Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Pillararene-Containing Polymers with Tunable Fluorescence Property Based on Host-Guest Interactions

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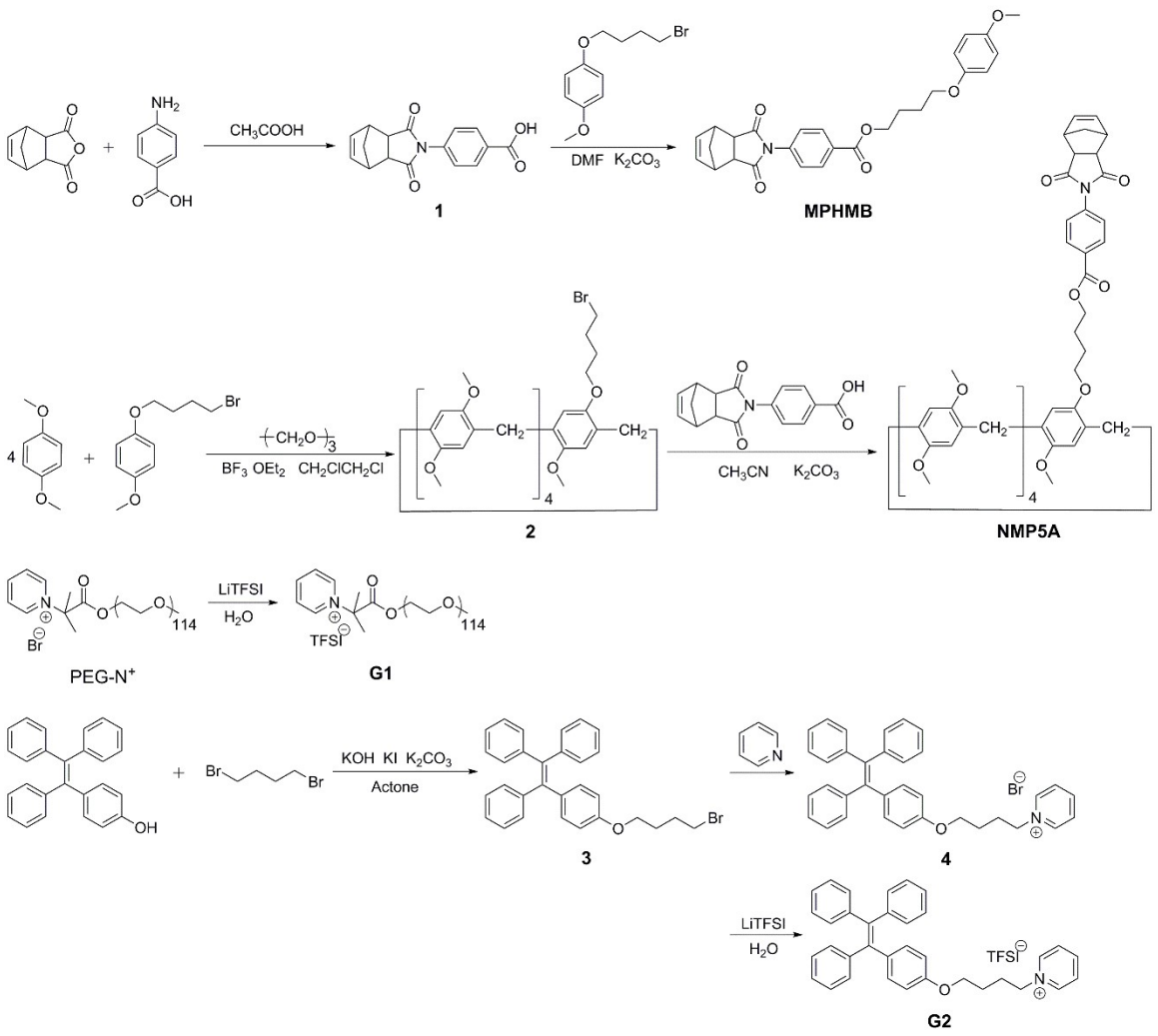
1. Materials and Methods

1-(4-Bromobutoxy)-4-methoxybenzene,[S1] PEG-N^+,[S2] and 4-(1,2,2-triphenylvinyl)phenol[S3] were prepared according to the previous procedures. 1,4-Dibromobutane (99%), 5-norbornene-2,3-dicarboxylic anhydride (98%+), 4-aminobenzoic acid (98%+), s-trioxane (99%+) and 4-methoxyphenol were purchased from Shanghai Titan Scientific Co. (Shanghai, Chain) and used as received. Boron trifluoride diethyl etherate was purchased from Sinopharm Chemical Reagent Co. (Shanghai, Chain). 1,4-Dimethoxybenzene was purchased from Aladdin Industrial Corporation (Shanghai, Chain). [1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] benzylidene ruthenium dichloride (**Ru-II**) was purchased from Aldrich, and [1,3-bis(2.4.6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][3-bromopyridine]$_2$ benzylidene ruthenium dichloride (**Ru-III**) was synthesized from **Ru-II** according to the synthetic procedures in the literature.[S4] Other materials were obtained from commercial suppliers, and were used directly without further purification. Ultrapure water was used in all relevant experiments.

^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker DPX500 spectrometer using tetramethylsilane as an internal standard in $CDCl_3$ or acetone-d6. Gel permeation chromatography (GPC) analysis was recorded on Malvern VISCOTEK GPCmax TDA305, using THF as the eluent, flow rate of 1 mL/min. ESI-TOF was recorded on maXis Impact + 1290 infinity with CH_3CN or CH_3OH as the eluent. MALDI-TOF was recorded on Bruker AUTOFLEX. Transmission electron microscopy (TEM) images were recorded on the FEI G2F20. For TEM sample preparation, a drop of dispersion was placed onto the carbon-coated copper grid and dried at room temperature. Dynamic light scattering (DLS) was performed on Malvern ZEN3600. UV-Vis spectra were recorded on a UV-1800 spectrophotometer. The fluorescence spectra were taken on a HITACHI F-7000 fluorescence spectrophotometer at room temperature. Fluorescence quantum yields were measured in solution using a commercial fluorometer with integrating sphere (RF-6000, shimadzu). Fluorescence lifetimes were recorded in a quartz cell (light path 10 mm) on the Edinburgh FLS980 transient fluorescence spectrometer.

2. Syntheses and Characterizations



Scheme S1. Syntheses of monomers and guest molecules.

Synthesis of 4-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-methanoisoindol-2-yl)benzoic acid 1

5-Norbornene-2,3-dicarboxylic anhydride (4.11 g, 30 mmol) and 4-aminobenzoic acid (4.59 g, 28 mmol) were dissolved in acetic acid (100 mL). The reaction mixture was heated and stirred at reflux for 9 h. Then the reaction mixture was precipitated in ultrapure water. Then the mixture was filtered and washed with ultrapure three times to afford the desired compound **1** as a yellow solid (6.90 g, 87%). The ^{1}H NMR spectrum of the compound **1** is shown in **Figure S1**. ^{1}H NMR (Acetone-d_6, 500 MHz, 298K) δ (ppm): 8.11 – 8.06 (m, 2H), 7.36 – 7.32 (m, 2H), 6.27 (t, J = 1.9 Hz, 2H), 3.57 – 3.52 (m, 2H), 3.41 (dp, J = 4.9, 1.5 Hz, 2H), 1.71 – 1.68 (m, 2H). The ^{13}C NMR spectrum of the compound **1** is shown in **Figure S2**. ^{13}C NMR (Acetone-d_6, 126 MHz, 298K) δ 205.30 (s), 205.14 (s), 176.01 (s), 166.00 (s), 134.57 (s), 129.93 (s), 126.85 (s), 51.81 (s), 45.77 (s), 45.30 (s), 28.95 (dp, J = 38.7, 19.4 Hz). HRMS (ESI) is shown in **Figure S3**. m/z called for $[C_{16}H_{12}O_4N]^-$: 282.077; found 282.0078.

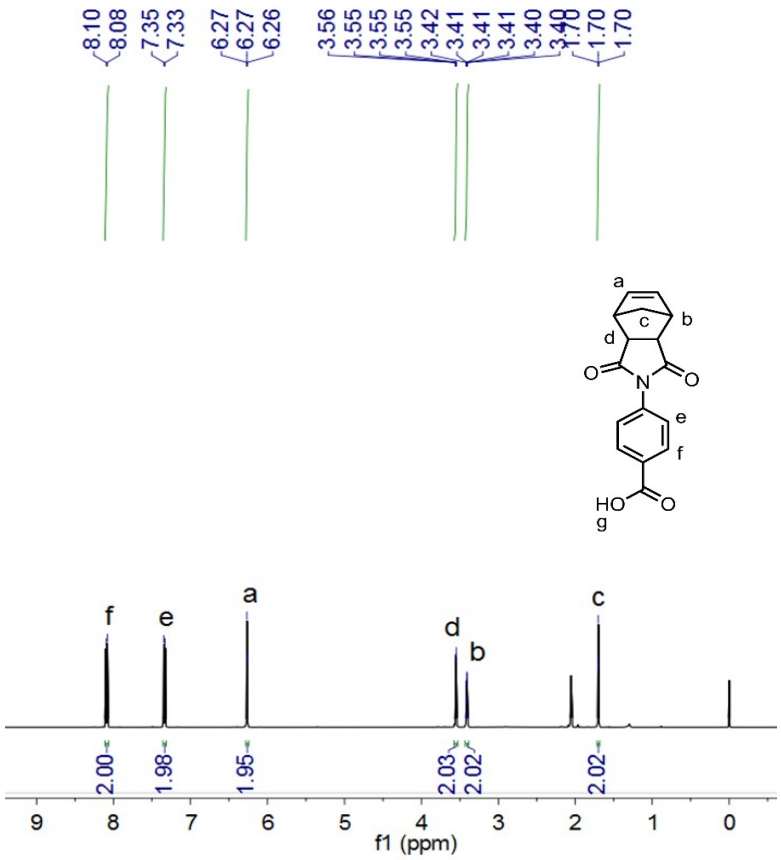


Figure S1. ^{1}H NMR spectrum (500 MHz, Acetone-d_6) of compound **1**.

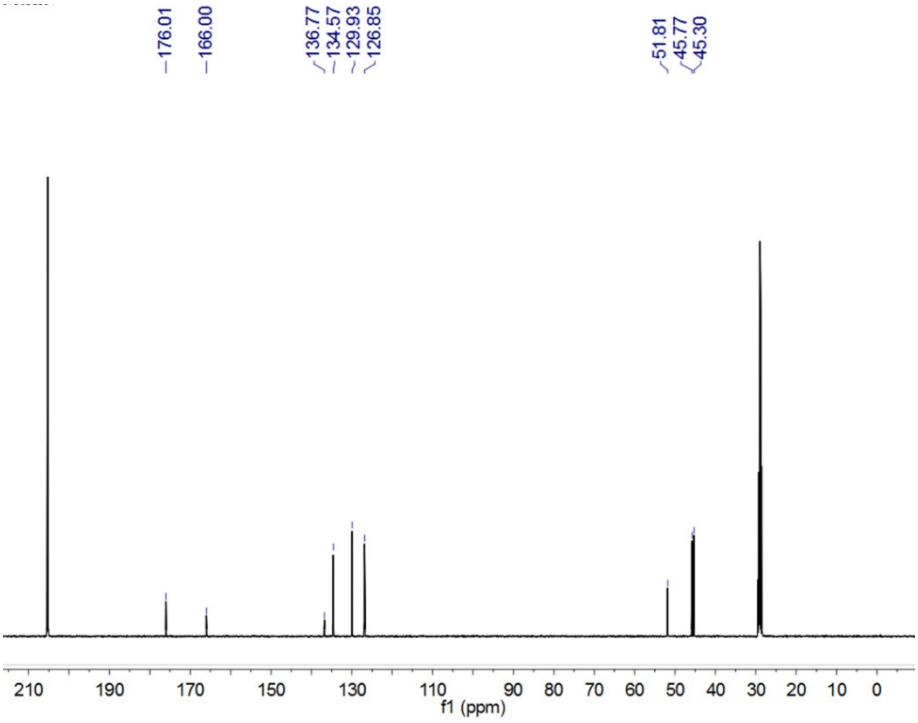


Figure S2. ^{13}C NMR spectrum (126 MHz, Acetone-d_6, 298K) of compound **1**.

