

Electronic Supplementary Information (ESI)

**Facile Surface Functionalization of Upconversion Nanoparticles with Phosphoryl Pillar[5]arenes
for Controlled Cargo Release and Cell Imaging**

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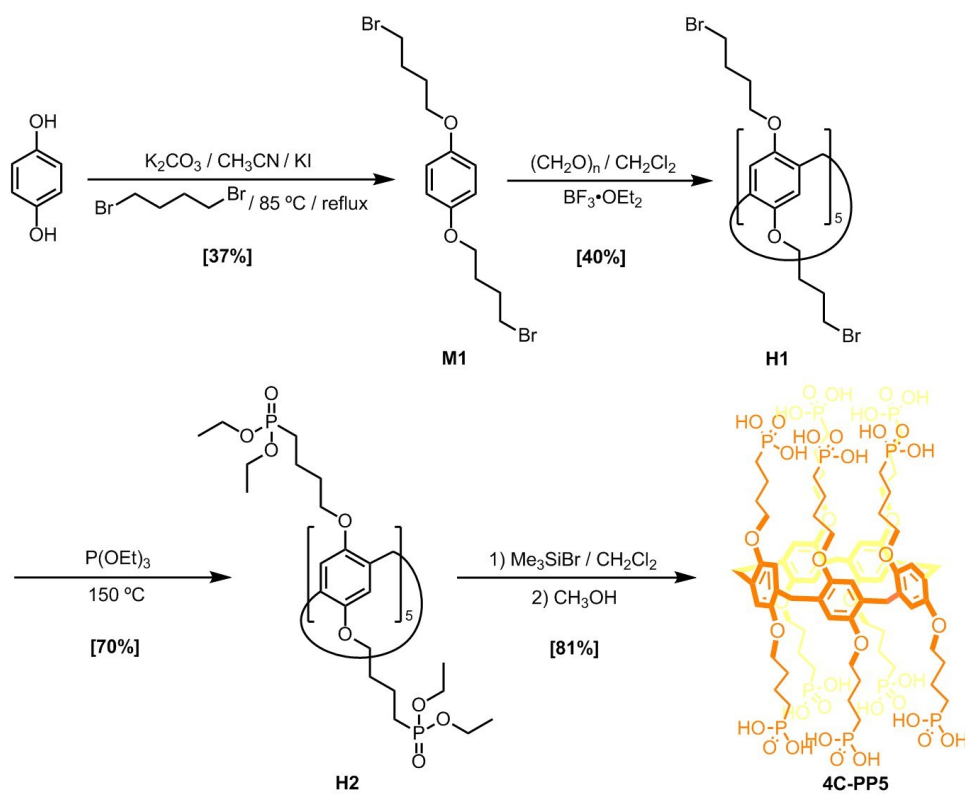
Email: ywyang@jlu.edu.cn

1. Materials and methods

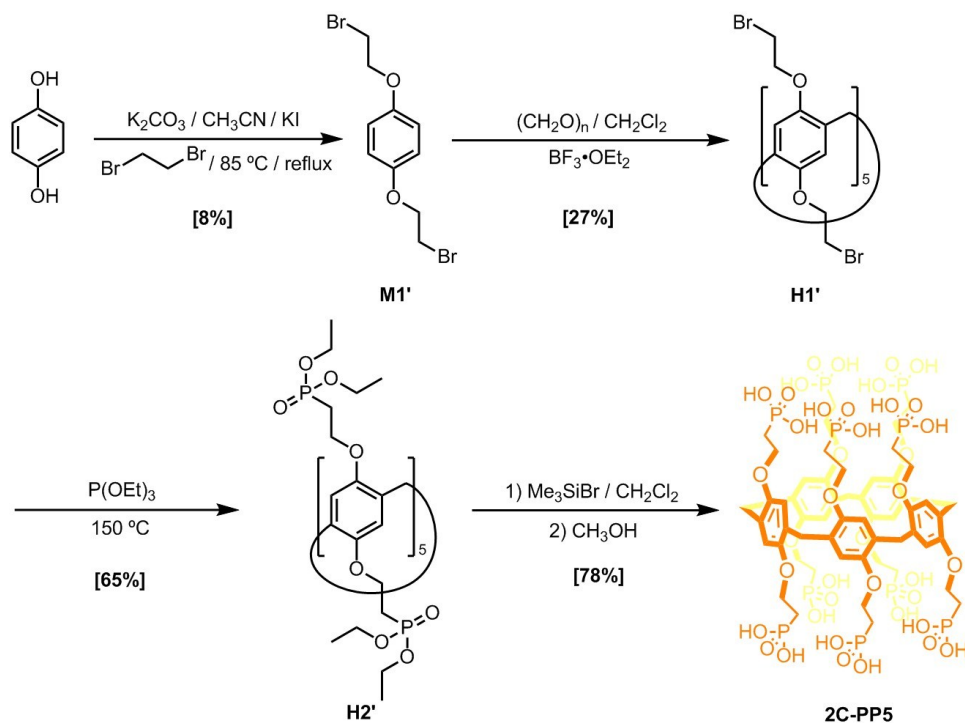
All reagents were commercially available. Hydroquinone, paraformaldehyde, 1, 4-dibromobutane, boron trifluoride diethyl etherate, bromotrimethylsilane, yttrium chloride hexahydrate, ytterbium chloride hexahydrate, erbium chloride hexahydrate, oleic acid and 1-octadecene were purchased from Aladdin, Sigma-Aldrich and Alfa Aesar Chemical Reagent Company without further purification. Deionized water was used in all experiments.

^1H NMR spectra were collected on a Varian 300 MHz NMR spectrometer at 298 K. ^{13}C NMR and ^{31}P NMR spectra were collected on a Bruker AVANCEIII 500MHz NMR spectrometer at 298 K. Scanning electron microscope (SEM) images were recorded on a HITACHI SU8082 instrument. Transmission electron microscopy (TEM) images were performed on a Tecnai G2 S-Twin F20 instrument. The crystalline structures of samples were characterized by powder X-ray diffraction (PXRD) measurements (Rigaku SmartLab III powder diffractometer using $\text{Cu}_{\text{K}\alpha}$ radiation source 1.39 Å). Fourier-transform infrared (FT-IR) absorption spectra were recorded on a Bruker Vertex 80 V spectrometer. Thermal gravimetric analysis (TGA) determinations were performed on a STA 449 Thermal gravimetric analyzer. Dynamic light scattering (DLS) measurements were performed on a Zetasizer Nano ZS instrument. Zeta potential measurements were tested on a Zetasizer Nano 9300 instrument. The upconversion emission spectra were recorded at 298 K using an Andor Shamrock SR-750 spectrometer with a 980 nm continuous diode laser. The controlled release experiments were collected via UV-vis spectroscopy on a Shimadzu UV-1800 spectrophotometer. Electrospray mass spectrometric analysis (ESI-MS) was performed on an Autoflex Speed TOF/TOF. Mass spectra were recorded on Bruker Daltonics Autoflex Speed Series: High-Performance MALDI-TOF Systems. Upconversion luminescence cell imaging was performed with an inverted fluorescence microscope (Nikon Ti-S), and an external CW 980 nm laser diode (~ 500 mW) was illuminated onto the samples.

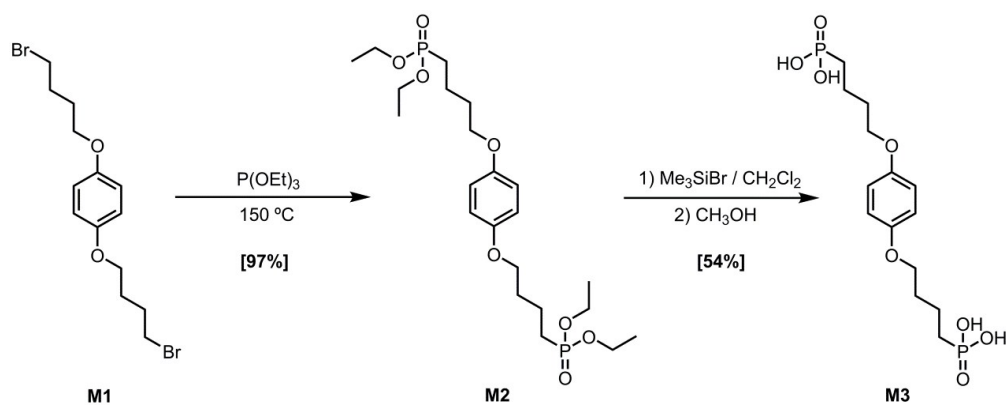
2. Experimental section



Scheme S1. Synthetic routes to the targeted compound **4C-PP5**



Scheme S2. Synthetic routes to the targeted compound **2C-PP5**



Scheme S3. Synthetic routes to the targeted monomer **M3**.

Phosphoryl-functionalized pillar[5]arene (2C-PP5) was prepared according to the reported procedures in literature.^{S1}

Synthesis of monomer 1, 4-bis(bromobutoxy)benzene (M1): A mixture of hydroquinone (3.3 g, 30 mmol) and K_2CO_3 (9 g, 65 mmol) in CH_3CN (250 mL) was stirred in a 500 mL round bottom flask at room temperature for 30 min. Then KI (30 mg, 0.2 mmol) and 1, 4-dibromobutane (17.8 mL, 82 mmol) were added in the above reaction, followed by stirring at 85 °C for 16 h. Next, the K_2CO_3 was removed by filtering and washing with CH_2Cl_2 . The crude product was purified by column chromatograph with petroleum ether/ethyl acetate (15:1 v/v) as the eluent to get pure product **M1** (4.2 g, 37%). $^1\text{H NMR}$ (300 MHz, CDCl_3 , 298 K), δ (ppm): 6.814 (s, 4 H), 3.944 (t, $J = 6$ Hz, 4H), 3.487 (t, $J = 6$ Hz, 4H), 2.041 (m, $J = 6$ Hz, 9 Hz, 4H), 1.912 (m, 4H).

Synthesis of bromo-functionalized pillar[5]arene (H1): To a solution of **M1** (3.8 g, 10 mmol) in 1, 2-dichloroethane (200 mL), paraformaldehyde (0.9 g, 30 mmol) was added under nitrogen atmosphere. Then boron trifluoride diethyl etherate (1.3 mL, 10 mmol) was added to the solution and the mixture was stirred at room temperature for 3 h to obtain a green solution. A green solution was got. After the solvent was removed, the organic phase was separated and washed with saturated aqueous NaHCO_3 , brine and H_2O , respectively. The obtained solid was purified by column chromatography on silica gel with petroleum ether/dichloromethane (1:2 v/v) as the eluent to get a white powder **H1** (1.6 g, 40%). $^1\text{H NMR}$ (300 MHz, CDCl_3 , 298 K), δ (ppm): 6.818 (s,

10H), 3.934 (t, $J = 6$ Hz, 20H), 3.751 (s, 10H), 3.447 (t, $J = 6$ Hz, 20H), 2.042 (m, 20H), 1.938 (m, 20H).

