images of (a) the monolayer with cationic surface and (b) bilayer with anionic surface.

**$^1\text{H}$  NMR spectra of a mixture of per-ethylated pillar[5]arene with *o*-DNB**



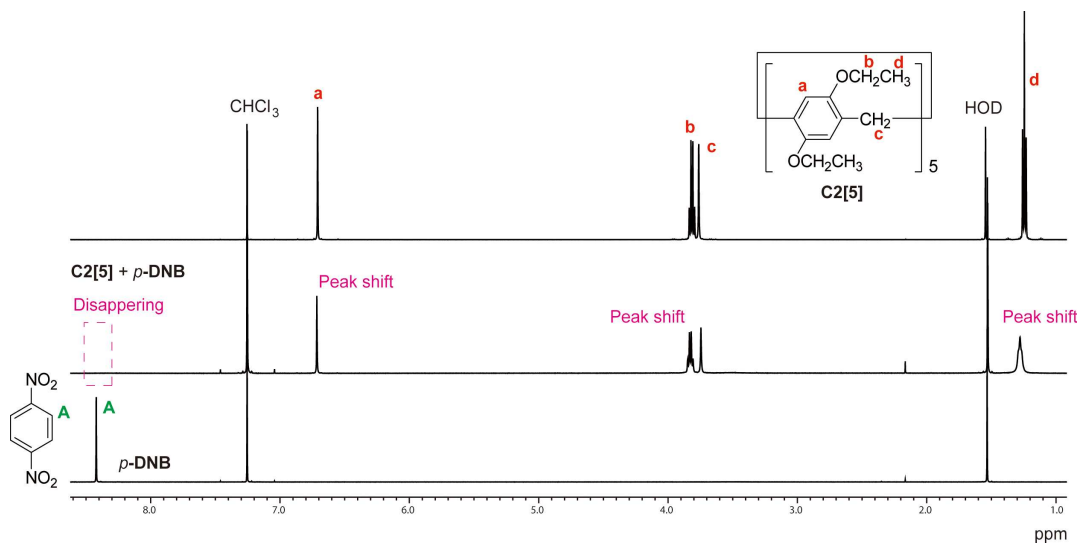
**Figure S3**  $^1\text{H}$  NMR spectra (1 mM, 25  $^\circ\text{C}$ ) of (a)  $\text{C2[5]}$ , (b) a mixture of  $\text{C2[5]}$  and *o*-DNB and (c) *o*-DNB. No peak shifts indicate no complexation between  $\text{C2[5]}$  and *o*-DNB.

**$^1\text{H}$  NMR spectra of a mixture of per-ethylated pillar[5]arene with *m*-DNB**



**Figure S4**  $^1\text{H}$  NMR spectra (1 mM, 25  $^{\circ}\text{C}$ ) of (a) C2[5], (b) a mixture of C2[5] and *m*-DNB and (c) *m*-DNB. No peak shifts indicate no complexation between C2[5] and *m*-DNB.

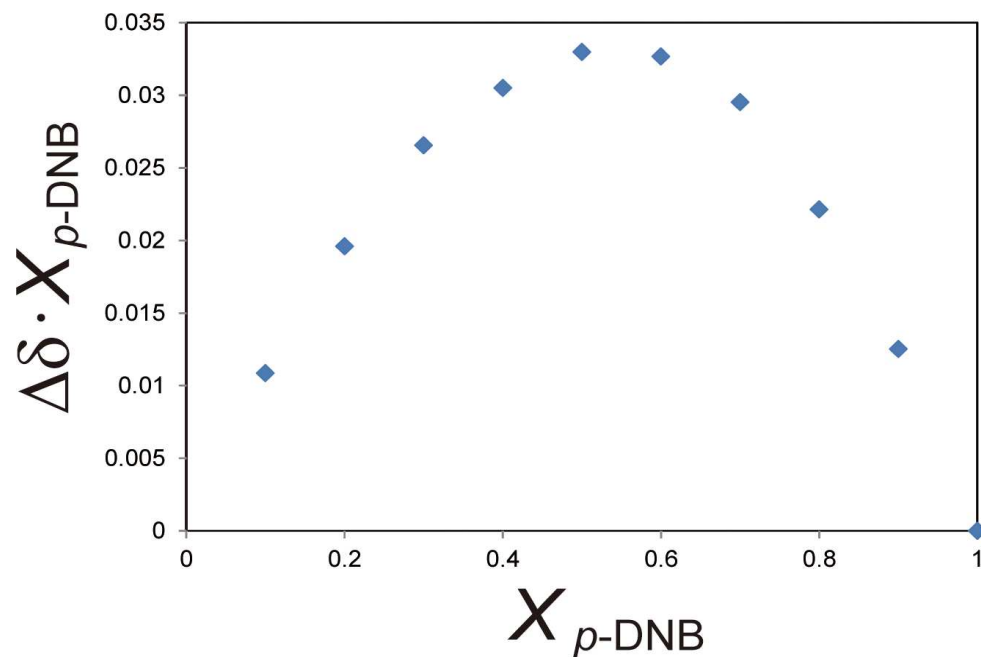
**$^1\text{H}$  NMR spectra of a mixture of per-ethylated pillar[5]arene with *p*-DNB**