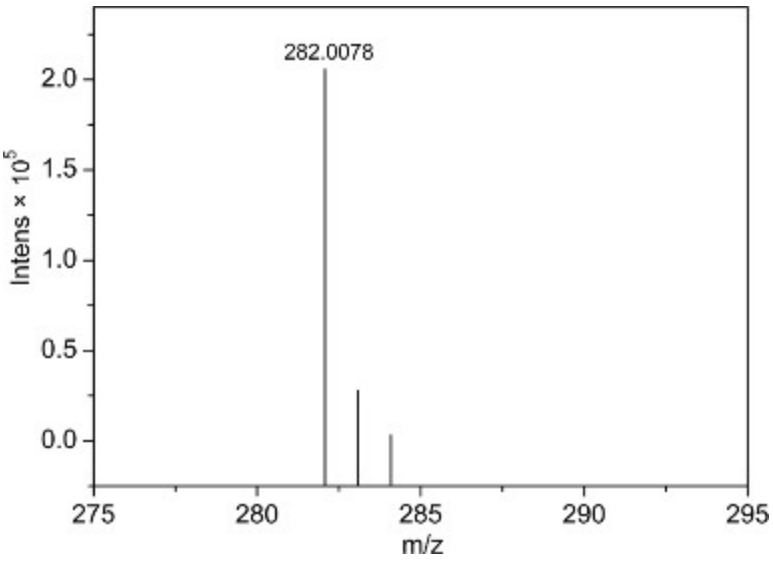


Figure S3. HRMS of compound **1**.

Synthesis of 4-(4-methoxyphenoxy)butyl 4-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-methanoisoindol-2-yl)benzoate（MPHMB）

compound **1** (5.66 g, 20 mmol), 1-(4-bromobutoxy)-4-methoxybenzene (7.77 g, 30 mmol) and potassium carbonate (4.14 g, 30 mmol) were added in dimethyl formamide (80 mL) under stirring at room temperature for 24 h. After the reaction was completed, the resulting mixture was filtered and the residue was washed with ethyl acetate. Evaporation of the solvent under reduced pressure and further purification was carried out by column chromatography (eluent: petroleum ether/ethyl acetate = 5:1, v/v) to afford the desired compound **MPHMB** as a white solid (7.25 g, 79%). The ^{1}H NMR spectrum of the monomer **MPHMB** is shown in **Figure S4**. ^{1}H NMR ($CDCl_3$, 500 MHz, 298K) δ (ppm): 8.12 – 8.08 (m, 2H), 7.27 (dd, *J* = 4.2, 2.3 Hz, 2H), 6.87 – 6.83 (m, 4H), 6.29 (t, *J* = 1.8 Hz, 2H), 4.42 (t, *J* = 6.2 Hz, 2H), 4.00 (t, *J* = 5.9 Hz, 2H), 3.79 (s, 3H), 3.56 – 3.51 (m, 2H), 3.50 – 3.44 (m, 2H), 2.02 – 1.89 (m, 4H), 1.82 (dt, *J* = 8.9, 1.5 Hz, 1H), 1.64 (d, *J* = 8.8 Hz, 1H). The ^{13}C NMR spectrum of the monomer **MPHMB** is shown in **Figure S5**. ^{13}C NMR ($CDCl_3$, 126 MHz, 298 K) δ (ppm): 176.32 (s), 165.68 (s), 153.80 (s), 153.03 (s), 135.79 (s), 134.67 (s), 130.33 (s), 130.17 (s), 126.40 (s), 115.45 (s), 114.66 (s), 77.30 (s), 77.05 (s), 76.79 (s), 67.87 (s), 64.92 (s), 55.74 (s), 52.32 (s), 45.90 (s), 45.61 (s), 26.06 (s), 25.52 (s). HRMS (ESI) is shown in **Figure S6**. m/z calcd for $[C_{27}H_{27}O_6NaN]^+$: 484.174; found 484.1721.

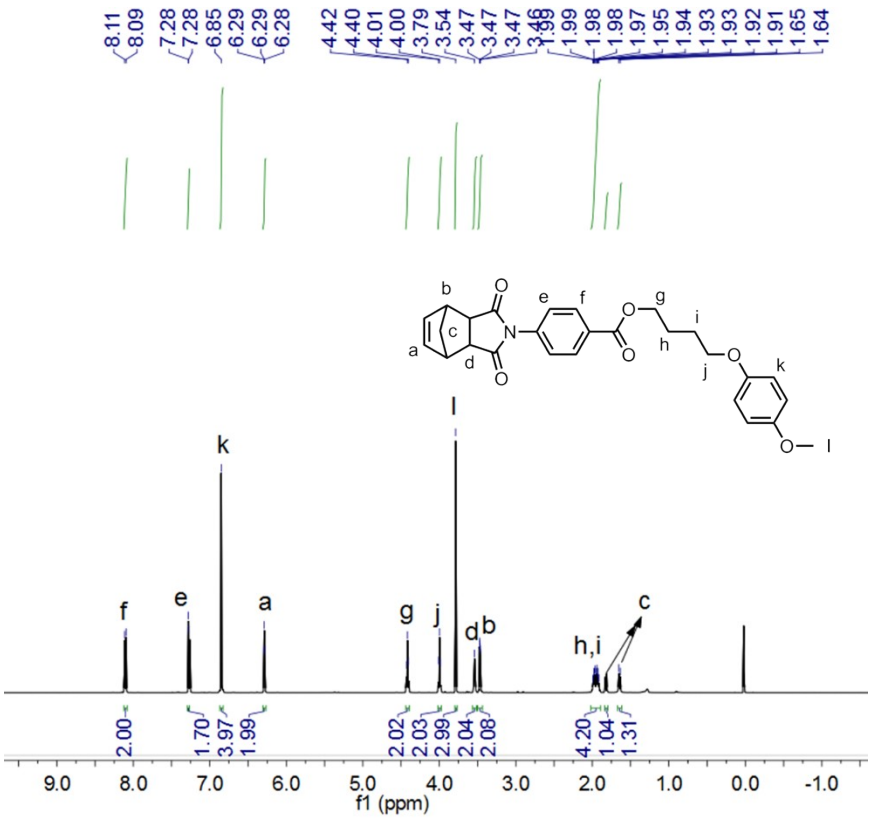


Figure S4. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of monomer **MPHMB**.

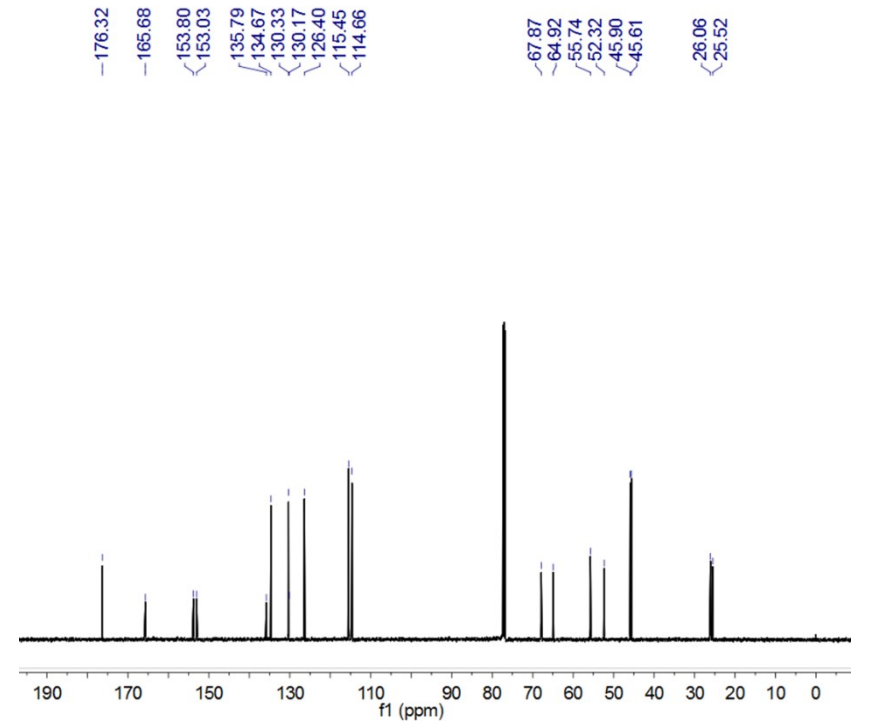


Figure S5. ^{13}C NMR spectrum (126 MHz, $CHCl_3$) of compound **MPHMB**.

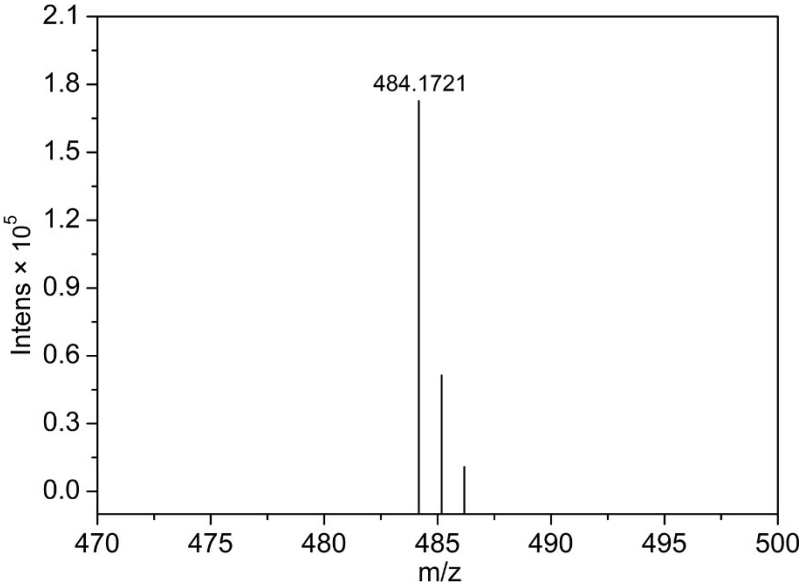


Figure S6. HRMS of monomer **MPHMB**.

Synthesis of monobromo-substituted pillar[5]arene 2

To a solution of 1-(4-bromobutoxy)-4-methoxybenzene (1.04 g, 4.0 mmol), 1,4-dimethoxybenzene (2.20 g, 16 mmol) and paraformaldehyde (1.80 g, 20 mmol) was added in $CHCl_2CHCl_2$ (230 mL). Boron trifluoride etherata [($BF_3 \cdot OEt_2$), 5.69 g, 5.2 mL, 40 mmol] was then added to the solution and the mixture was stirred at room temperature for 10 min. After the color of solution changed from white to light yellow to olivine to dark-green, water (200 mL) was poured into the solution to quench the reaction. The solvent was removed under vacuum and the residue was purified by column chromatography (eluent: petroleum ether/dichloromethane=1:3, v/v) to afford monobromo-substituted pillar[5]arene compound **2** as a white solid (946 mg, 27%). The ^{1}H NMR spectrum of compound **2** is shown in **Figure S7**. ^{1}H NMR ($CDCl_3$, 500 MHz, 298K) δ (ppm): 6.82, 3.84, 3.77, 3.72, 3.71, 3.69, 3.68, 3.24, 1.82. The ^{13}C NMR spectrum of compound **2** is shown in **Figure S8**. ^{13}C NMR ($CDCl_3$, 126 MHz, 298K) δ (ppm): 150.68 (s), 149.84 (s), 128.25 (s), 114.75 (s), 113.99 (s), 67.34 (s), 55.82 (dd, J = 25.4, 9.6 Hz), 33.46 (d, J = 3.7 Hz), 29.57 (d, J = 12.1 Hz), 28.36 (s). MALDI-TOF of compound **2** is shown in **Figure S9**. m/z calcd for $C_{48}H_{55}O_{10}Br$: 872.862, found m/z 872.200. m/z calcd for $C_{48}H_{55}O_{10}BrNa^+$: 895.852, found m/z 895.196; m/z calcd for $C_{48}H_{55}O_{10}Br \subset CHCl_3$: 992.230, found m/z 992.145; m/z calcd for $C_{48}H_{55}O_{10}BrNa^+ \subset CHCl_3$: 1015.220, found m/z 1015.141.

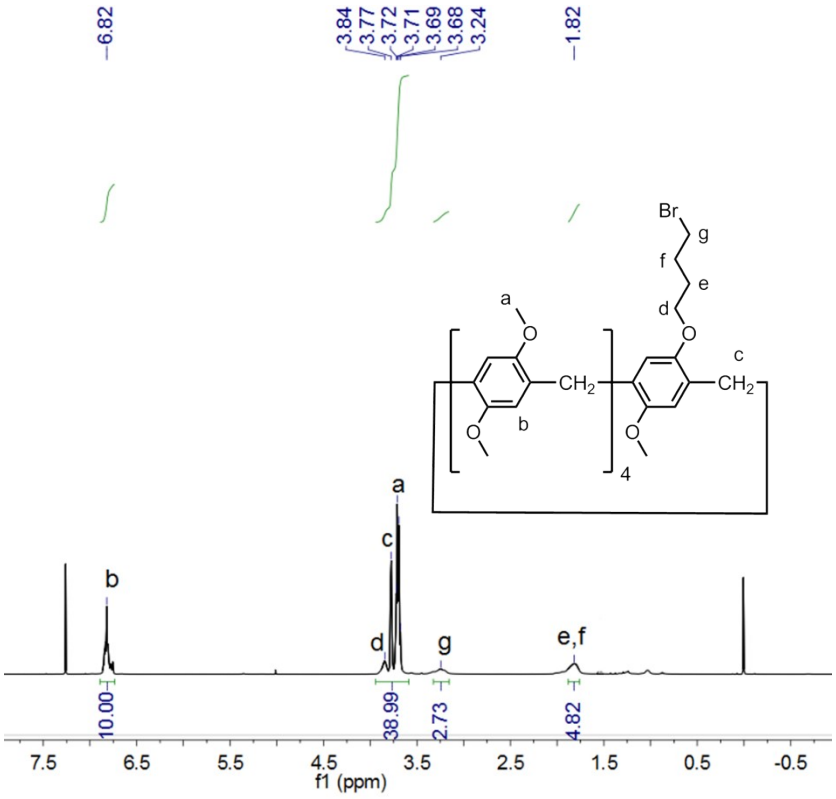


Figure S7. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **2**.