Synthesis of phosphonate-substituted pillar[5]arene (H2): **H1** (530 mg, 0.3 mmol) was dissolved in triethyl phosphite (3 mL, 17 mmol). The mixture was stirred at 150 °C for 60 h. After the solvent was removed, the obtained solid was purified by column chromatography on silica gel with chloroform/methanol (20:1 v/v) as the eluent to get a viscous liquid **H2** (483 mg, 70%). ¹H NMR (300 MHz, CDCl₃, 298 K), δ (ppm): 6.793 (s, 10H), 4.122 – 4.072 (m, 60H), 3.714 (s, 10H), 1.902 – 1.818 (m, 60H), 1.310 – 1.257 (m, 60H). ¹³C NMR (126 MHz, CDCl₃, 298 K), δ (ppm): 146.616, 128.351, 114.777, 67.479, 61.475, 29.274, 26.071, 24.894, 19.493, 16.478. ³¹P NMR (202 MHz, CDCl₃, 298 K), δ (ppm): 31.695. MS (MALDI-TOF): C₁₁₅H₂₀₀O₄₀P₁₀ calcd. [M+Na]⁺ m/z 2555.0918, found m/z 2555.0914.

Synthesis of phosphoryl-functionalized pillar[5]arene (4C-PP5): A solution of bromotrimethylsilane (2 mL, 15.2 mmol) in CH₂Cl₂ (10 mL) was added dropwise to CH₂Cl₂ solution (10 mL) containing **H2** (483mg, 0.2 mmol) and the reaction mixture was stirred at room temperature for 24 h. Then, the solvent was evaporated under reduced pressure and methanol was added into the obtained yellow oil. The reaction mixture was stirred for an additional 12 h. The crude product was washed with acetone for three times and dried under high vacuum oven to get a white powder **4C-PP5** (300 mg, 81%). ¹H NMR (300 MHz, DMSO-*d*₆, 298 K), δ (ppm): 8.137 (s, 20H), 6.806 (s, 10H), 3.940 – 3.745 (m, 20H), 3.643 (s, 10H), 1.884 – 1.677 (m, 60H); ¹³C NMR (126 MHz, DMSO-*d*₆, 298 K), δ (ppm): 149.115, 127.734, 114.045, 67.610, 28.867, 27.923, 26.838, 19.439. ³¹P NMR (202 MHz, DMSO-*d*₆, 298 K), δ (ppm): 27.239. MS (MALDI-TOF): C₇₅H₁₂₀O₄₀P₁₀ calcd. [M] m/z 1970.4727, found m/z 1970.4761.

Synthesis of monomer 1, 4-bis(bromobutoxy)benzene (M1'): A solution of containing CH₃CN (300 mL) hydroquinone (4.4 g, 40 mmol) and K₂CO₃ (12.0 g, 88 mmol) was stirred in a 500 mL round bottom flask at room temperature for 30 min. Then KI (30 mg, 0.2 mmol) and 1, 2-dibromoethane (50 mL, 578 mmol) were added into the above solution and the mixture was stirred

at 85 °C for 16 h. Next, the K_2CO_3 was removed by filtering and washing with CH_2Cl_2 (50 mL \times 2). The crude product was purified by column chromatograph with petroleum ether/ethyl acetate (15:1 v/v) as the eluent to get pure product **M1'** (1.0 g, 8%). 1H NMR (300 MHz, $CDCl_3$, 298 K), δ (ppm): 6.862 (s, 4 H), 4.246 (t, $J = 6$ Hz, 4H), 3.615 (t, $J = 6$ Hz, 4H).

Synthesis of bromo-functionalized pillar[5]arene (H1'): To a solution of **M1'** (1.0 g, 3 mmol) in 1, 2-dichloroethane (100 mL), paraformaldehyde (0.3 g, 10 mmol) was added under nitrogen atmosphere. Then boron trifluoride diethyl etherate (0.5 mL, 4 mmol) was added into the solution and the mixture was stirred at room temperature for 3 h to obtain a green solution. After the solvent was removed, the organic phase was separated and washed with saturated aqueous $NaHCO_3$, brine and H_2O respectively. The obtained solid was purified by column chromatography on silica gel with petroleum ether/dichloromethane (1:2 v/v) as the eluent to get a white powder **H1'** (278 mg, 27%). 1H NMR (300 MHz, $CDCl_3$, 298 K), δ (ppm): 6.917 (s, 10H), 4.231 (t, $J = 6$ Hz, 20 H), 3.843 (s, 10H), 3.636 (t, 20H).

Synthesis of phosphonate-substituted pillar[5]arene (H2'): **H1'** (500 mg, 0.3 mmol) was dissolved in triethyl phosphite (4 mL, 23 mmol). The mixture was stirred at 150 °C for 60 h. After the solvent was removed, the obtained solid was purified by column chromatography on silica gel with chloroform/methanol (20:1 v/v) as the eluent to get a viscous liquid **H2'** (440 mg, 65%). 1H NMR (300 MHz, $CDCl_3$, 298 K), δ (ppm): 6.861 (s, 10H), 4.170 – 4.086 (m, 60H), 3.742 (s, 10H), 2.411 – 2.235 (m, 60H), 1.310 – 1.257 (m, 60H).

Synthesis of phosphoryl-functionalized pillar[5]arene (2C-PP5): A solution of bromotrimethylsilane (2 mL, 15.2 mmol) in CH_2Cl_2 (10 mL) was added dropwise to CH_2Cl_2 solution (10 mL) containing **H2'** (500 mg, 0.2 mmol) and the reaction mixture was stirred at room temperature for 24 h. Then, the solvent was evaporated under reduced pressure and methanol was added into the obtained yellow oil. The reaction mixture was stirred for an additional 12 h. The crude product was washed with acetone for three times and dried under high vacuum oven to get a

white powder **2C-PP5** (290 mg, 78%). ¹H NMR(300 MHz, DMSO-*d*₆, 298 K), δ (ppm): 7.940 (s, 20H), 6.873 (s, 10H), 4.081 – 4.055 (m, 20H), 3.669 (s, 10H), 2.262 – 2.209 (m, 20H).

Synthesis of 1, 4-phosphonatebutoxybenzene (M2): Compound **M1** (500 mg, 1 mmol) was dissolved in triethyl phosphite (4.5 mL, 26 mmol). The reaction mixture was heated to 150 °C and the resulting clear solution was stirred for another 36 h at 150 °C. After the solvent was removed, the product was obtained as a viscous liquid **M2** (633 mg, 97%). ¹H NMR (300 MHz, CDCl₃, 298 K), δ (ppm): 6.804 (s, 4 H), 4.131 – 4.047 (m, 8 H), 3.936 – 3.897 (t, *J* = 6 Hz, 4 H), 1.852 – 1.777 (m, 12 H), 1.325 (t, *J* = 6 Hz, 12 H). ¹³C NMR (126 MHz, CDCl₃, 298 K), δ (ppm): 153.083, 115.342, 67.714, 61.456, 61.405, 25.938, 24.816, 19.321, 16.441. ³¹P NMR (202 MHz, CDCl₃, 298 K), δ (ppm): 31.892. ESI-MS: C₂₂H₄₀O₈P₂ calcd. [M+H]⁺ m/z 495.2271, found m/z 495.2255.

Synthesis of 1, 4-(phosphonic acid)butoxybenzene (M3): A solution of bromotrimethylsilane (4.4 mL, 33.3 mmol) in CH₂Cl₂ was added dropwise to CH₂Cl₂ solution (10 mL) containing **M2** (633 mg, 1.3 mmol) and the reaction mixture was stirred at room temperature for 24 h. Then, the solvent was evaporated under reduced pressure and methanol was added into the obtained yellow oil. The reaction mixture was stirred for an additional 12 h. The crude product was washed with acetone for three times and dried under high vacuum oven to get a white powder **M3** (265 mg, 54%). ¹H NMR (300 MHz, DMSO-*d*₆, 298 K), δ (ppm): 6.835 (s, 4 H), 3.884 (t, *J* = 6 Hz, 4 H), 1.751 (t, 4 H), 1.710 – 1.515 (t, 8 H). ¹³C NMR (126 MHz, DMSO-*d*₆, 298 K), δ (ppm): 152.679, 115.317, 67.509, 27.709, 26.618, 19.578. ³¹P NMR (202 MHz, DMSO-*d*₆, 298 K), δ (ppm): 28.851. MS (MALDI-TOF): C₁₄H₂₄O₈P₂ calcd. [M+Na-H] m/z 404.0760, found m/z 404.0765.

Hexagonal-phase NaYF₄: 20% Yb³⁺, 2% Er³⁺ nanoparticles (OA-UCNPs) were synthesized following a previously reported process:^{S2} Herein, 1 mmol of lanthanide chlorates (0.78 mmol YCl₃·6H₂O, 0.20 mmol YbCl₃·6H₂O and 0.02 mmol ErCl₃·6H₂O) were mixed with oleic acid (6 mL) and octadecene (ODE, 15 mL) in a 100 mL 3-necked flask. The mixture was heated to 160 °C and kept at the high reaction temperature for half an hour to form a homogeneous solution. Then the solution was cooled down to room temperature and methanol solution (5 mL) containing 2.5

mmol NaOH and 4 mmol NH₄F was slowly added dropwise into the flask. The resulting solution was stirred for 30 min at room temperature and heated slowly to 110 °C and then maintained at this temperature until the methanol was evaporated. Then the mixed solution was heated up to 300 °C and held for 90 min under the protection of a gentle flow of nitrogen. After the solution was cooled down to room temperature, adding ethanol (20 mL) into the as-prepared solution. The nanoparticles were isolated by centrifuge at 10000 rpm. The product was washed with ethanol and deionized water for several times to remove the NaF residue.

Ligand exchange on OA-UCNPs with phosphoryl-functionalized pillar[5]arene ligands (2C-PP5/4C-PP5):^{S3} Methanol solution (50 mL) containing excess 2C-PP5/4C-PP5 (500 mg) was added into the THF (50 mL) solution containing OA-UCNPs (50 mg). The reaction mixture was then heated slowly to 70 °C in an oil bath and stirred at 70 °C for a minimum of 5 h or overnight. Then the reaction was cooled down to room temperature and hexanes was added to precipitate out the 2C-PP5/4C-PP5 coated UCNPs (2C-PP5-UCNPs/4C-PP5-UCNPs). The 2C-PP5-UCNPs/4C-PP5-UCNPs were isolated via centrifugation at 10000 rpm and washed with hexane for three times. To remove excess ligands, the exchanged UCNPs were washed with deionized water and ethanol, respectively.

Ligand exchange on OA-UCNPs with M3 ligands: Methanol solution (50 mL) containing excess M3 (500 mg) was added into the THF (50 mL) solution containing OA-UCNPs (50 mg). The reaction mixture was then heated slowly to 70 °C in an oil bath and stirred at 70 °C for a minimum of 5 h or overnight. Then the reaction was cooled down to room temperature and hexanes was added to precipitate out the M3 coated UCNPs (M3-UCNPs). The M3-UCNPs were isolated via centrifugation at 10000 rpm and washed with hexane for three times. To remove excess ligands, the exchanged UCNPs were washed with deionized water and ethanol, respectively.

Drug loading: Rhodamine B (RhB) was employed as a kind of drug model compound for loading into the prepared nanomaterials by dispersing 4C-PP5-UCNPs nanomaterials (8 mg) in RhB (4 mL) aqueous solution and stirred at room temperature for 12 h. Finally, the obtained RhB loaded 4C-PP5-UCNPs (4C-PP5-UCNPs@RhB) nanocomposites were isolated via centrifugation at 10000 rpm, washed with deionized

water for three times, and dried under vacuum. Similarly, the 5-ASA loaded 4C-PP5-UCNPs (4C-PP5-UCNPs@5-ASA) nanocomposites were prepared in a similar method, but replaced RhB aqueous solution (4 mL) with 5-ASA aqueous solution (4 mL).