**Figure S5**  $^1\text{H}$  NMR spectra (1 mM, 25 °C) of (a) C2[5], (b) a mixture of C2[5] and *p*-DNB and (c) *p*-DNB. Broadening of proton signal from *p*-DNB and peak shifts of proton signals from C2[5] indicate complexation between C2[5] and *p*-DNB.

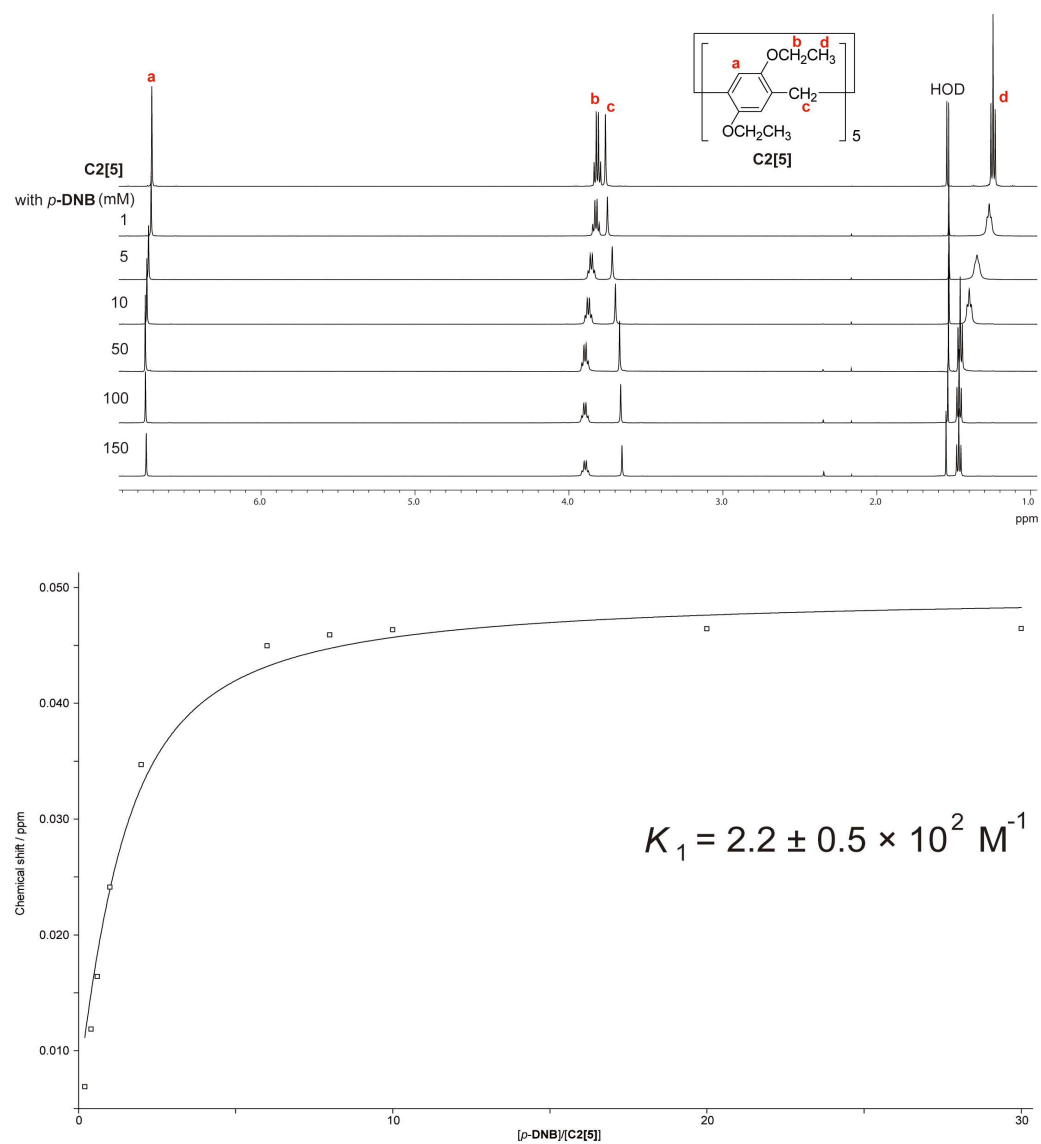


**Job plot for a mixture of *p*-DNB and C2[5]**



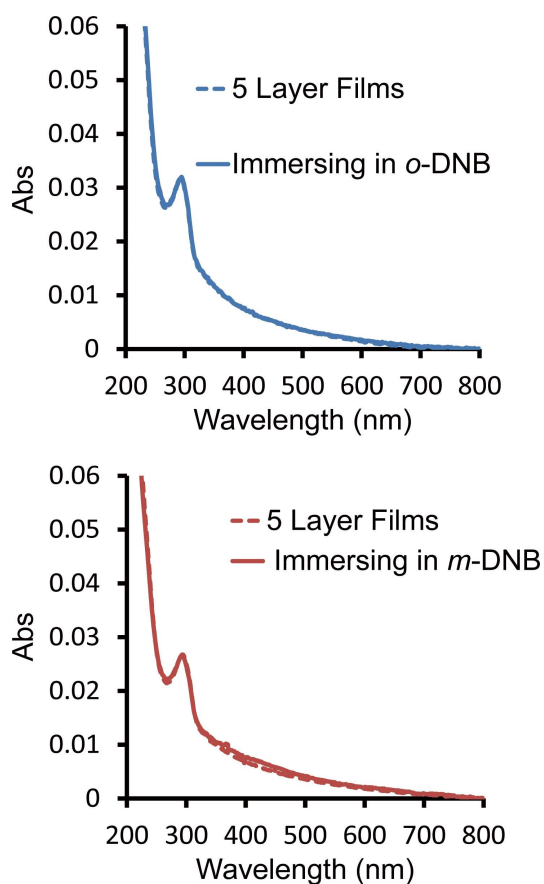
**Figure S6** Job plot between *p*-DNB (guest) and C2[5] (host) was collected by plotting the  $\Delta\delta$  in chemical shift of the proton signal of C2[5] (**Figure S5**, peak d) of C2[5] observed by  $^1\text{H}$  NMR spectroscopy against the change in the mole fraction of the guest ( $X_{p\text{-DNB}}$ ). Concentration:  $[p\text{-DNB}] + [\text{C2[5]}] = 1 \text{ mM}$ . The plot indicates a 1:1 binding between the host and guest.

## <sup>1</sup>H NMR titration



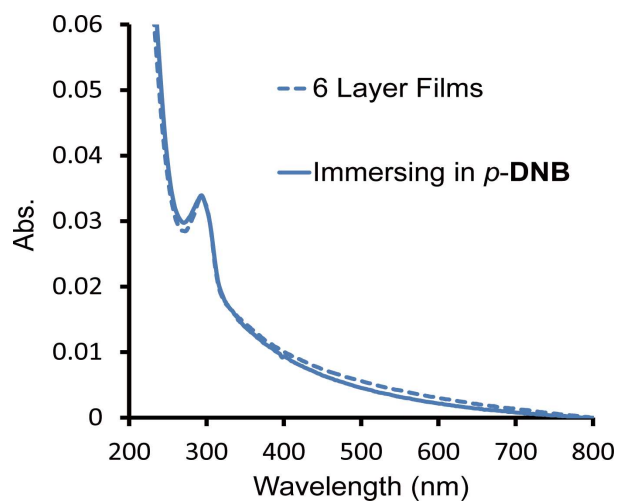
**Figure S7** <sup>1</sup>H NMR titration of C2[5] (peak d) with *p*-DNB in CDCl<sub>3</sub> at 25 °C.

**UV-vis absorption spectra of LBL assembled five layer film (5L) before and after immersing in *o*- and *m*-DNB in chloroform**



**Figure S8** UV-vis absorption spectra of LbL-assembled five-layer films (dash line) after immersing in (a) *o*-DNB (blue solid line) and (b) *m*-DNB (brown solid line) in chloroform. An increase in absorption was not observed for *o*-DNB and *m*-DNB, indicating no complexation with *o*-DNB and *m*-DNB.

**UV-vis absorption spectra of LBL assembled six layer film (6L) with anionic surface before and after immersing in *p*-DNB in chloroform**



**Figure S9** UV-vis absorption spectra of LbL-assembled six-layer films with anionic surface (dash line) after immersing in (a) *p*-DNB (solid line). An increase in absorption was not observed for *p*-DNB, indicating no complexation with *p*-DNB.

## References

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