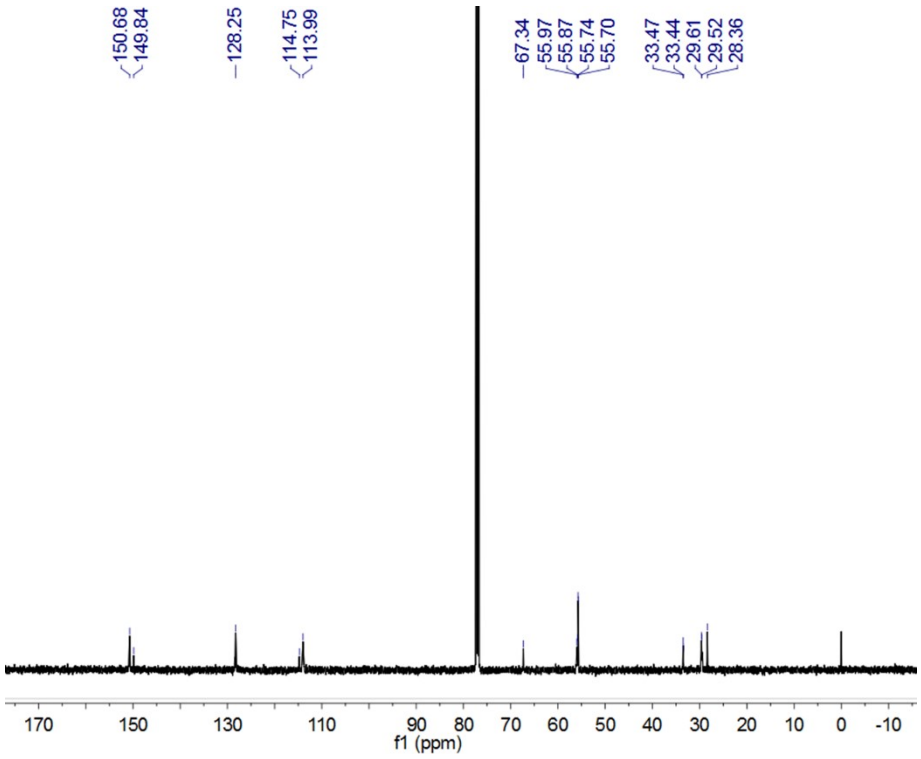


Figure S8. ^{13}C NMR spectrum (126 MHz, $CHCl_3$) of compound **2**.

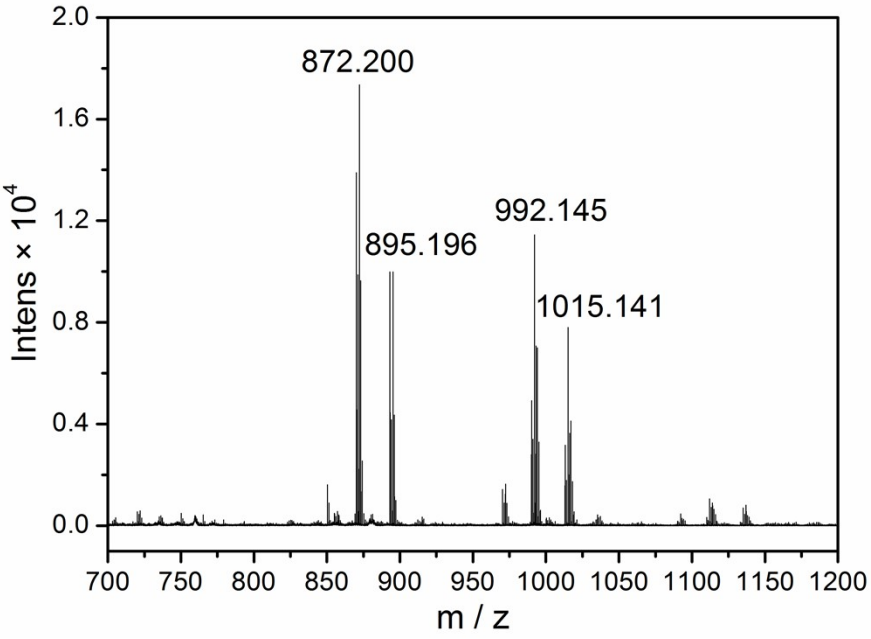


Figure S9. MALDI-TOF of compound **2**.

Synthesis of NMP5A

Monobromo-substituted pillar[5]arene (1.25 g, 1.4 mmol), compound **1** (1.98 g, 7 mmol) and potassium carbonate (1.90 g, 14 mmol) were added in acetonitrile (80 mL) under stirring at 80 ° C for 24 h. After the reaction was completed, the resulting mixture was filtered and the residue was washed with ethyl acetate. Evaporation of the solvent under reduced pressure and further purification was carried out by column chromatography (eluent: petroleum ether/ethyl acetate = 1:1, v/v) to afford the desired monomer **NMP5A** as a white solid (0.862 g, 69%). The ^{1}H NMR spectrum of the monomer **NMP5A** is shown in **Figure S10**. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K) δ (ppm): 8.10 (d, *J* = 8.4 Hz, 2H), 7.28 (s, 2H), 6.79 (s, 10H), 6.27 (s, 2H), 4.41 (s, 2H), 3.91 (s, 2H), 3.77 (s, 11H), 3.65 (s, 27H), 3.53 (s, 2H), 3.46 (s, 2H), 2.01 (s, 2H), 1.92 (s, 2H), 1.81 (d, *J* = 8.9 Hz, 1H), 1.63 (d, *J* = 8.8 Hz, 1H). The ^{13}C NMR spectrum of the monomer **NMP5A** is shown in **Figure S11**. ^{13}C NMR ($CDCl_3$, 126 MHz, 298 K) δ (ppm): 176.33 (s), 165.69 (s), 150.72 (s), 149.82 (s), 135.87 (s), 134.68 (s), 130.31 (s), 130.12 (s), 128.24 (s), 126.44 (s), 114.84 (s), 113.97 (s), 67.76 (s), 64.89 (s), 55.69 (d, *J* = 7.6 Hz), 52.33 (s), 45.91 (s), 45.63 (s), 29.99 – 28.61 (m), 28.36 (s), 26.46 (s), 25.77 (s). The melting point of **NMP5A** was 109.2 °C.

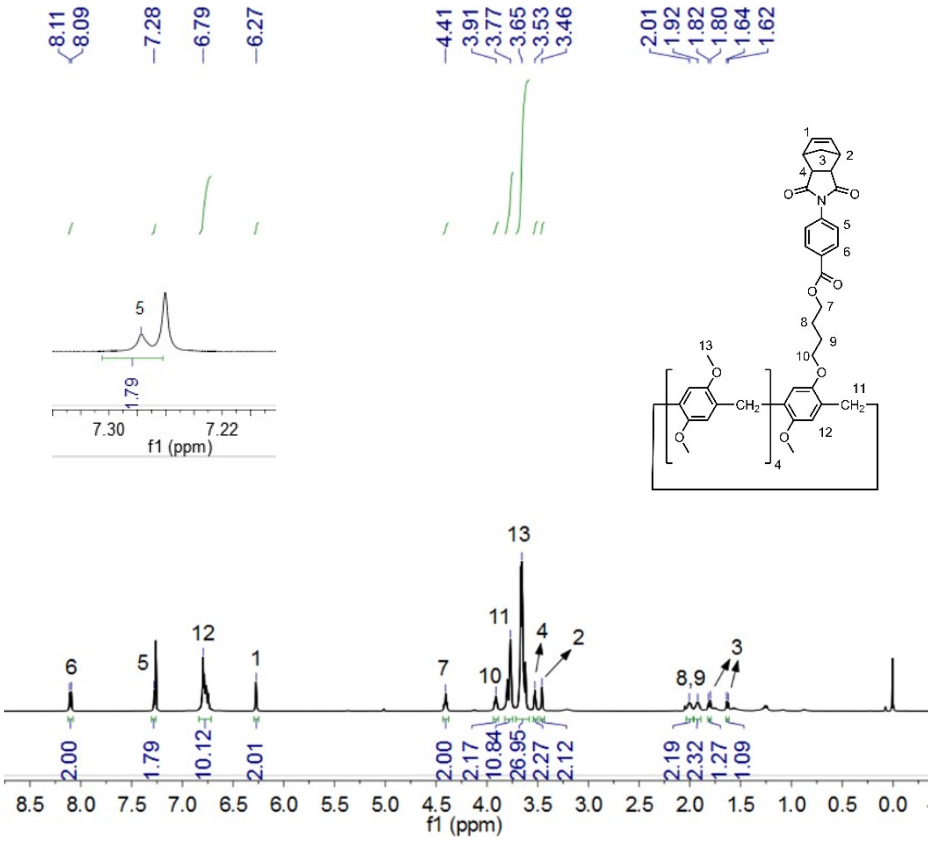


Figure S10. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **NMP5A**.

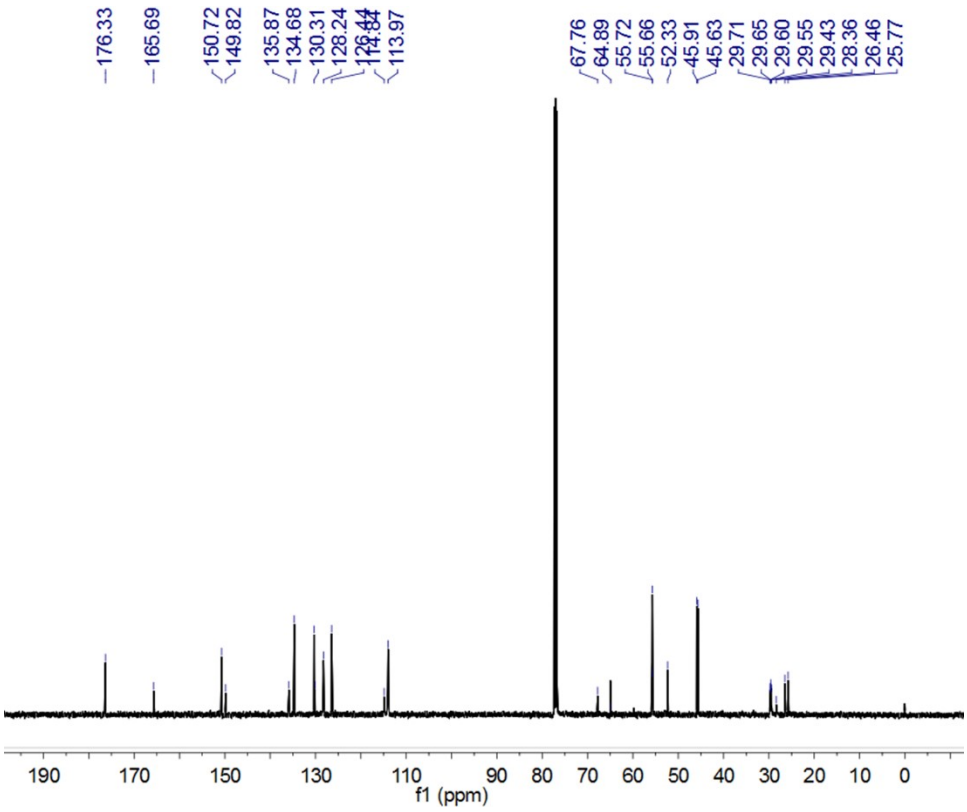
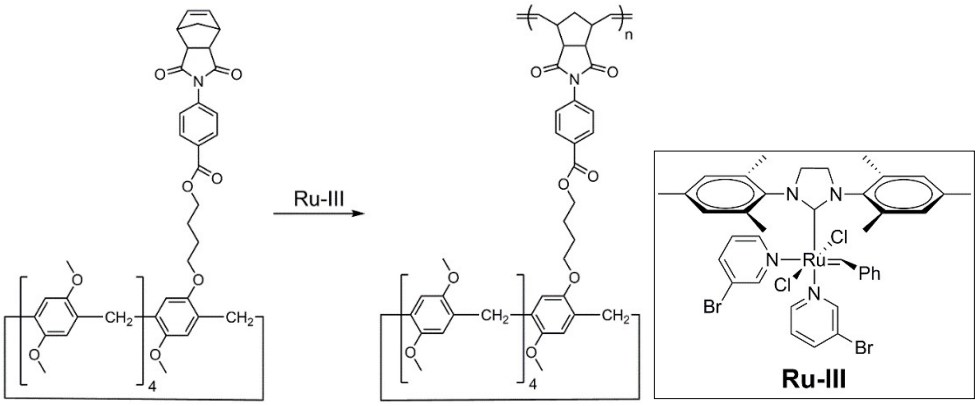


Figure S11. ^{13}C NMR spectrum (126 MHz, $CHCl_3$) of **NMP5A**.