Controlled drug release: Drug release experiments were determined by monitoring the UV-vis absorption spectra of the released RhB at the preset time interval. Briefly, the 4C-PP5-UCNPs@RhB nanocomposites (0.5 mg) were putted into dialysis bag and then immersed into the cuvette containing phosphate-buffered saline (PBS, 10 mL) under gentle stirring. The release of RhB was controlled by changing pH. The amount of released drug was determined by plotting the standard curve of the RhB concentration and absorbance, then, quantified by Lambert-Beer Law.

3. Particle size distribution

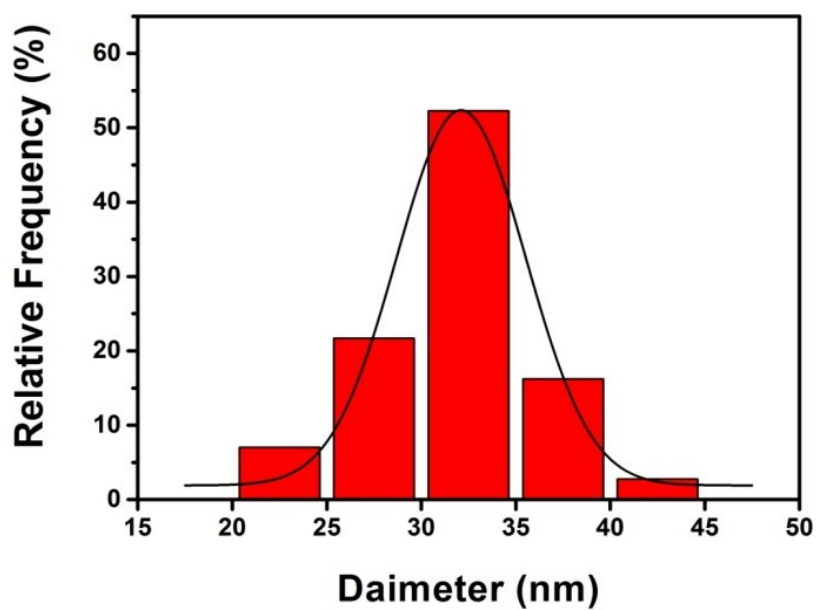


Figure S1. The corresponding histograms of the 4C-PP5-UCNPs sizes based on 327 particles. The diameter is 31.4 ± 4.2 nm.

4. SEM images

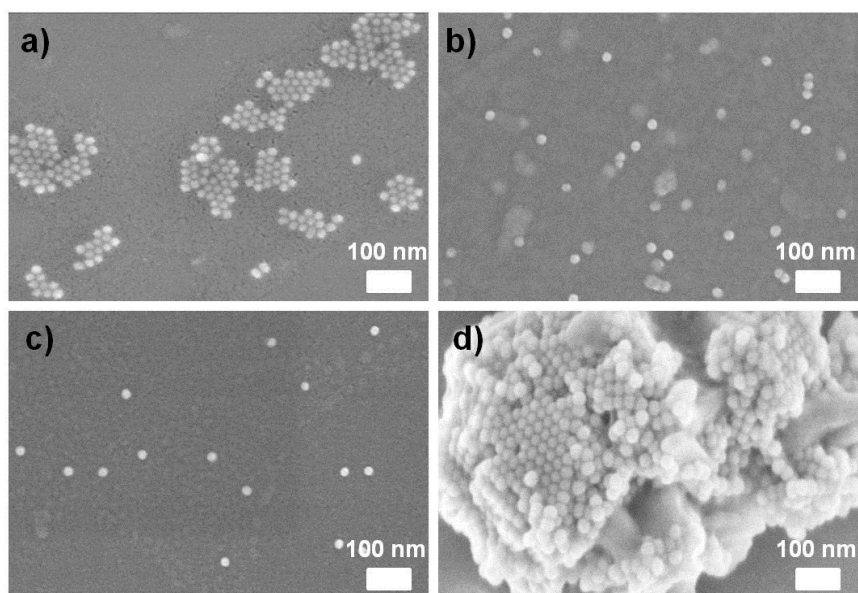


Figure S2. SEM images of (a) OA-UCNPs, (b) 2C-PP5-UCNPs, (c) 4C-PP5-UCNPs and (d) M3-UCNPs.

5. XRD patterns and FT-IR spectra

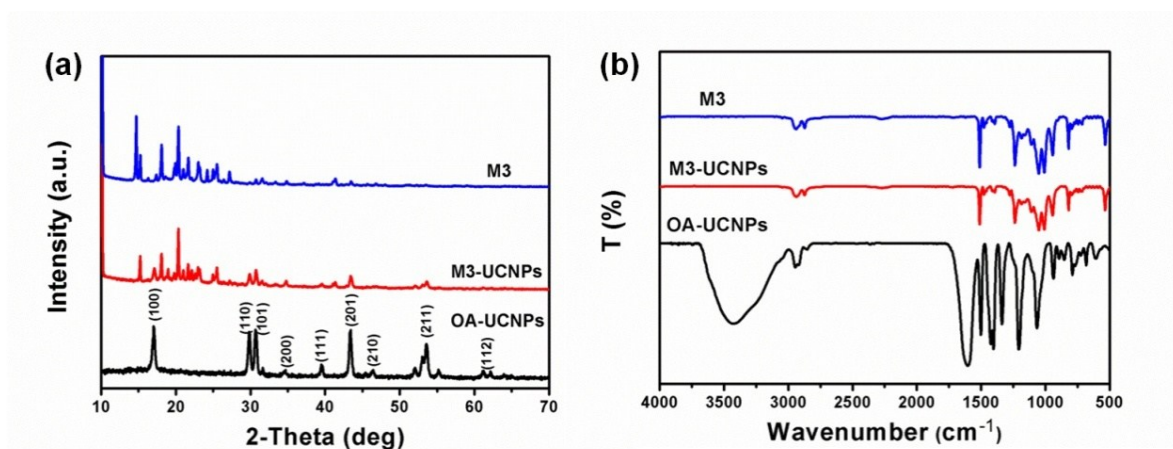


Figure S3. (a) PXRD patterns of OA-UCNPs (black), M3-UCNPs (red) and M3 (blue); (b) FT-IR spectra of OA-UCNPs (black), M3-UCNPs (red) and M3 (blue).

6. Dynamic light scattering measurements

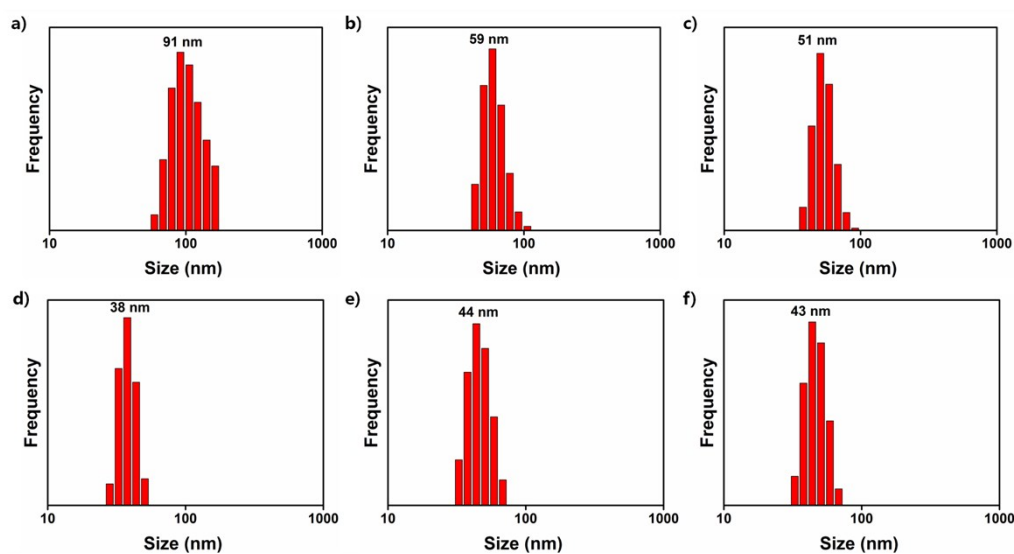


Figure S4. Dynamic light scattering (DLS) analysis of (a) 4C-PP5-UCNPs, (b) 4C-PP5-UCNPs@RhB and (c) 4C-PP5-UCNPs@5-ASA in PBS (pH = 5.0); (d) 4C-PP5-UCNPs, (e) 4C-PP5-UCNPs@RhB and (f) 4C-PP5-UCNPs@5-ASA in PBS (pH = 7.4).

7. Zeta potential measurements

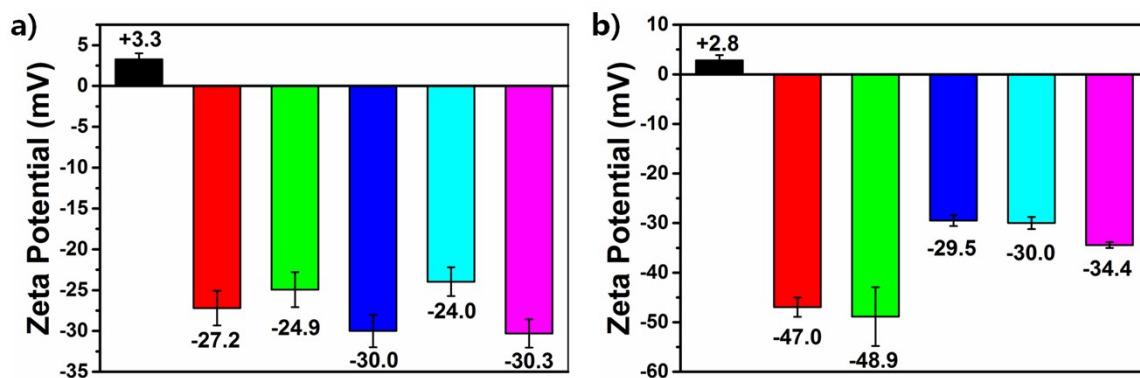


Figure S5. Zeta potentials of OA-UCNPs (black), 2C-PP5-UCNPs (red), 4C-PP5-UCNPs (green), M3-UCNPs (blue), 4C-PP5-UCNPs@RhB (cyan) and 4C-PP5-UCNPs@5-ASA (pink) in PBS of (a) pH 5.0 and (b) pH 7.4, respectively.