Synthesis of pillar[5]arene functionalized homopolymer pNMP5A

Scheme S2. Synthesis of pillar[5]arene functionalized homopolymer **pNMP5A**.



A 25 mL Schlenk flask was charged with **NMP5A** (214.6 mg, 0.2 mmol) dissolved in 0.5 mL of $CHCl_3$. In another 25 mL flask, **Ru-III** (3.5 mg, 4 μmol) was dissolved in 0.5 mL of $CHCl_3$. After being degassed with three freeze-vacuum-thaw cycles, the catalyst solution was then injected into the pre-heated monomer solution via a syringe under vigorous stirring at 50 °C for 3 h. Then an excess of vinyl ethyl ether was added to the mixture and stirring for another 1 h. The solution was precipitated into acetone and dried under vacuum to afford homopolymer **pNMP5A** as a dark yellow solid (115.5 mg, 58%). The polymer was characterized by ^{1}H NMR (**Figure S12**).

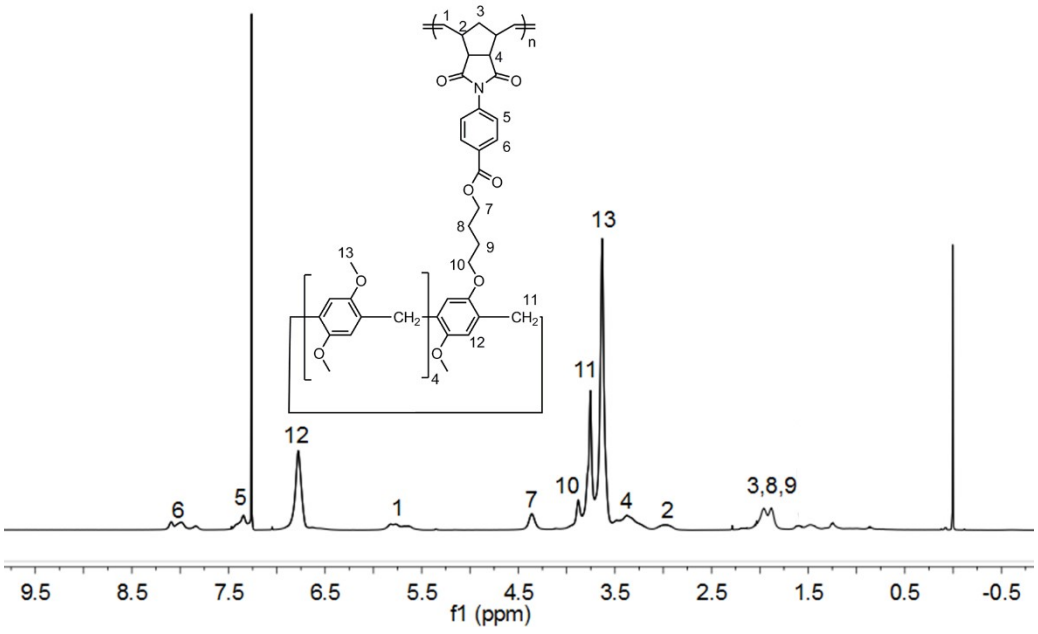


Figure S12. ^{1}H NMR spectrum of **pNMP5A**.

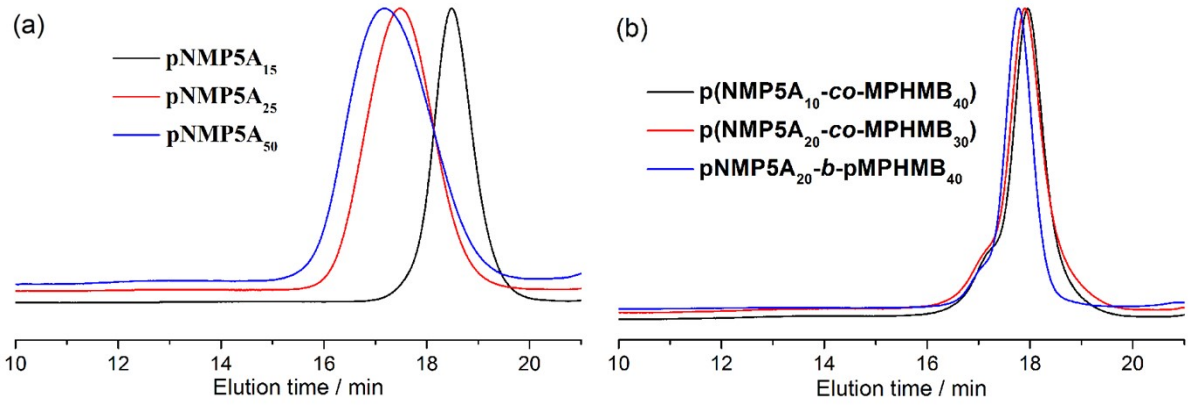


Figure S13. GPC traces of **pNMP5A** (a), **p(NMP5A-*co*-MPHMB)**, and **pNMP5A-*b*-pMPHMB** (b).

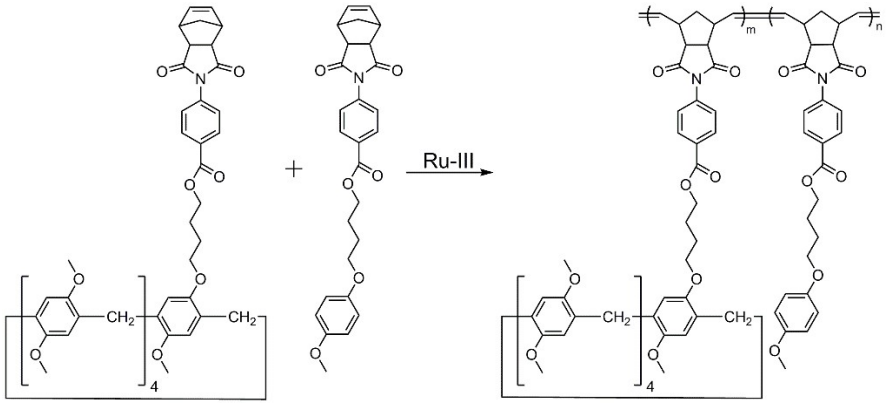
Table S1. Characteristics for polymers.[a]

run	polymers	[**NMP5A**]:[**MPHMB**]:[Cat.][b]	M_n [c] (kDa)	PDI [c]	Yield (%)
1	**pNMP5A$_{15}$**	15:0:1	15.2	1.10	74
2	**pNMP5A$_{25}$**	25:0:1	21.6	1.35	66
3	**pNMP5A$_{50}$**	50:0:1	60.4	1.37	58
4	**p(NMP5A$_{10}$-*co*-MPHMB$_{40}$)**	10:40:1	22.8	1.15	83
5	**p(NMP5A$_{20}$-*co*-MPHMB$_{30}$)**	20:30:1	32.7	1.20	65
6	**pNMP5A$_{20}$-*b*-pMPHMB$_{40}$**	20:40:1	38.0	1.09	81

[a] Polymerization conditions: using Ru-III as catalyst, $CHCl_3$ as solvent, temperature = 50 °C. Polymerization time: 180 min for runs 1, 2, 3, 4, 5 and 15 + 180 min for run 6. [b] The molar feeding ratios of monomers to catalyst. [c] Values corresponding to the polymer chain determined by GPC eluted with THF.

Synthesis of pillar[5]arene functionalized block polymer pNMP5A-*b*-pMPHMB

Scheme S3. Synthesis of **pNMP5A-*b*-pMPHMB**.



A 25 mL Schlenk flask was charged with **NMP5A** (107.4 mg, 0.1 mmol) dissolved in 0.5 mL of $CHCl_3$. **MPHMB** (92.2 mg, 0.2 mmol) was dissolved in 0.75 mL of $CHCl_3$ in the second 25 mL flask. In the third 25 mL flask, **Ru-III** (4.4 mg, 5 μmmol) was dissolved in 0.25 mL of $CHCl_3$. After being degassed with three freeze-vacuum-thaw cycles, the catalyst solution was then injected into the pre-heated **NMP5A** solution via a syringe under vigorous stirring at 50 °C for 15 min. Then the solution of **MPHMB** was injected into the same flask via a syringe under vigorous stirring at 50 °C for 3 h. Then an excess of vinyl ethyl ether was added to the mixture and stirring for another 1 h. The solution was precipitated into ether thrice and dried under vacuum to afford block polymer **pNMP5A-*b*-pMPHMB** as a yellow solid (159.6 mg, 80%). The polymer was characterized by ^{1}H NMR (**Figure S14**).

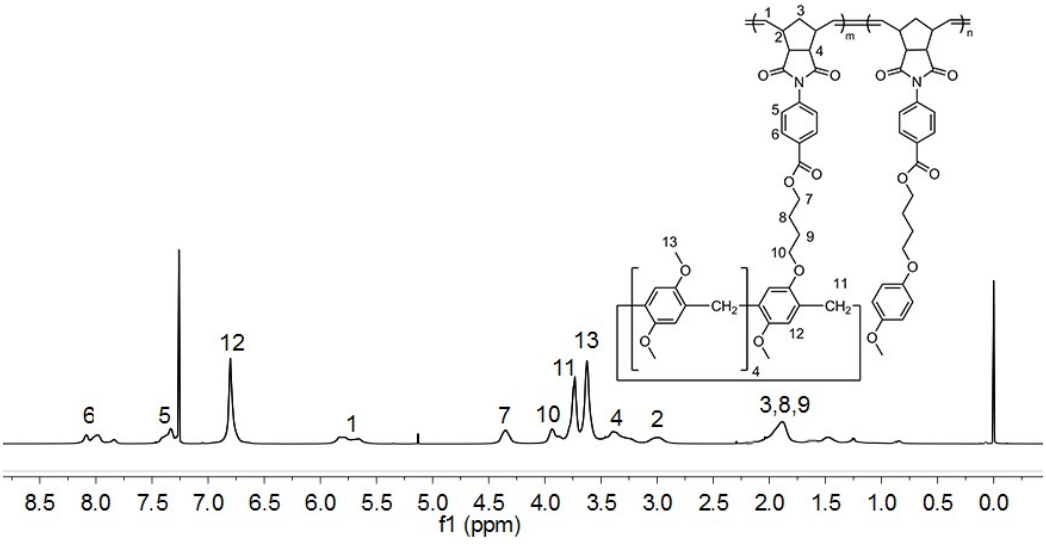
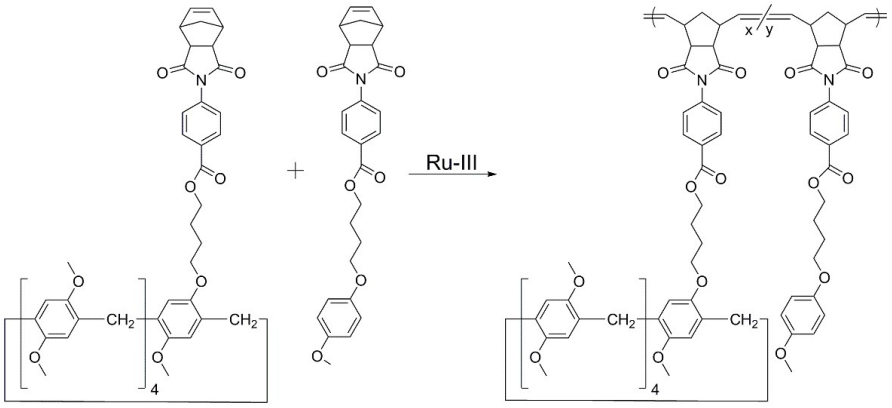


Figure S14. ^{1}H NMR spectrum of **pNMP5A-*b*-pMPHMB.**

Synthesis of pillar[5]arene functionalized copolymer p(NMP5A-*co*-MPHMB)

Scheme S4. Synthesis of **p(NMP5A-*co*-MPHMB)**.