8. Thermogravimetric analysis

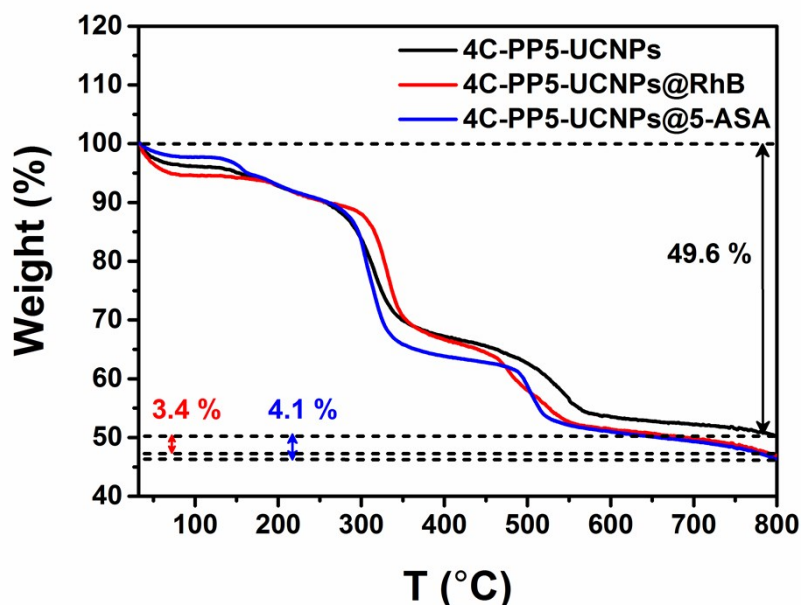


Figure S6. Thermogravimetric analysis of 4C-PP5-UCNPs (black), 4C-PP5-UCNPs@RhB (red) and 4C-PP5-UCNPs@5-ASA (blue).

9. The form changes of RhB and 4C-PP5 at different pH values.

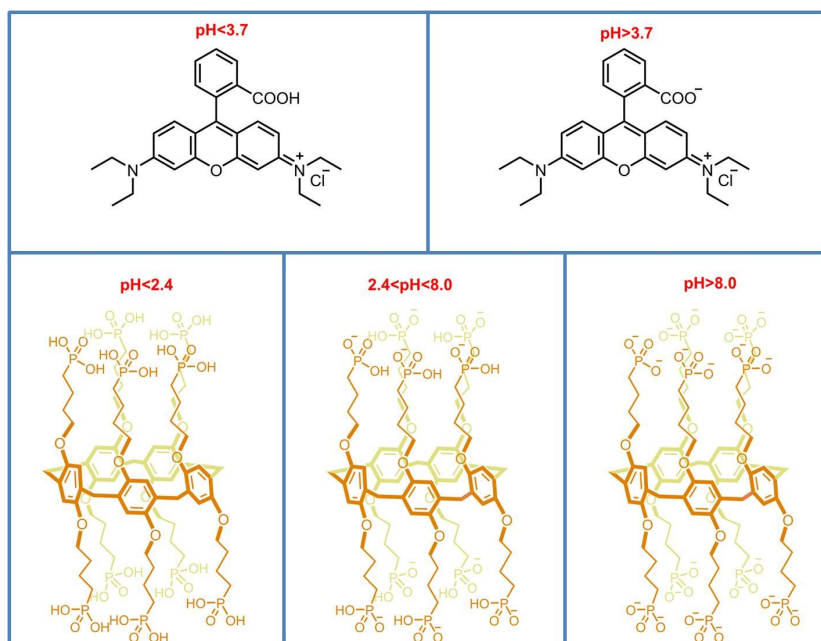


Figure S7. The different forms of RhB and 4C-PP5 at different pHs.

10. Determination of host-guest association constants.

To quantitatively assess the inclusion complexation behavior, fluorescence titrations of 4C-PP5 with RhB and 5-ASA were performed at 298 K in PBS (pH 5.0 and 7.4), respectively. Using a nonlinear least-squares curve-fitting method,^{S4} the association constant was obtained for each host-guest combination from the following equation:

$$\Delta I = 0.5 * (\alpha) * ((G_0/2 + H_0 + (1/K_a)) - \sqrt{((G_0/2 + H_0 + (1/K_a))^2 - 4 * G_0/2 * H_0)})$$

Where ΔI is the fluorescence intensity change of guest at $[H]_0$ compared with at $[G]_0$, $[G]_0$ is the fixed initial concentration of the guest, and $[H]_0$ is the initial concentration of host.

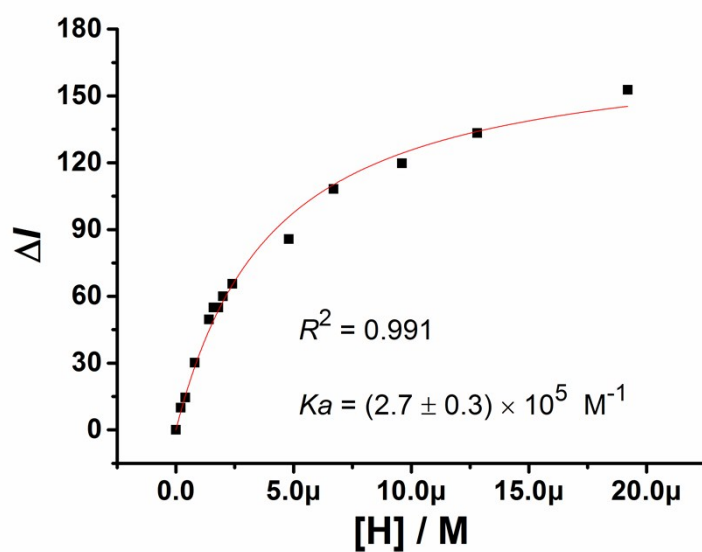


Figure S8. The nonlinear least-squares analysis to calculate the association constant (Ka) of 4C-PP5 with RhB in PBS (pH 5.0).

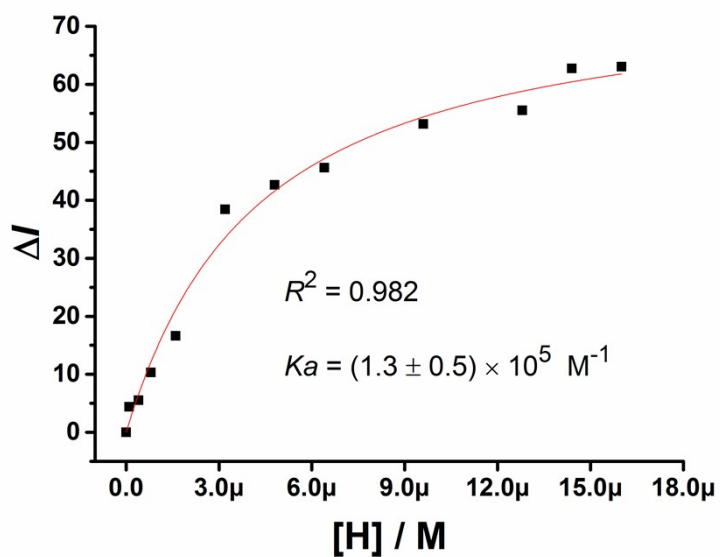


Figure S9. The nonlinear least-squares analysis to calculate the association constant (Ka) of 4C-PP5 with RhB in PBS (pH 7.4).

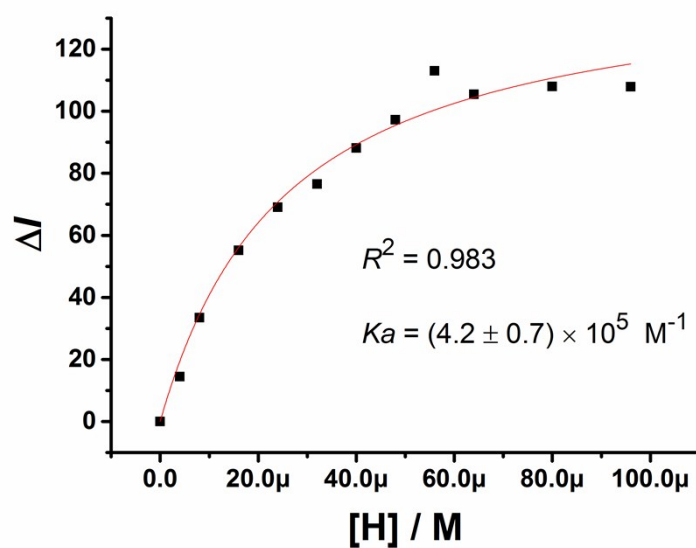


Figure S10. The nonlinear least-squares analysis to calculate the association constant (Ka) of 4C-PP5 with 5-ASA in PBS (pH 5.0).

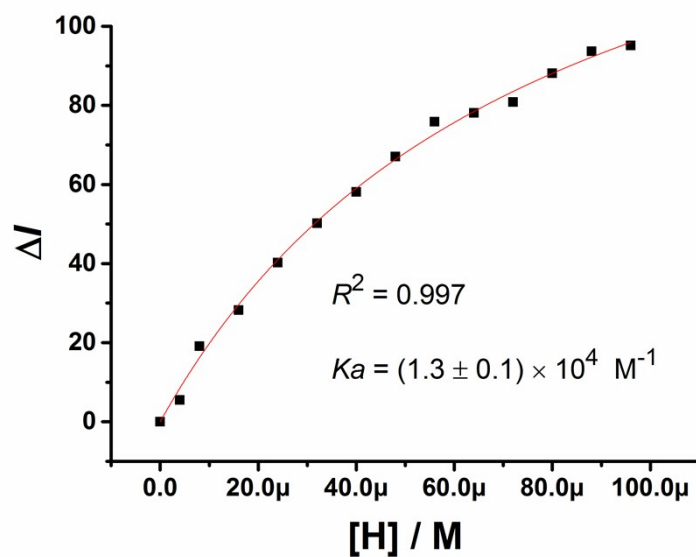


Figure S11. The nonlinear least-squares analysis to calculate the association constant (Ka) of 4C-PP5 with 5-ASA in PBS (pH 7.4).

11. Release profiles measurements

To further verify the release performance, 4C-PP5-UCNPs@RhB was put in PBS at the pH of 4.0, 5.0, 6.0, 7.4 and 8.0 and released for 10 min at each pH. The results indicated that the release efficiencies increased with the increase of pHs. Then we shorten the release time to 5 min to investigate the release performance.

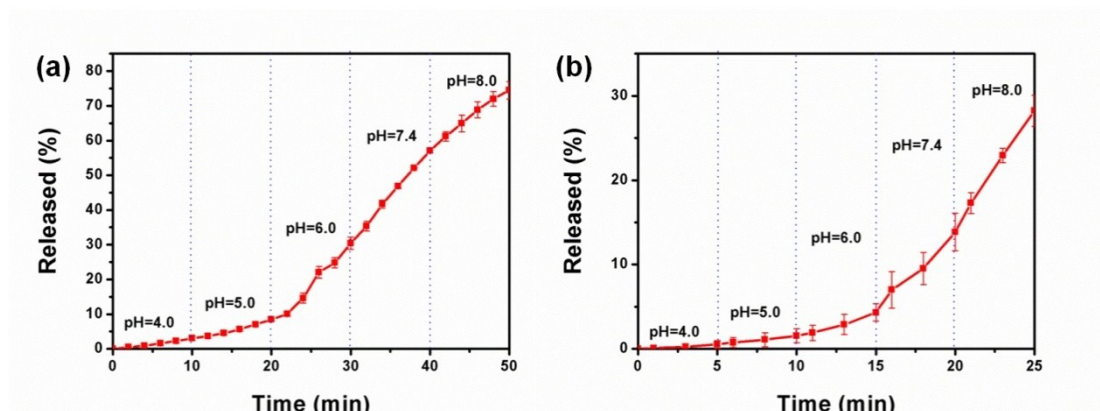


Figure S12. Release profiles of RhB from 4C-PP5-UCNPs@RhB upon triggering by change of pH.

12. In vitro upconversion luminescence (UCL) cell imaging

4C-PP5-UCNPs, 4C-PP5-UCNPs@RhB and 4C-PP5-UCNPs@5-ASA (100 $\mu\text{g}/\text{mL}$) were added to the macrophages and incubated for 6 h at 37 $^{\circ}\text{C}$, respectively. The cells were rinsed with PBS (0.01 M) for three times to remove excess nanoparticles and kept in PBS at room temperature for the subsequent experiments. UCL emissions in green and red regions were collected at 520-560 and 630-680 nm, respectively. Meanwhile, the macrophages incubated with culture medium acted as the control group. All images were obtained under the same instrumental conditions.

13. In vitro luminescence cell imaging

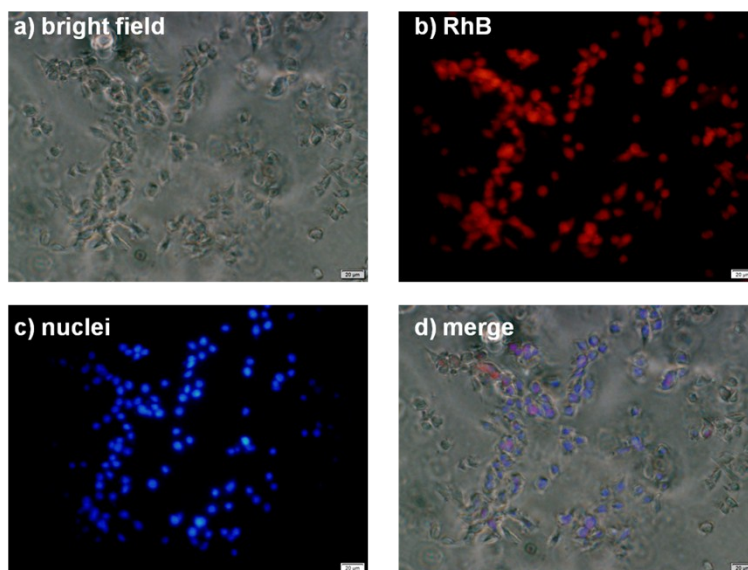


Figure S13. a) The bright field, b) red fluorescence from RhB, c) the nuclei of macrophages and d) the merge of the first three fluorescence microscope images of macrophages incubated with 100 $\mu\text{g/mL}$ of 4C-PP5-UCNPs@RhB for 6h. Scale bar: 20 μm .

14. NMR spectra

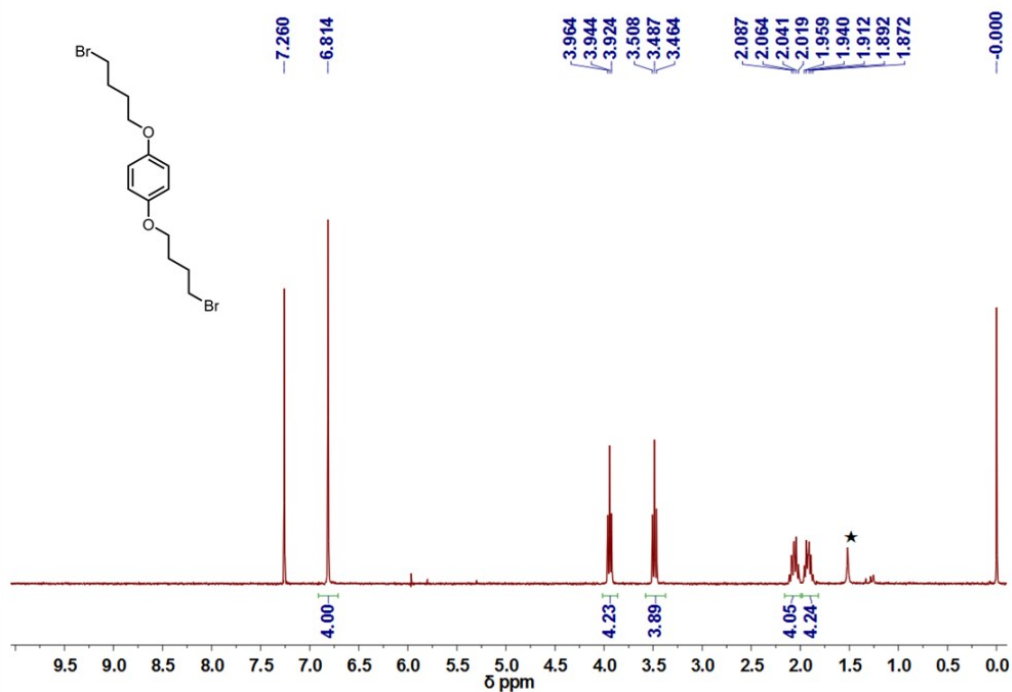


Figure S14. ^1H NMR spectrum of 1, 4-bis(bromobutoxy)benzene (M1) in CDCl_3 .

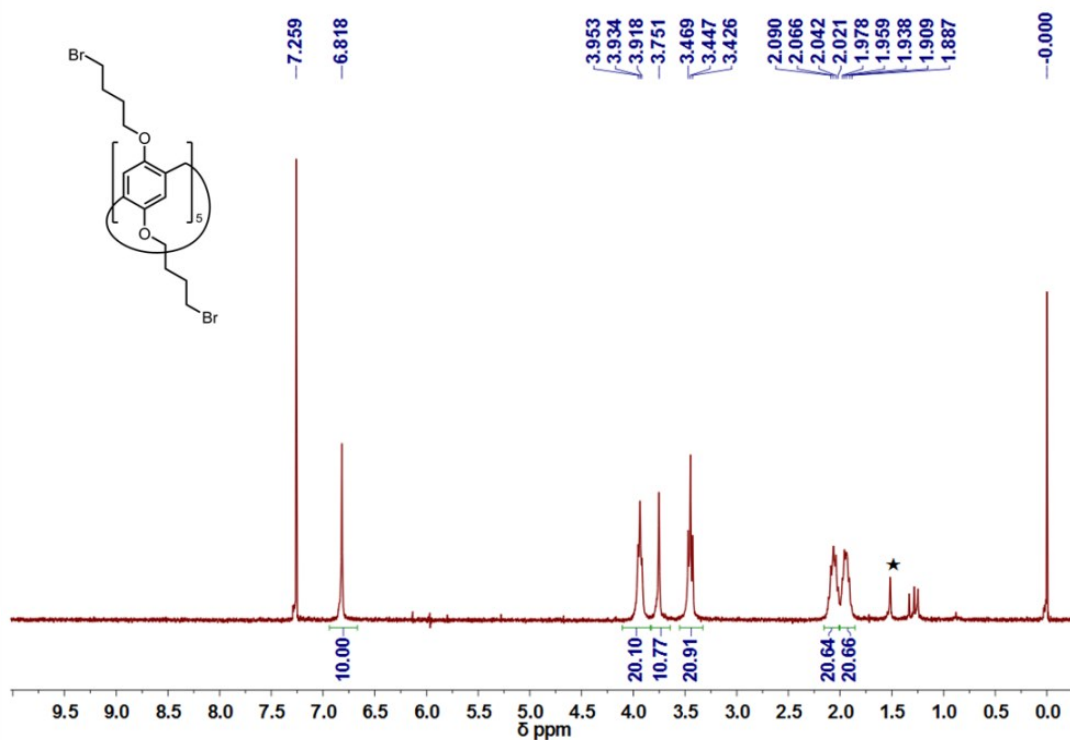


Figure S15. ^1H NMR spectrum of bromo-functionalized pillar[5]arene (H1) in CDCl_3 .

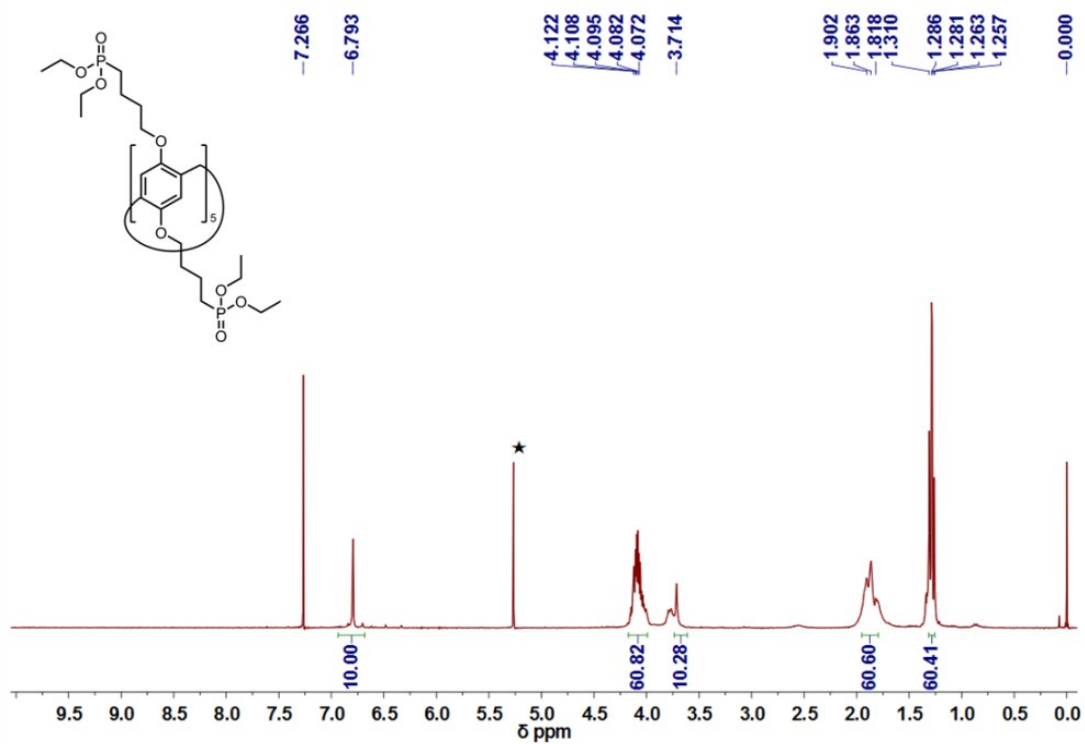


Figure S16. ^1H NMR spectrum of phosphonate-substituted pillar[5]arene (H2) in CDCl_3 .