A 25 mL Schlenk flask was charged with **NMP5A** (107.4 mg, 0.1 mmol) and **MPHMB** (115.2 mg, 0.25 mmol) dissolved in 0.7 mL of $CHCl_3$. In another 25 mL flask, catalyst **Ru-III** (6.2 mg, 7 μmmol) was dissolved in 0.7 mL of $CHCl_3$. After degassed with three freeze-vacuum-thaw cycles, the catalyst solution of **Ru-III** was then injected into the monomer solution via a syringe under vigorous stirring at 50 °C. After stirred for 3 h, an excess of vinyl ethyl ether was added to the mixture and stirring for another 1 h. The solution was precipitated into ether thrice and dried under vacuum to afford copolymer **p(NMP5A-*co*-MPHMB)** as a purple solid (198.1 mg, 89%). The polymer was characterized by ^{1}H NMR (**Figure S15**).

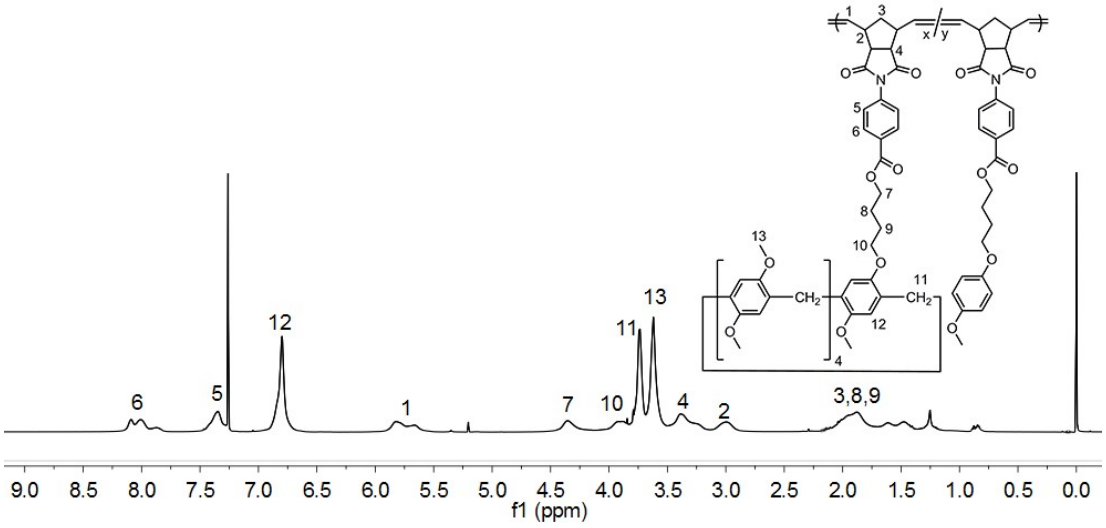


Figure S15. ^{1}H NMR spectrum of **p(NMP5A-*co*-MPHMB).**

Synthesis of G1

A solution of PEG-N^+ (1.02g, 0.2 mol) and LiTFSI (172 mg, 0.6 mmol) in ultrapure water (50 mL) was stirring at room temperature for 24 h. Then dialysis method was used to remove small molecules in

the solution. Evaporation of the solution under reduced pressure to afford **G1** as a brown solid (714 mg, 66%). The ^{1}H NMR spectrum of **G1** in $CDCl_3$ is shown in **Figure S16**. The melting point of **G1** was 59.3 ^{o}C.

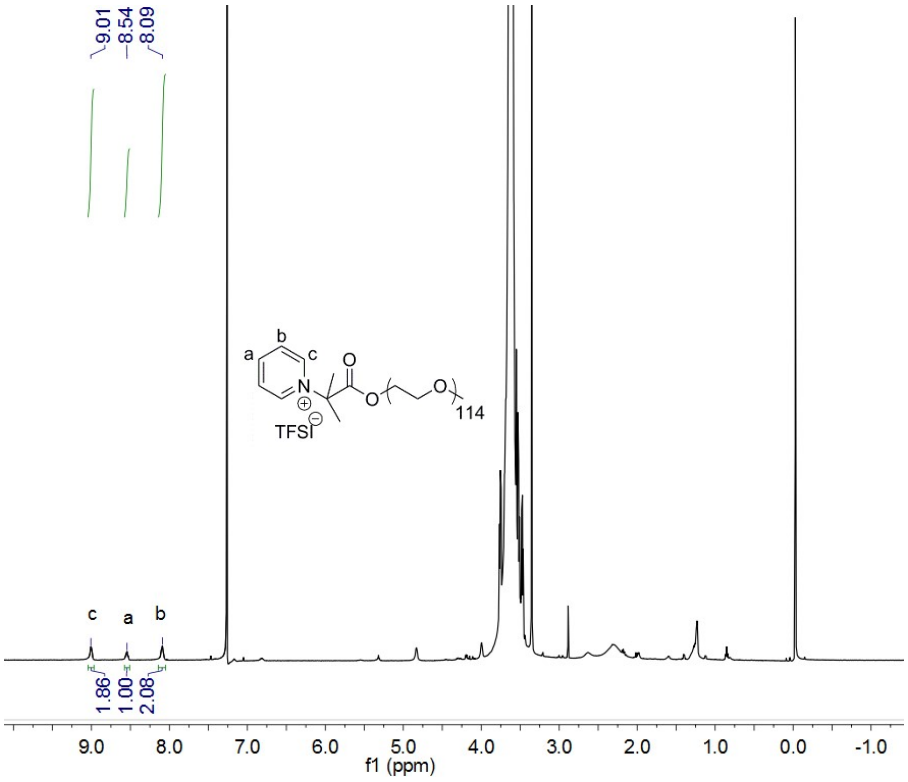


Figure S16. ^{1}H NMR spectrum of **G1**.

Synthesis of G2

Under a nitrogen atmosphere, 4-(1,2,2-triphenylvinyl)phenol (626 mg, 1.8 mmol) and 1,4-dibromobutane (1.9 g, 9 mmol) were dissolved in acetone (100 mL), followed by addition of potassium carbonate (621 mg, 4.5 mmol), potassium hydroxide (157 mg, 2.8 mmol), and potassium iodide (30 mg, 0.18 mmol). The reaction mixture was stirred at reflux for 8h. Then the cooled reaction mixture was filtered and washed with dichloromethane. The filtrate was concentrated and purified by column chromatography (eluent: petroleum ether/dichloromethane = 5:1, v/v) to afford the desired compound **3** as a withe solid (770 mg, 89%). The ^{1}H NMR spectrum of the compound **3** is shown in **Figure S17**. ^{1}H NMR ($CDCl_3$, 500 MHz, 298K) δ (ppm): 7.08, 7.07, 7.03, 6.91, 6.61, 3.91, 3.47, 2.03, 1.91.

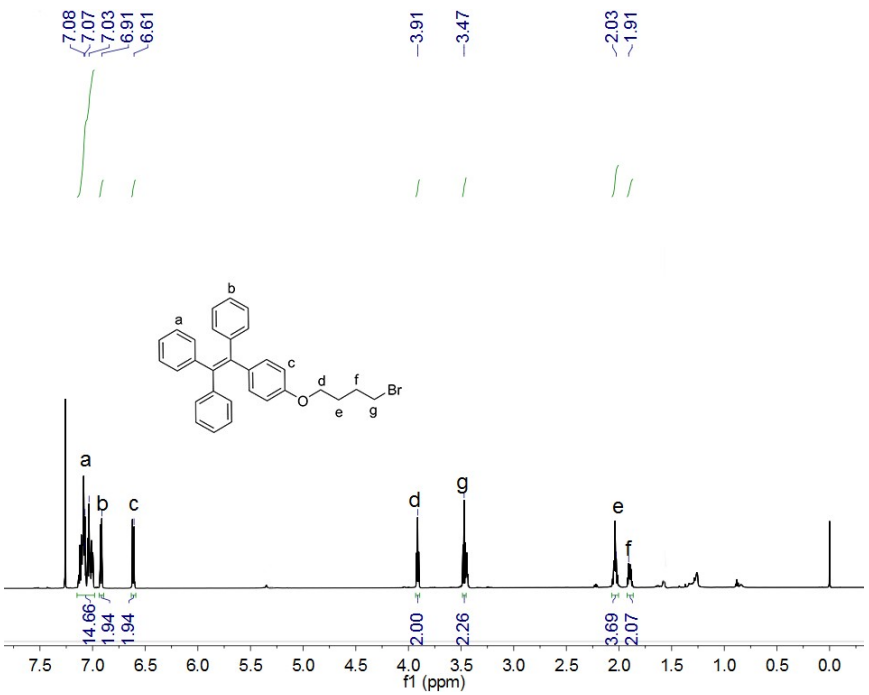


Figure S17. ^{1}H NMR spectrum of compound **3**.

Compound **3** (770 mg, 1.6 mmol) was dissolved in 40 mL pyridine under stirring at 80 °C temperature for 8 h. Then the solution was precipitated in 100 mL ethyl acetate to obtain a white solid compound **4** (878 mg, 98%). The ^{1}H NMR spectrum of compound **4** in $CDCl_3$ is shown in **Figure S18**. ^{1}H NMR (600 MHz, $CDCl_3$, 298K) δ (ppm): 9.48 (s, 2H), 8.40 (s, 1H), 8.07 (s, 2H), 7.04 (d, J = 33.5 Hz, 16H), 6.92 (s, 2H), 6.57 (d, J = 11.7 Hz, 2H), 5.10 (s, 2H), 3.92 (d, J = 11.6 Hz, 2H), 2.25 (s, 2H), 1.86 (s, 2H).

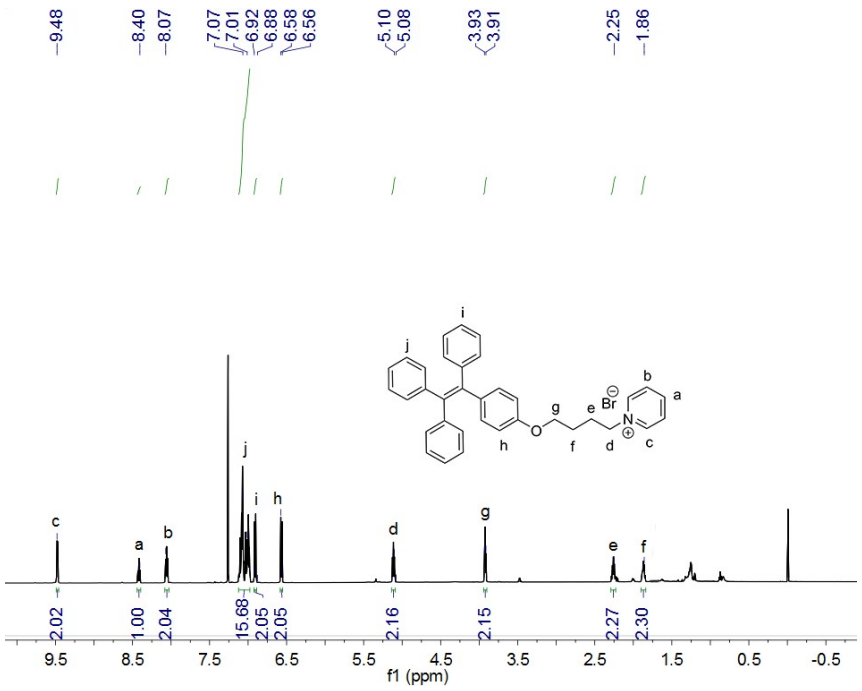


Figure S18. [1]H NMR spectrum of compound **4**.

Synthesis of G2

A solution of compound **4** (169 mg, 0.3 mmol) and LiTFSI (258 mg, 0.9 mmol) in 50 mL ultrapure water was stirring at room temperature for 2 h. The reaction mixture was filtered and the residue was washed with ultrapure water to afford **G2** as a white solid (196.5 mg, 86%). The [1]H NMR spectrum of **G2** in $CDCl_3$ is shown in **Figure S19**. [1]H NMR (600 MHz, $CDCl_3$, 298K) δ (ppm): 8.83 (d, *J* = 5.9 Hz, 2H), 8.44 (t, *J* = 7.8 Hz, 1H), 8.03 (t, *J* = 7.0 Hz, 2H), 7.04 (d, *J* = 45.8 Hz, 15H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.58 (d, *J* = 8.7 Hz, 2H), 4.72 (t, *J* = 7.6 Hz, 2H), 3.93 (t, *J* = 5.6 Hz, 2H), 2.22 (s, 2H), 1.83 (s, 2H). The melting point of **G2** was 106.2 °C.