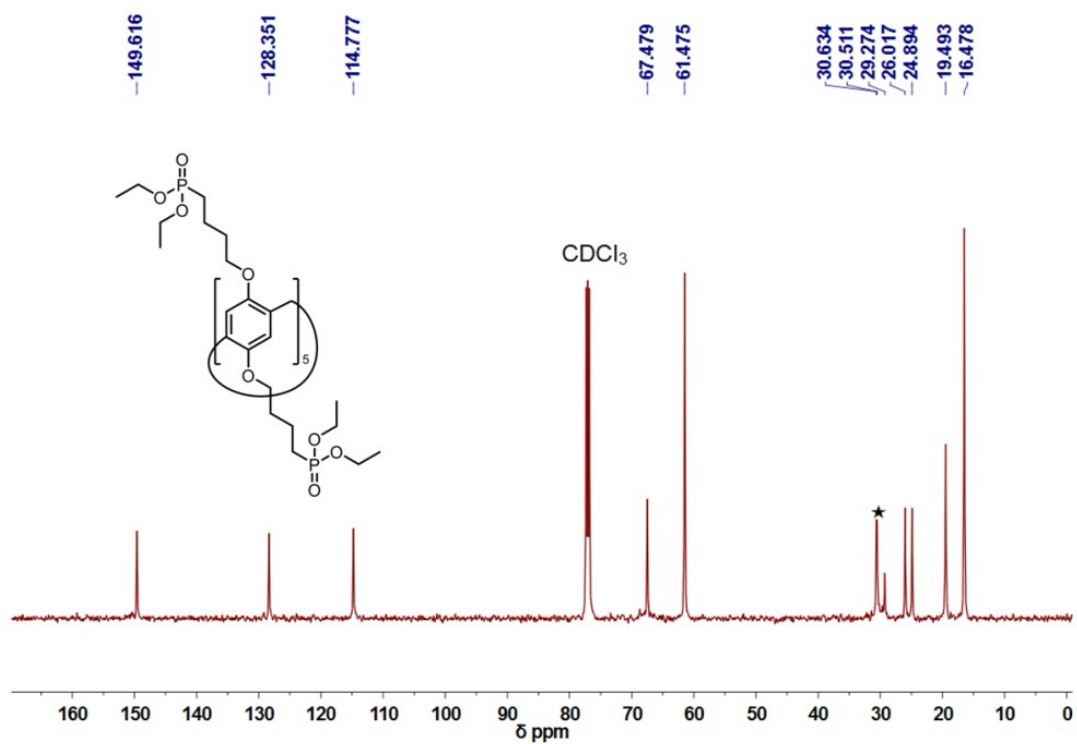


Figure S17. ¹³C NMR spectrum of phosphonate-substituted pillar[5]arene (H2) in CDCl₃.

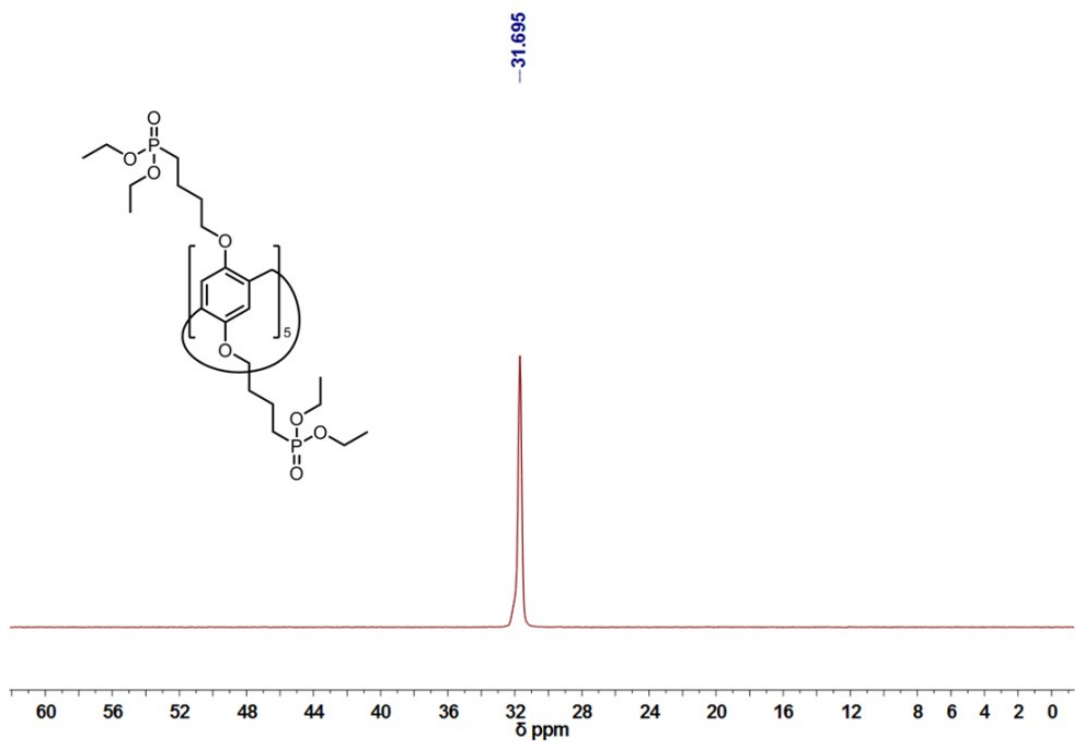


Figure S18. ³¹P NMR spectrum of phosphonate-substituted pillar[5]arene (H2) in CDCl₃.

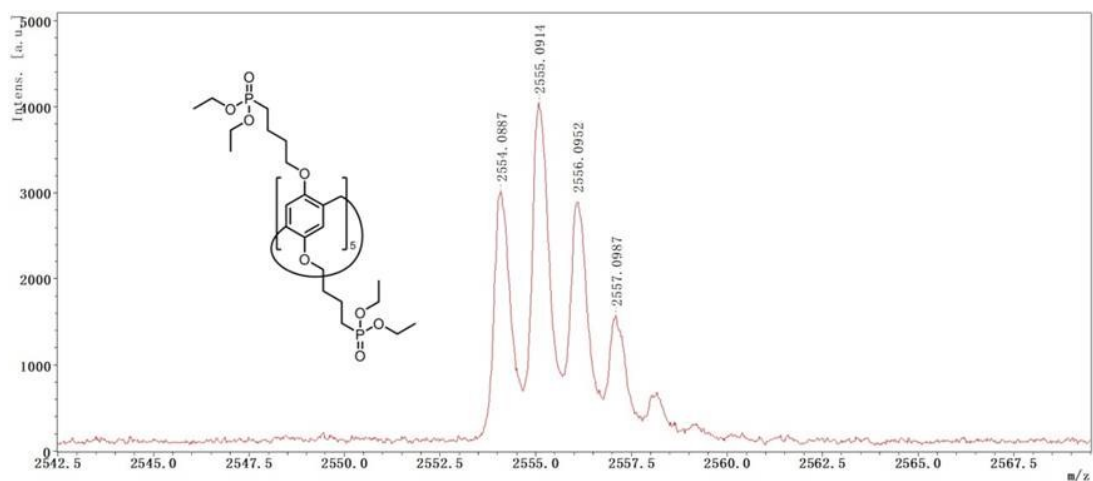


Figure S19. Maldi-tof spectrum of phosphonate-substituted pillar[5]arene (H2).

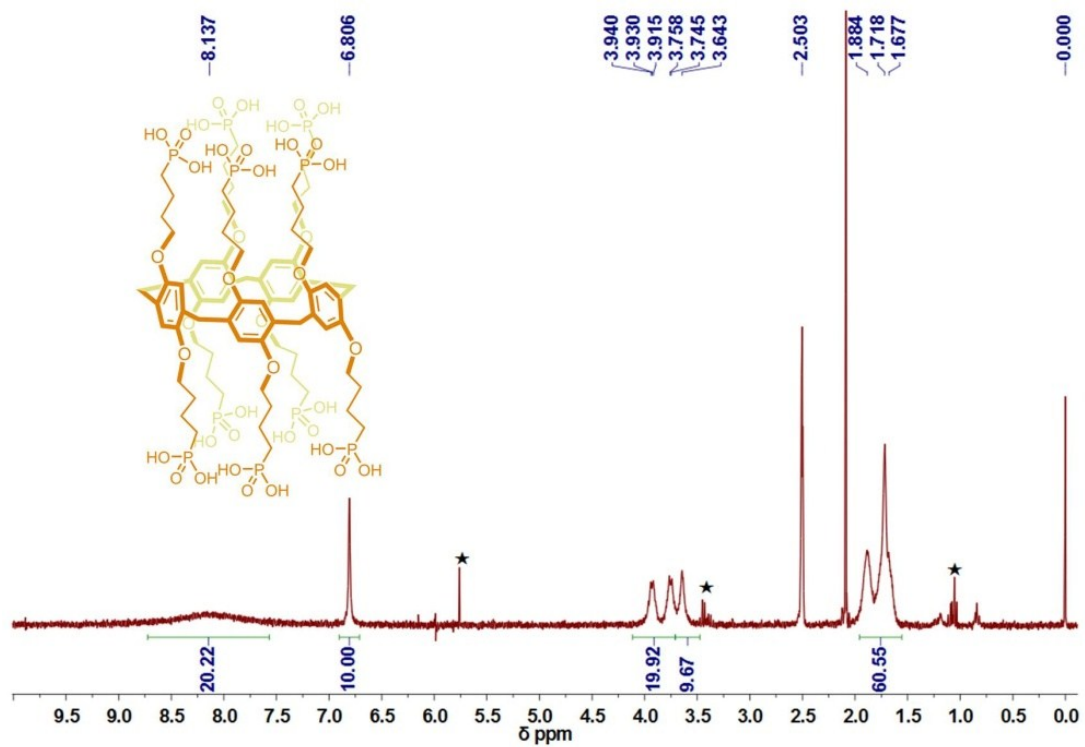


Figure S20. ^1H NMR spectrum of phosphoryl-functionalized pillar[5]arene (4C-PP5) in $\text{DMSO-}d_6$.

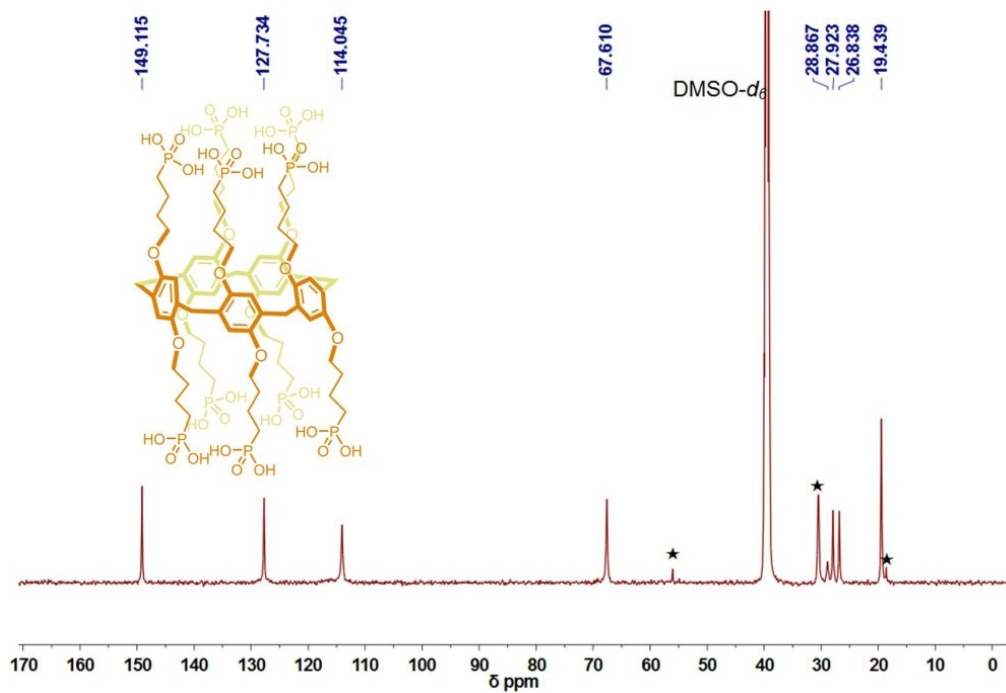


Figure S21. ^{13}C NMR spectrum of phosphoryl-functionalized pillar[5]arene (4C-PP5) in DMSO- d_6 .

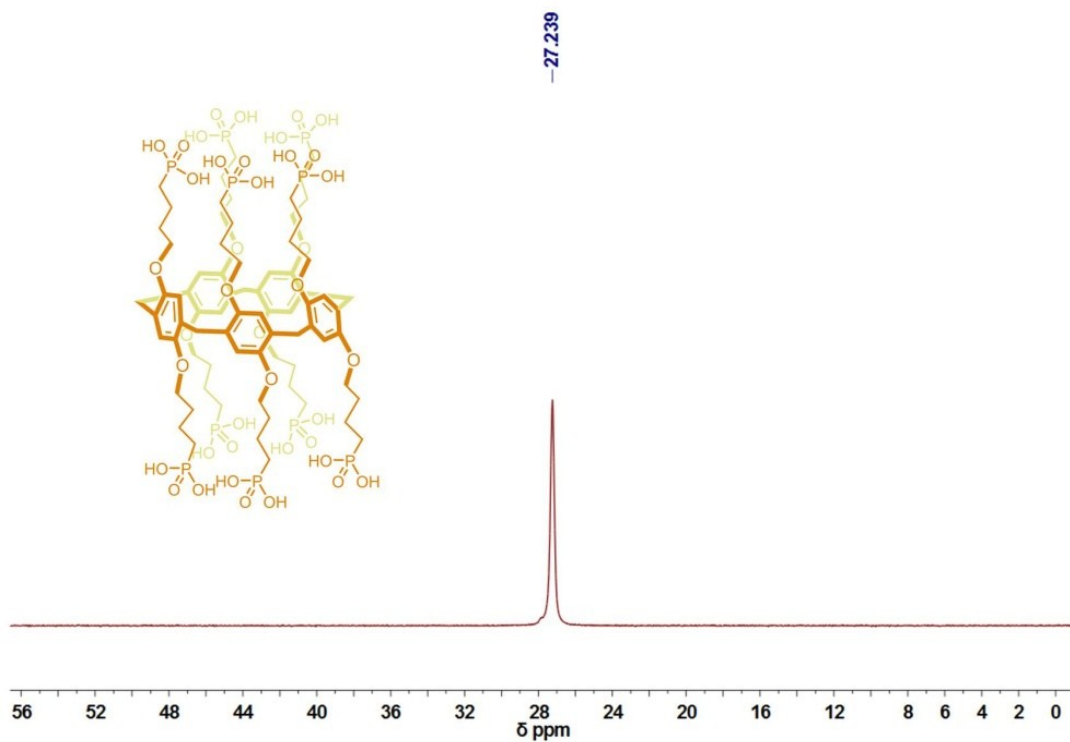


Figure S22. ^{31}P NMR spectrum of phosphoryl-functionalized pillar[5]arene (4C-PP5) in DMSO- d_6 .

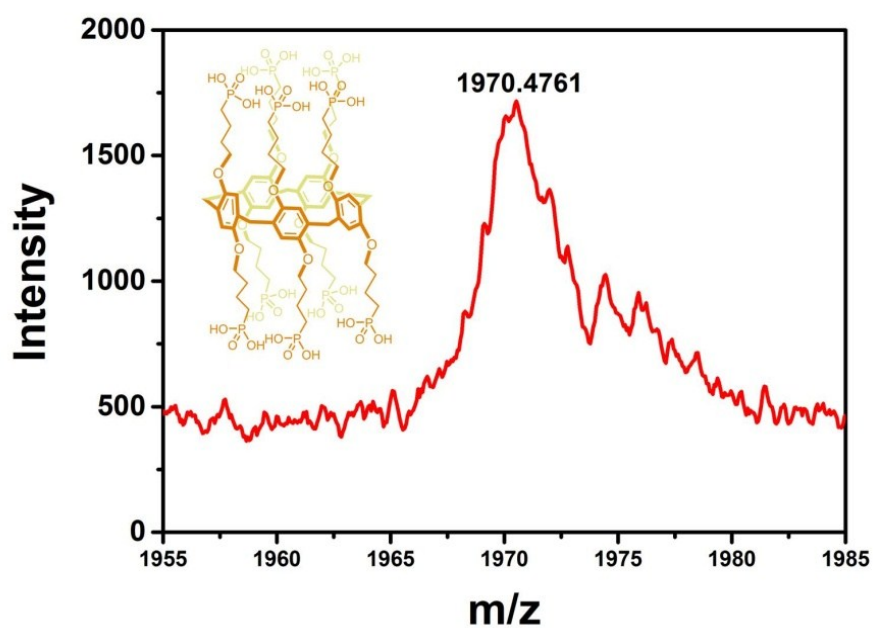


Figure S23. MALDI-TOF spectrum of phosphoryl-functionalized pillar[5]arene (4C-PP5).

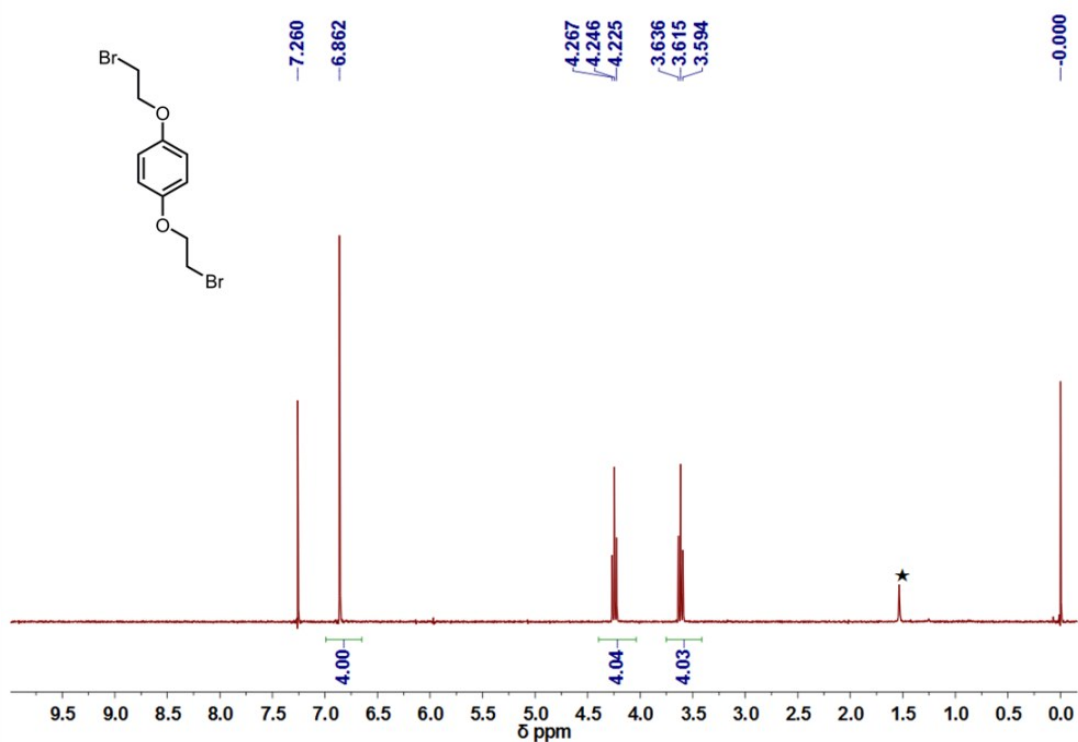


Figure S24. ^1H NMR spectrum of 1,4-bis(bromoethoxy)benzene (M1') in CDCl_3 .

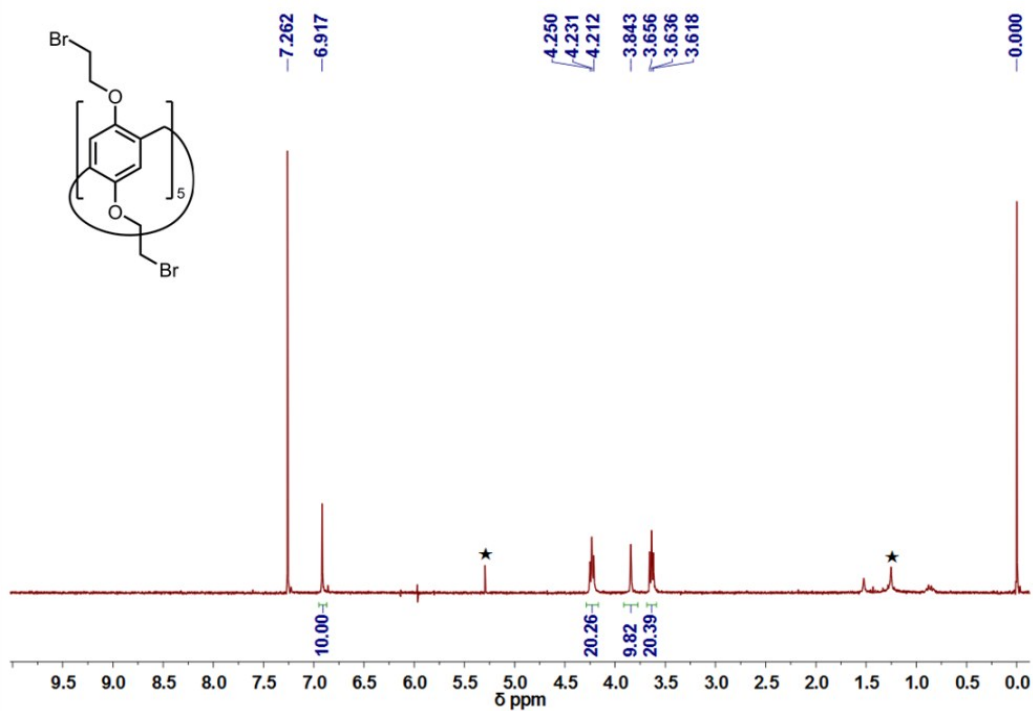


Figure S25. ^1H NMR spectrum of bromo-functionalized pillar[5]arene (H1') in CDCl_3 .

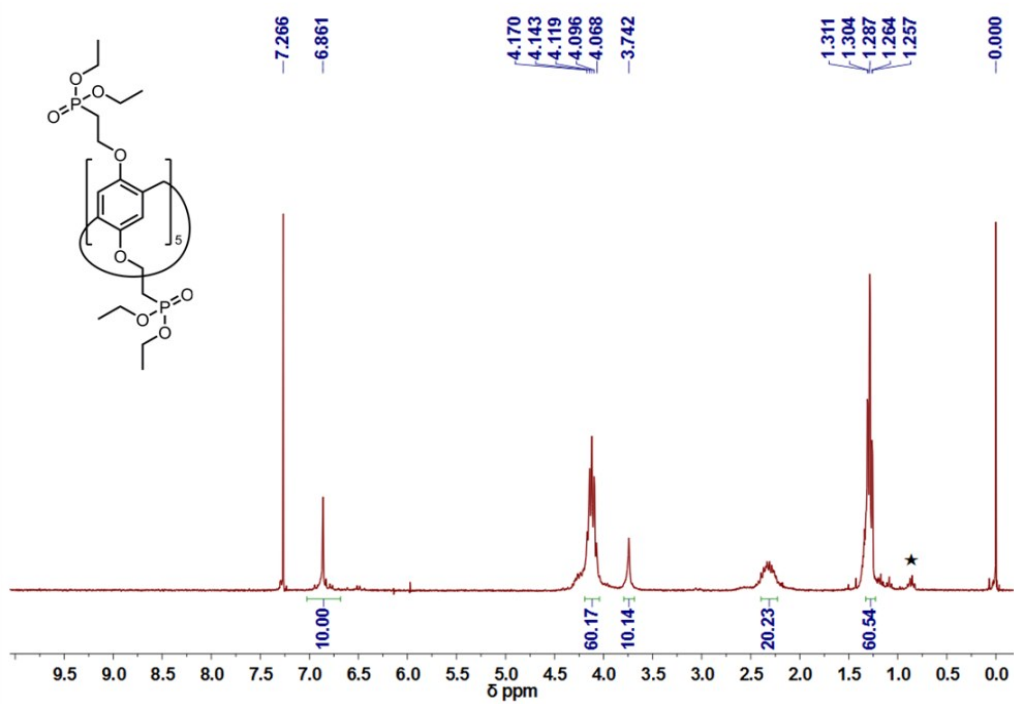


Figure S26. ^1H NMR spectrum of phosphonate-substituted pillar[5]arene (H2') in CDCl_3 .