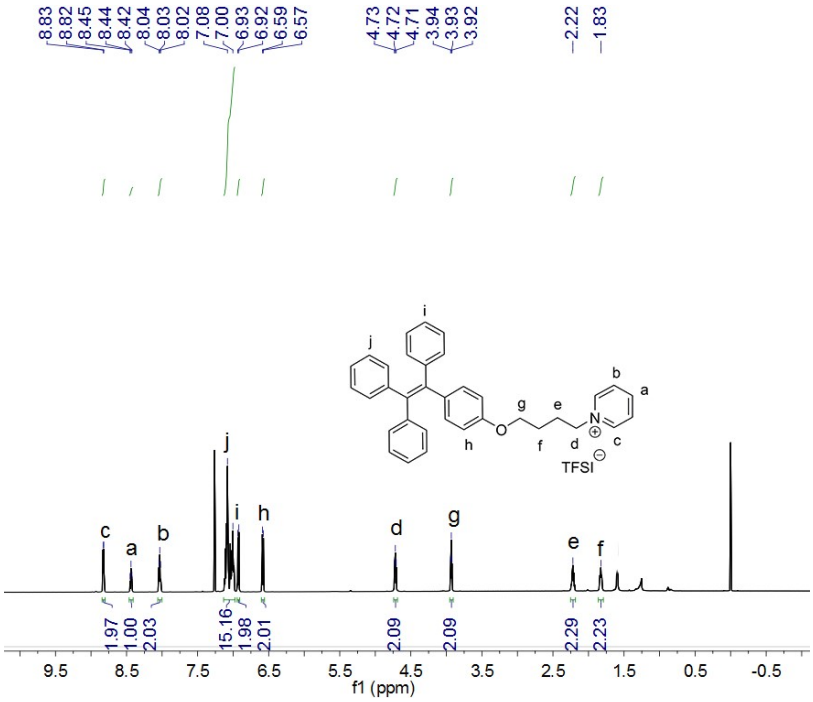


Figure S19. [1]H NMR spectrum of **G2**.

3. Complexation between NMP5A and different Guests.

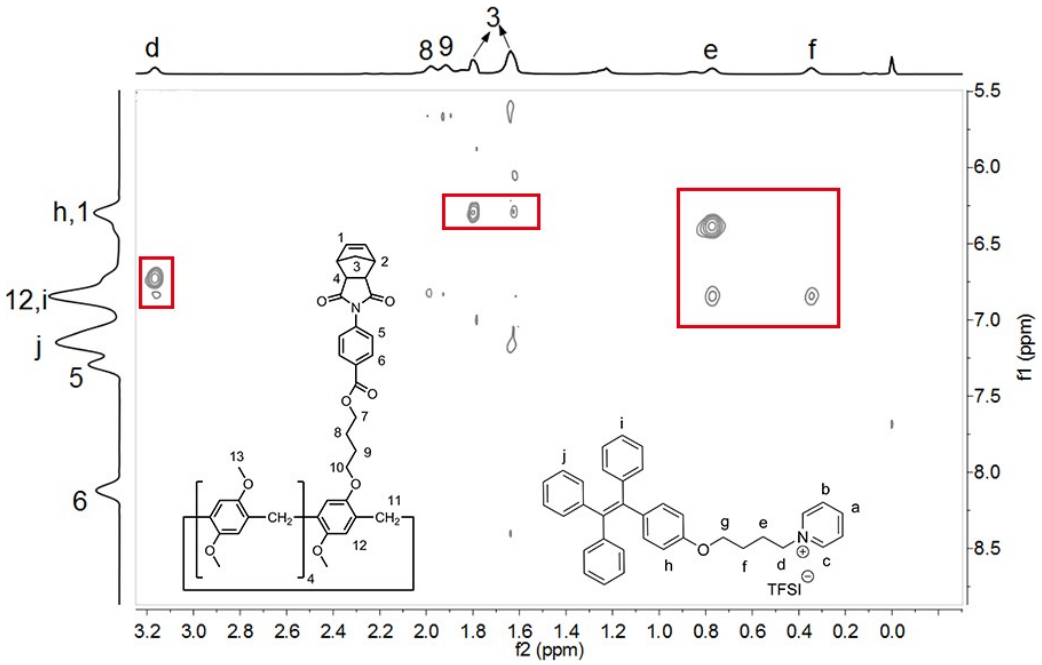


Figure S20. NOESY spectrum of a mixture of **NMP5A** (50.0 mM) and **G2** (25.0 mM) (600 MHz, $CDCl_3$, 298K).

The binding constant K_a of **NMP5A⊃G1** and **NMP5A⊃G2** was determined by ^{1}H NMR titration (***Figure S21***) and calculated as (132 ± 32) M^{-1} and (3120 ± 1159) M^{-1} as shown in ***Figure S22***. This values were obtained by the non-linear curve-fitting method, using the equation:[S5]

$\Delta\delta = (\delta_\infty / [G]_0) * (0.5 * [H]_0 + 0.5 * ([G]_0 + 1 / K_a) - (0.5 * ([H]_0 \wedge 2 + (2*[H]_0 (1 / K_a - [G]_0)) + (1/ K_a + [G]_0) \wedge 2) \wedge 0.5))$

Where $\Delta\delta$ is the chemical shift change of pyridinium aromatic proton (H_b) owing to **G1** or **G2**, δ_∞ is the chemical shift change of these protons when the guest is completely complexed, $[\mathbf{G}]_0$ is the initial concentration of **G1** or **G2**, and $[H]_0$ is the varying concentrations of **NMP5A**.

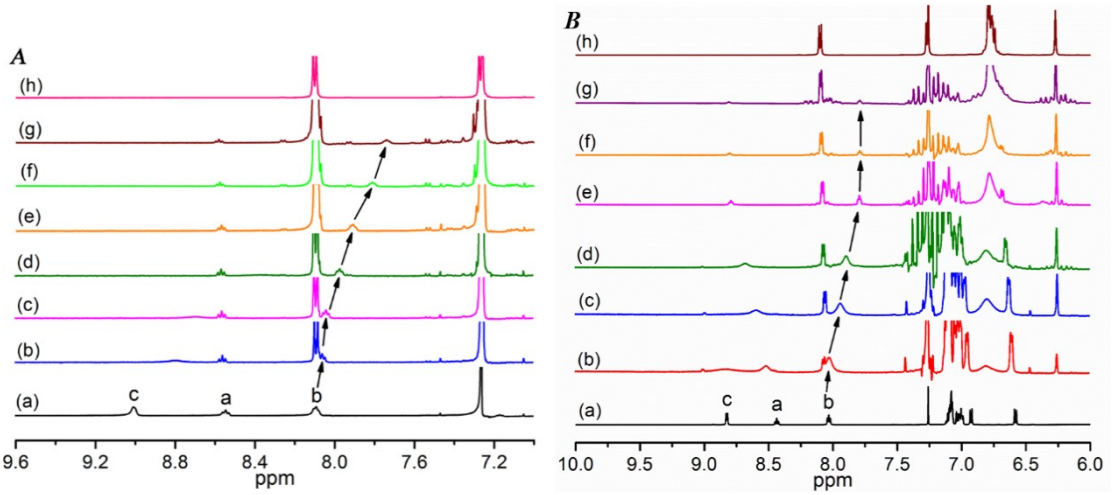


Figure S21 Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298K) of (**A**): **G1** at a concentration of 2 mM upon addition of **NMP5A**: 0.0 mM (a), 1 mM (b), 2 mM (c), 3 mM (d), 6 mM (e), 10 mM (f), 20 mM (g) and **NMP5A** (h) at 8

mM; (**B**): **G2** at a concentration of 2 mM upon addition of **NMP5A**: 0.0 mM (a), 0.4 mM (b), 1 mM (c), 1.6 mM (d), 5 mM (e), 10 mM (f), 20 mM (g) and **NMP5A** (h) at 8 mM.

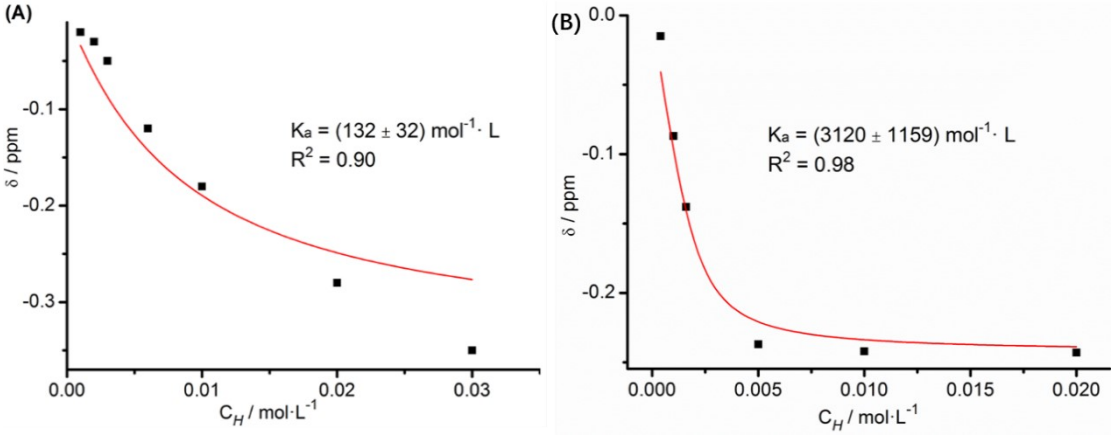


Figure S22 Fitting plot for the chemical shift changes of (**A**): pyridinium aromatic proton(H_b) from **G1**; (**B**): pyridinium aromatic proton (H_b) from **G2** upon addition of **NMP5A**.

^{1}H NMR titration of butanedinitrile (**G3**) and **NMP5A** was also carried out (***Figure S23***). The ethylene proton from **G3** upshifted to -1.31 ppm when 0.5 equiv of **NMP5A** was added into the **G3** solution and this peak did not move to higher field with1 equiv of **NMP5A**, revealing the binding constant K_a for complexes between **G3** and **NMP5A** is too large (>10^5 M^{-1}) to be determined by ^{1}H NMR titration, which is in agreement with the literatures.[S6]

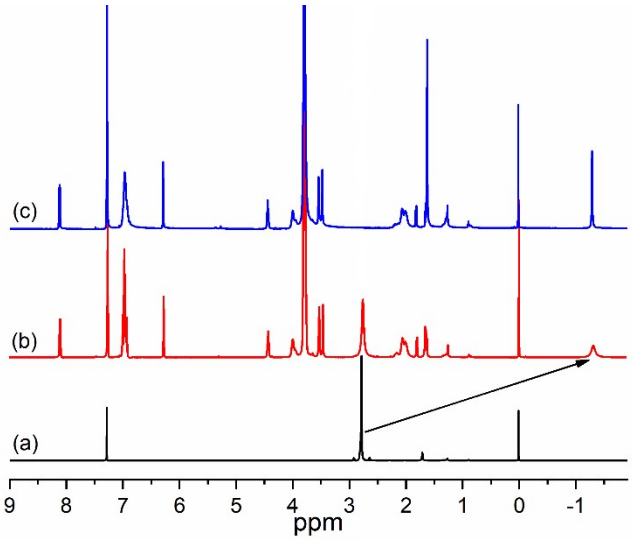


Figure S23 ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298K) of **G3** (a), *n*(**NMP5A**):*n*(**G3**)= 1:2 (b); *n*(**NMP5A**):*n*(**G_3**) = 1:1 (c) in $CDCl_3$.

4. Host-Guest Complexations between Polymers and G1.

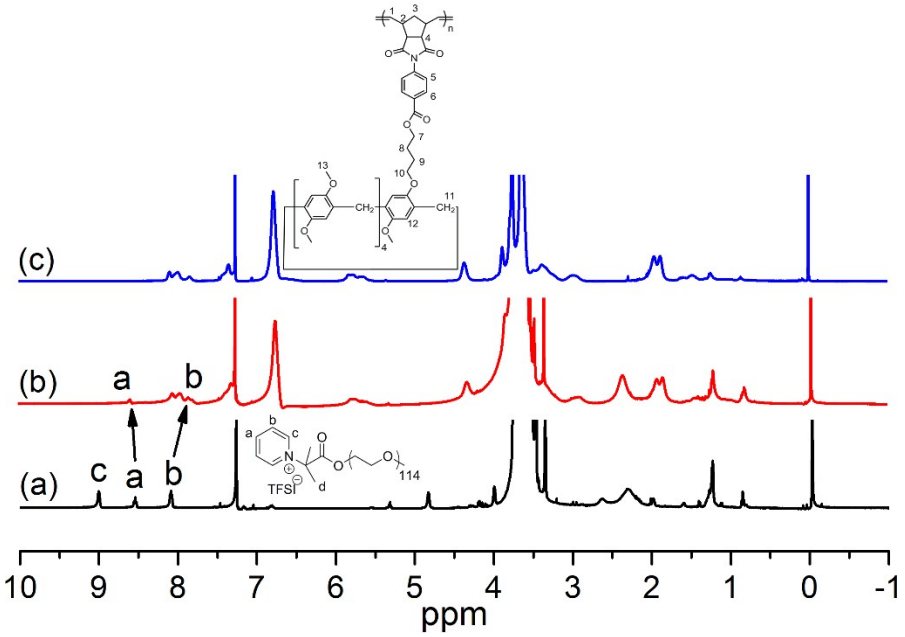


Figure S24. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K): 4 mM **G1** (a), 4 mM **G1** + 8 mM **pNMP5A** (b) and 8 mM **pNMP5A** (c).

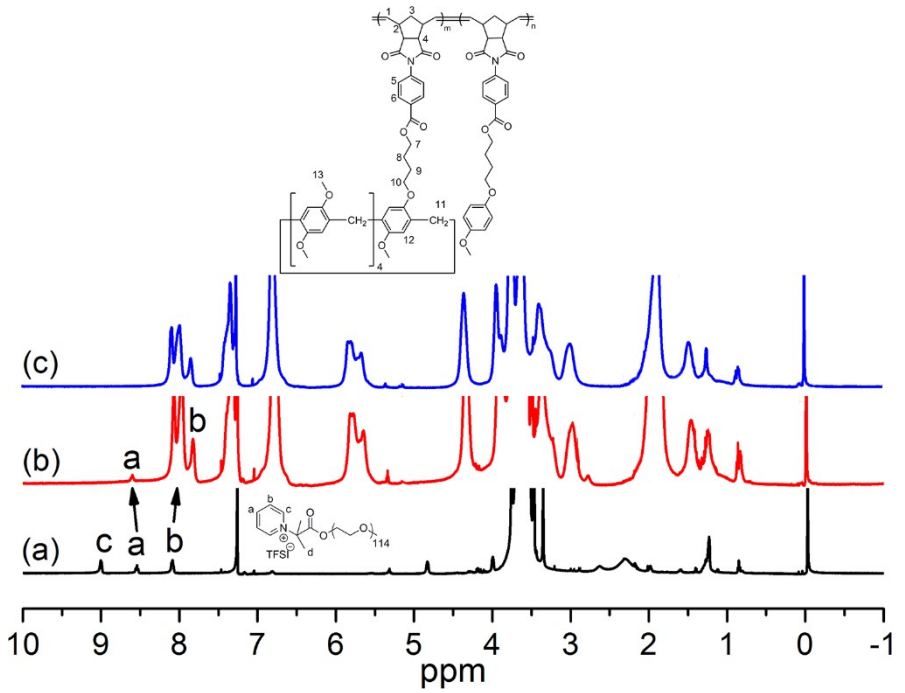


Figure S25. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K): 4 mM **G1** (a), 4 mM **G1** + 8 mM **pNMP5A-*b*-pMPHNB** (b) and 8 mM **pNMP5A-*b*-pMPHMB** (c).

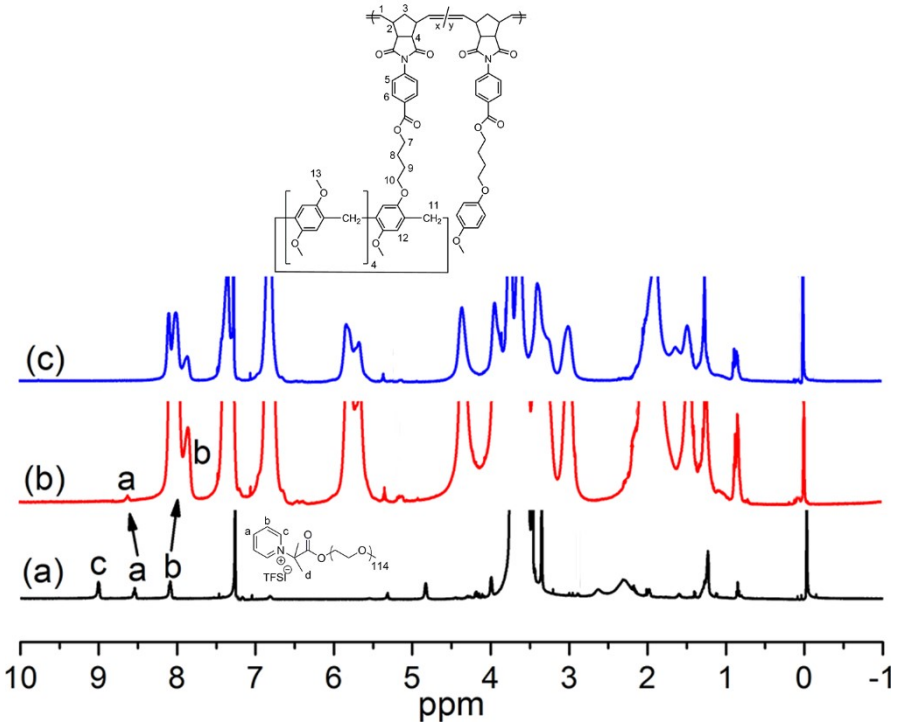


Figure S26. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K): 4 mM **G1** (a), 4 mM **G1** + 8 mM **p(NMP5A-*co*-MPHNB)** (b) and 8 mM **p(NMP5A-*co*-MPHMB)** (c).

5. TEM and DLS Measurements of Assemblies Formed from Supramolecular Brush Polymers.

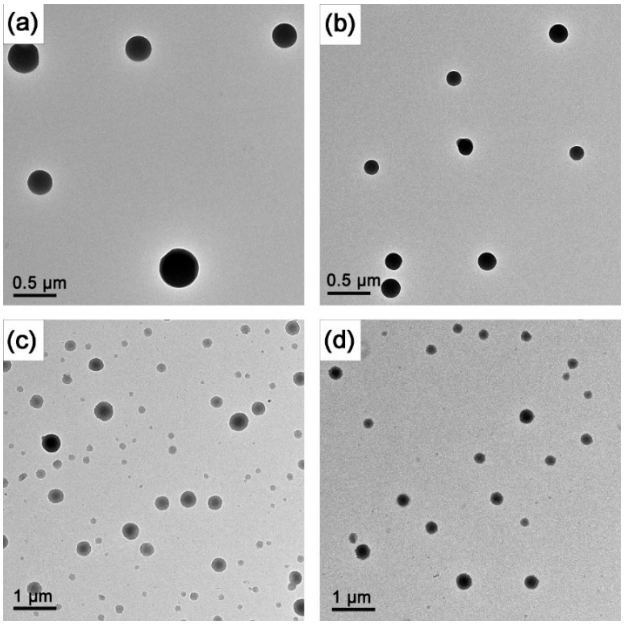


Figure S27. TEM images of micelles from polymer **p(NMP5A-*co*-MPHMB)** (a and b) and **pNMP5A** (c and d) with different molar ratios of **G1**, **H**:**G1**=1:0.3 (a and c), **H**:**G1**=1:4 (b and d) at 1.4 mg mL^{-1}.

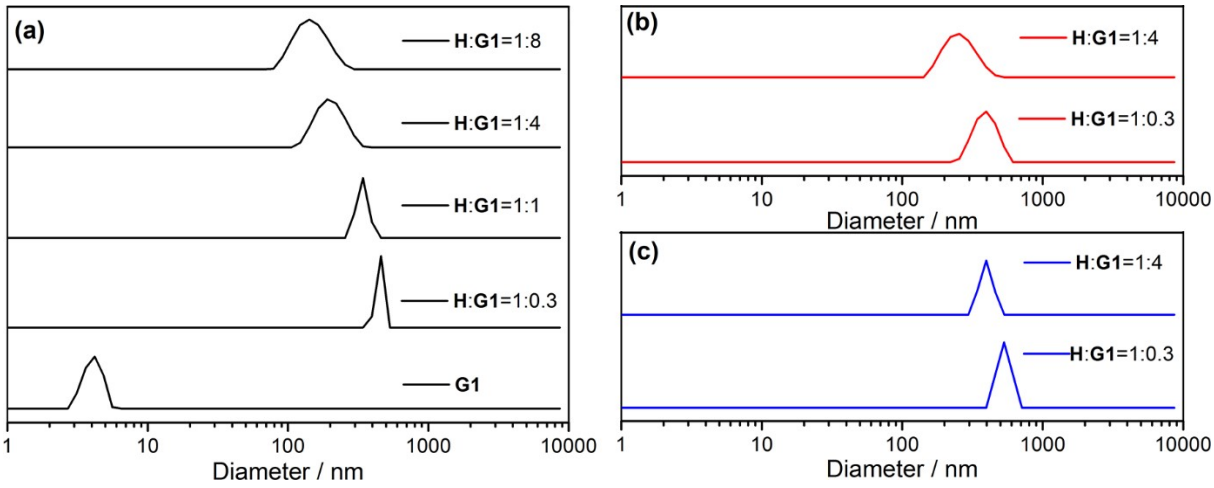


Figure S28. DLS results of micelles from block polymer (a), statistical polymer (b), and homopolymer (c) with different molar rations of **G1** at 1.4 mg mL^{-1}.

Figure S29. Photo of **pNMP5A-*b*-pMPHNB** suspension with laser light irradiation.

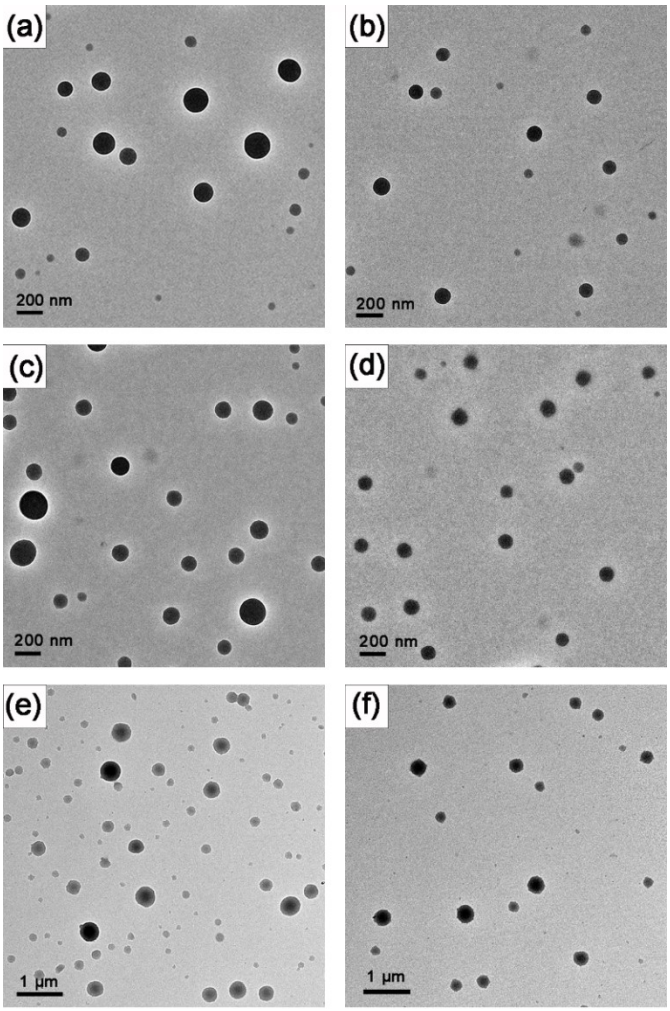


Figure S30. TEM images of the micelles self-assembled from **pNMP5A-*b*-pMPHMB**(a) (b), **p(NMP5A-*co*-MPHMB)** (c) (d), and **pNMP5A**(e) (f) in **H**:**G1:G2**=1:0.3:0.5(a) (c) (e), **H**:**G1:G2**=1:1:0.5(b) (d) (f) at 1.4 mg mL^{-1}.

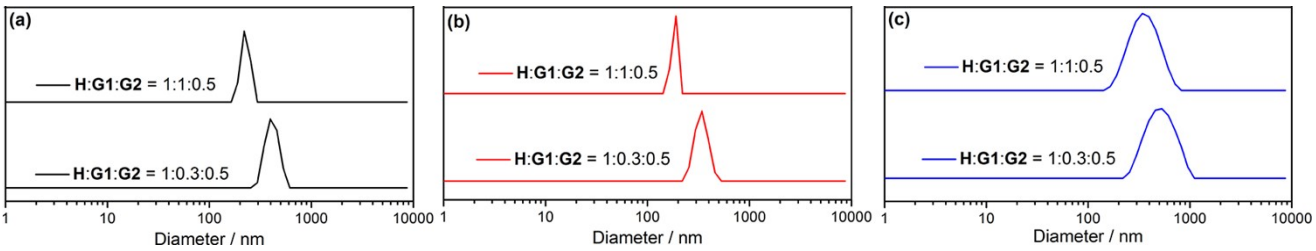


Figure S31. DLS results of micelles self-assembled from block polymer (a), statistical polymer (b), and homopolymer (c) with different molar rations of **G1** and **G2** at 1.4 mg mL^{-1}.

6. Study of Competitive Complexation.

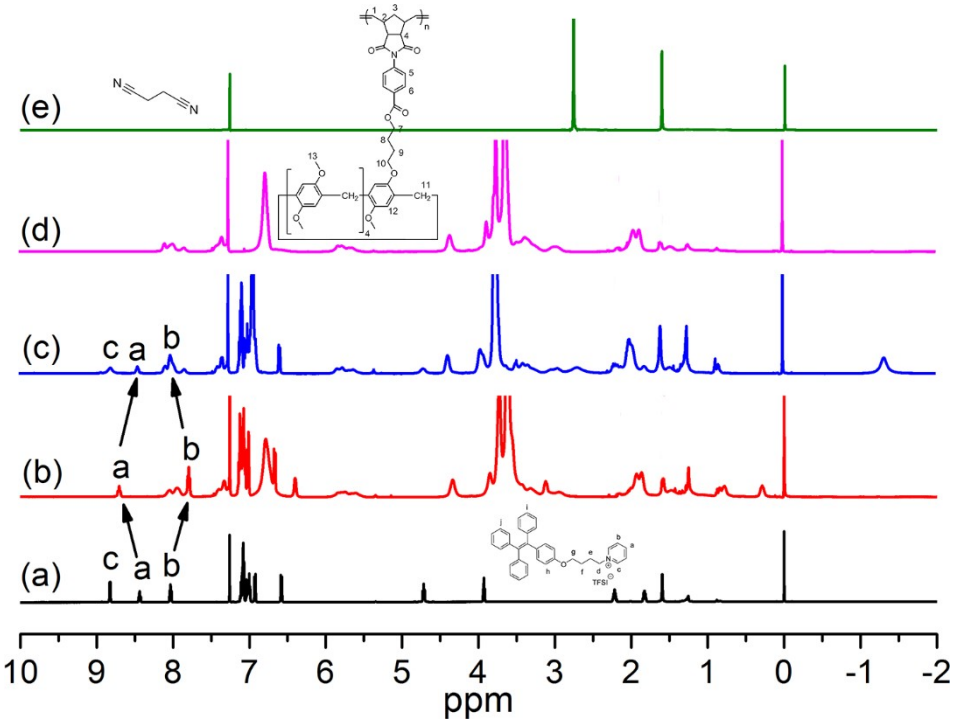


Figure S32. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 25 ^{o}C): 8mM **G2** (a), 16 mM **H** + 8 mM **G2** (b), 16 mM **H** + 8 mM **G2** + 16 mM **G3** (c), 16 mM **H** (d), and 16 mM **G3** (e).

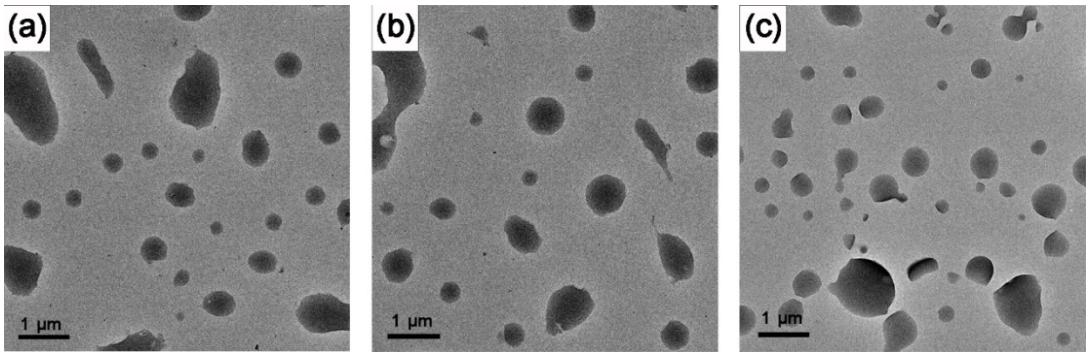


Figure S33. TEM images of the micelles self-assembled from **pNMP5A-*b*-pMPHMB**(a), **p(NMP5A-*co*-MPHMB)** (b), and **pNMP5A**(c) with **G3**.

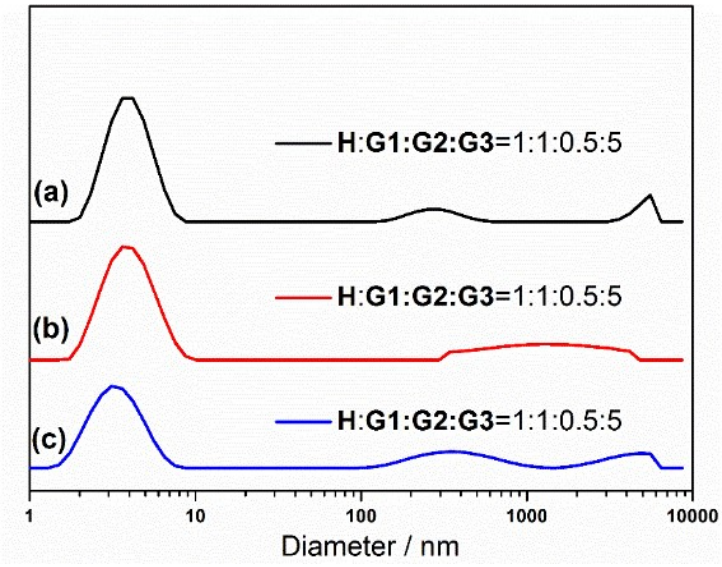
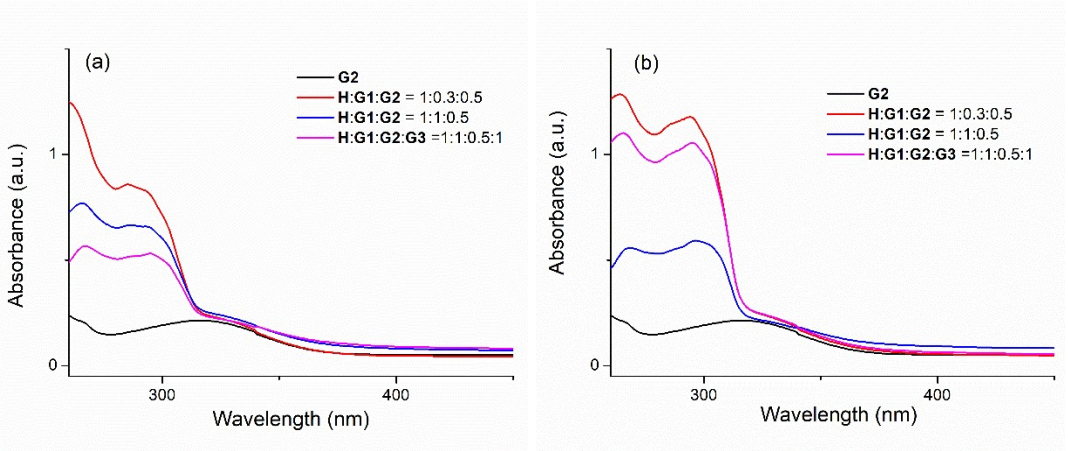


Figure S34. DLS results of micelles constructed by block polymer (a), statistical polymer (b), and homopolymer (c) fixed with **G3**.

7. UV-Vis spectra of the supramolecular brush polymers.

UV-Vis absorption spectra of **G2**, mixture of pillararene-containing polymers (**H**) with different molar ratio of **G1** and **G2**, as well as the mixture of **H**, **G1**, **G2** and **G3** in $CHCl_3$/MeOH (v/v = 8/3) solution were measured. As shown in ***Figure S35***, similar spectral patterns were observed for the self-assemblies, and absorption peaks at ~260, 300 and 330 nm were attributed to the π-π* transition of phenyl rings.



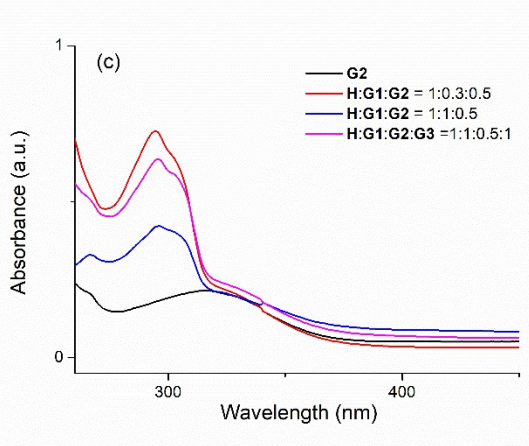


Figure S35. UV-Vis absorption spectra of supramolecular brush polymers composed of **pNMP5A-*b*-pMPHMB** (a), **p(NMP5A-*co*-MPHMB)** (b), and **pNMP5A** (c) with different molar ratios of **G1**, **G2**, and competitive guest **G3** in $CHCl_3$/MeOH (v/v = 8/3) solution ([**G2**] is 8.3×10^{-3} mg·ml^{-1}).

8. Fluorescence lifetimes and quantum yields.

The fluorescence lifetimes and quantum yields were shown in ***Figure S36*** and **Table S2**. The fluorescence lifetime increased a little after increasing the amount of **G1** from molar ratio of pillar[5]arene unit:**G1**:**G2** with 1:0.3:0.5 to 1:1:0.5. After competitive guest **G3** was added, this value decreased to a small extent. However, all these samples showed low quantum yields with less than 8.00%, which were obtained from an integrating sphere.

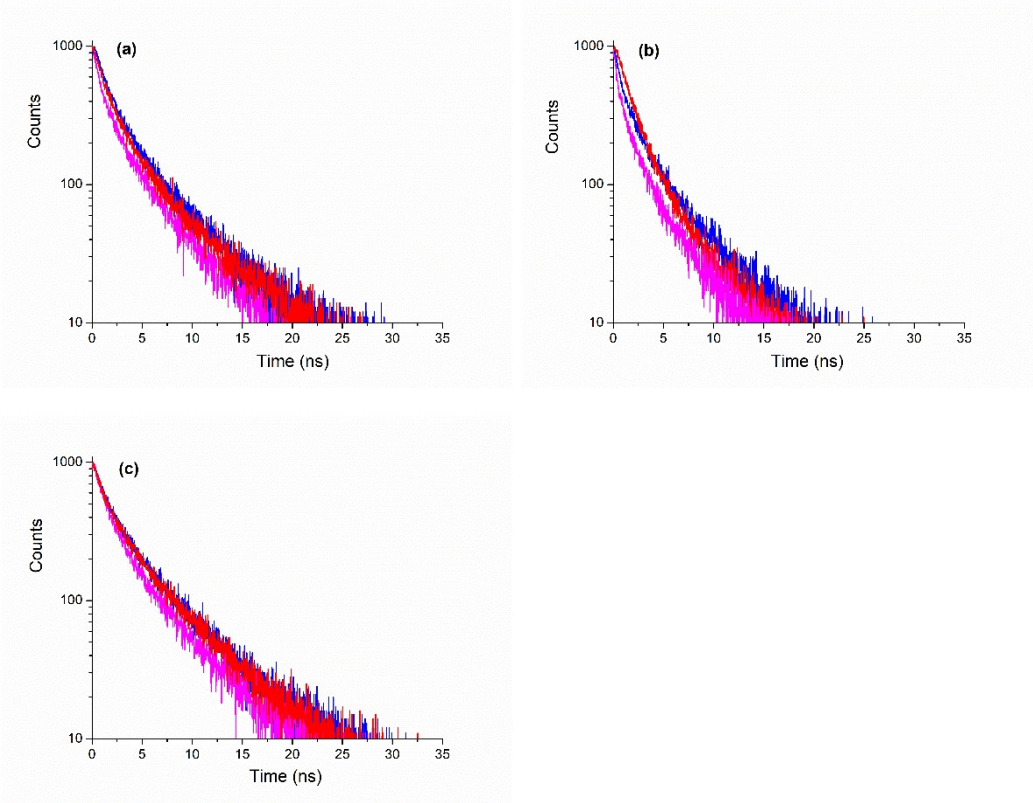


Figure S36. Fluorescence lifetime tests of supramolecular brush polymers composed of **pNMP5A-*b*-pMPHMB** (a),

p(NMP5A-*co*-MPHMB) (b), and **pNMP5A** (c) with different molar ratios of **G1**, **G2**, and competitive guest **G3** in $CHCl_3$/MeOH (v/v = 8/3) solution: **H**:**G1**:**G2** = 1:0.3:0.5 (red lines), **H**:**G1**:**G2** = 1:1:0.5 (blue lines), and **H**:**G1**:**G2**:**G3** = 1:1:0.5:1 (purple lines).

Table S2. The quantum yields and lifetimes of supramolecular polymers in solution

Samples[a]	φ (%)[b]	τ (ns)
H1:**G1**:**G2** = 1:0.3:0.5	6.24	2.63
H1:**G1**:**G2** = 1:1:0.5	7.34	2.72
H1:**G1**:**G2:G3** = 1:1:0.5:1	3.12	2.38
H2:**G1**:**G2** = 1:0.3:0.5	5.78	1.84
H2:**G1**:**G2** = 1:1:0.5	6.93	2.36
H2:**G1**:**G2:G3** = 1:1:0.5:1	2.56	1.60
H3:**G1**:**G2** = 1:0.3:0.5	5.88	2.62
H3:**G1**:**G2**= 1:1:0.5	7.87	2.70
H3:**G1**:**G2:G3** = 1:1:0.5:1	3.92	2.47

[a] **H1**, **H2** and **H3** refers to **pNMP5A-*b*-pMPHMB**, **p(NMP5A-*co*-MPHMB)**, and **pNMP5A**, respectively.

[b] Quantum yield is the absolute value obtained from an integrating sphere.

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