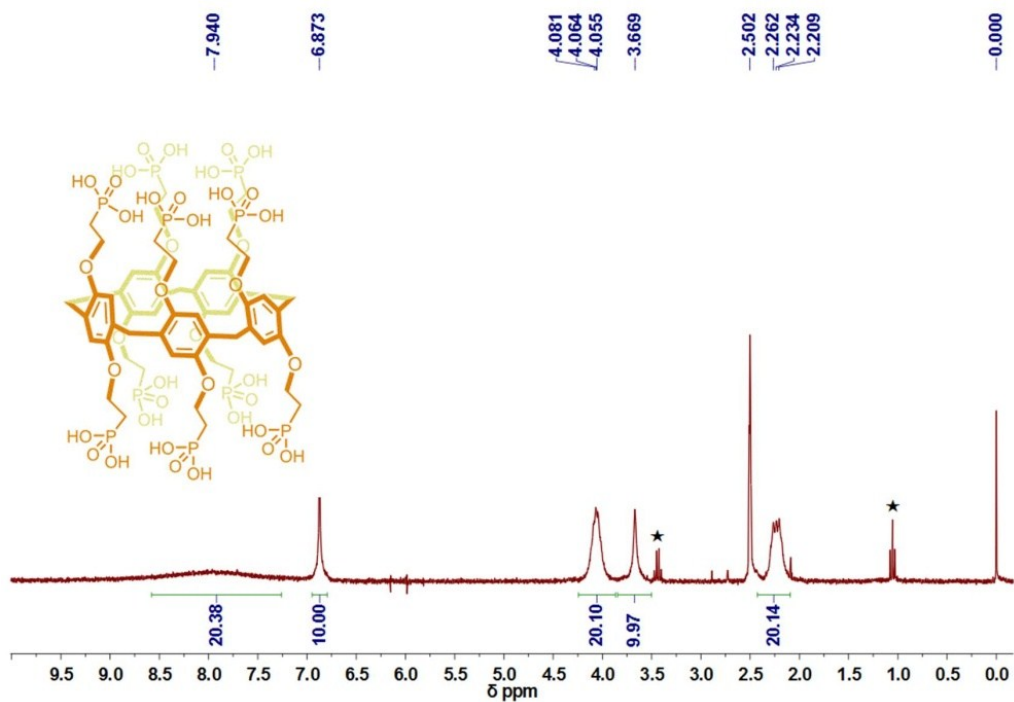


Figure S27. ^1H NMR spectrum of phosphoryl-functionalized pillar[5]arene (2C-PP5) in $\text{DMSO-}d_6$.

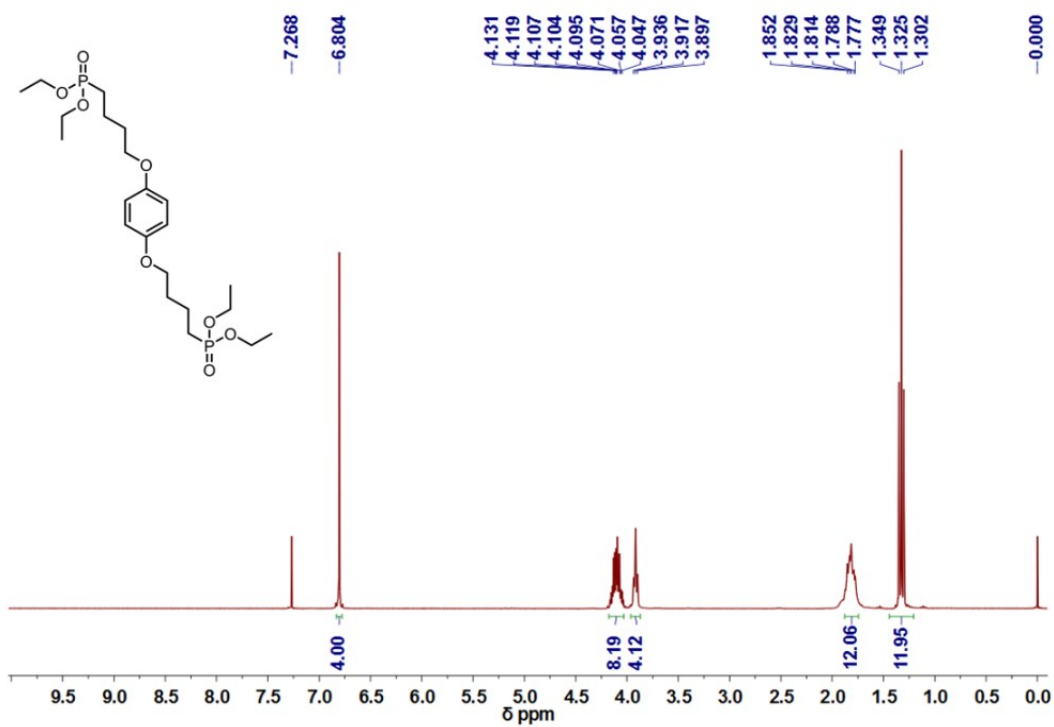


Figure S28. ^1H NMR spectrum of 1, 4-(phosphonate)butoxybenzene (M2) in CDCl_3 .

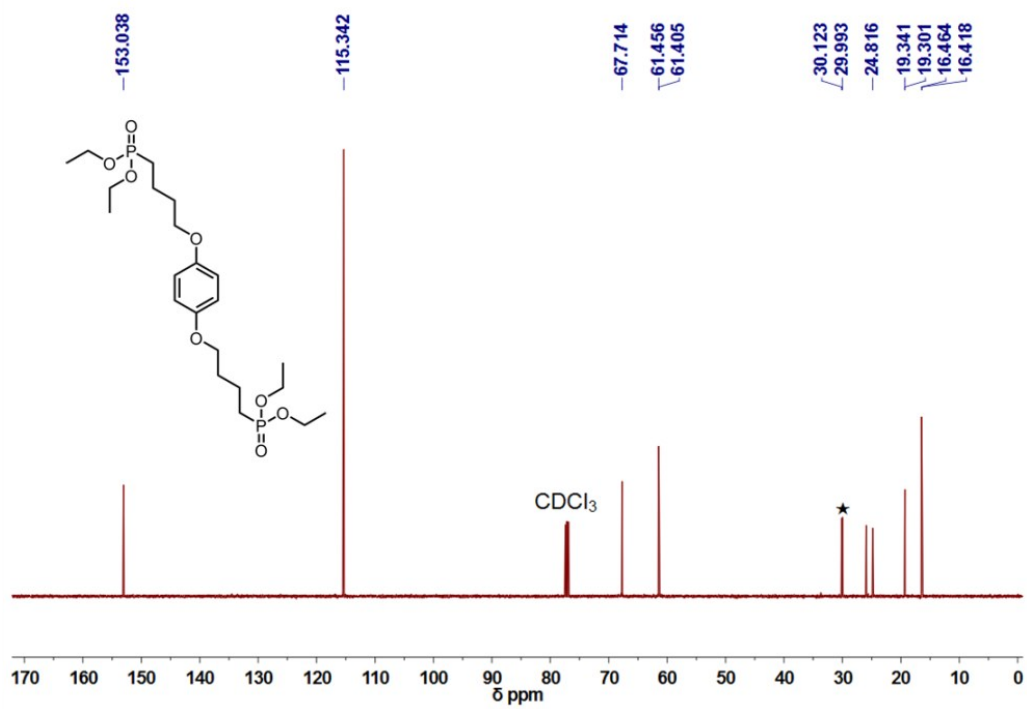


Figure S29. ^{13}C NMR spectrum of 1, 4-(phosphonate)butoxybenzene (M2) in CDCl_3 .

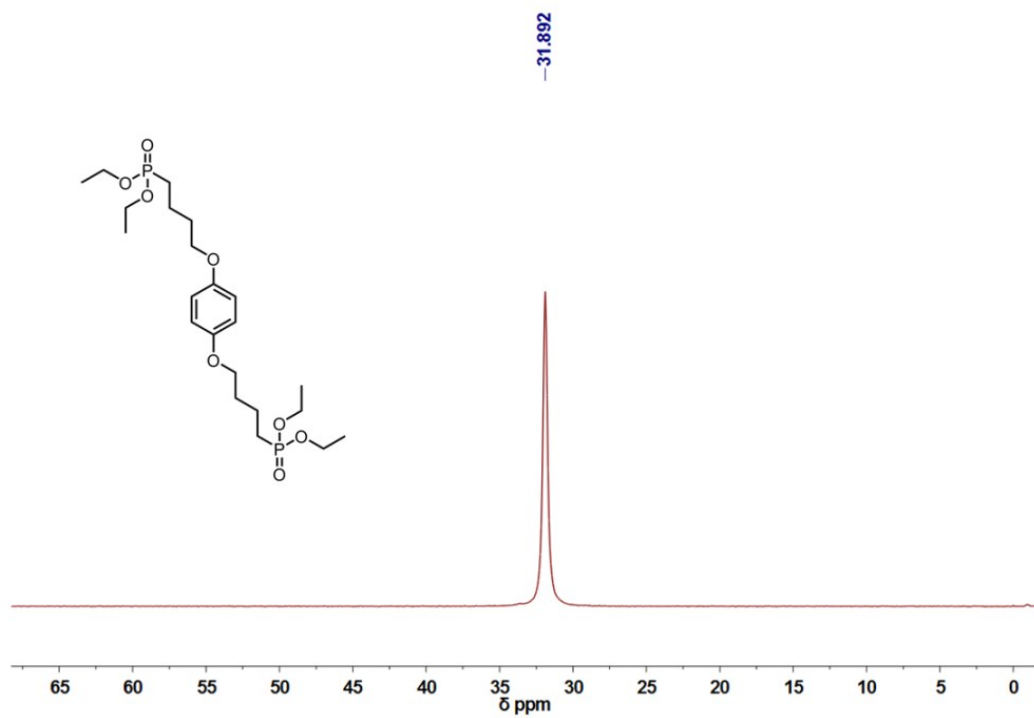


Figure S30. ^{31}P NMR spectrum of 1, 4-(phosphonate)butoxybenzene (M2) in CDCl_3 .

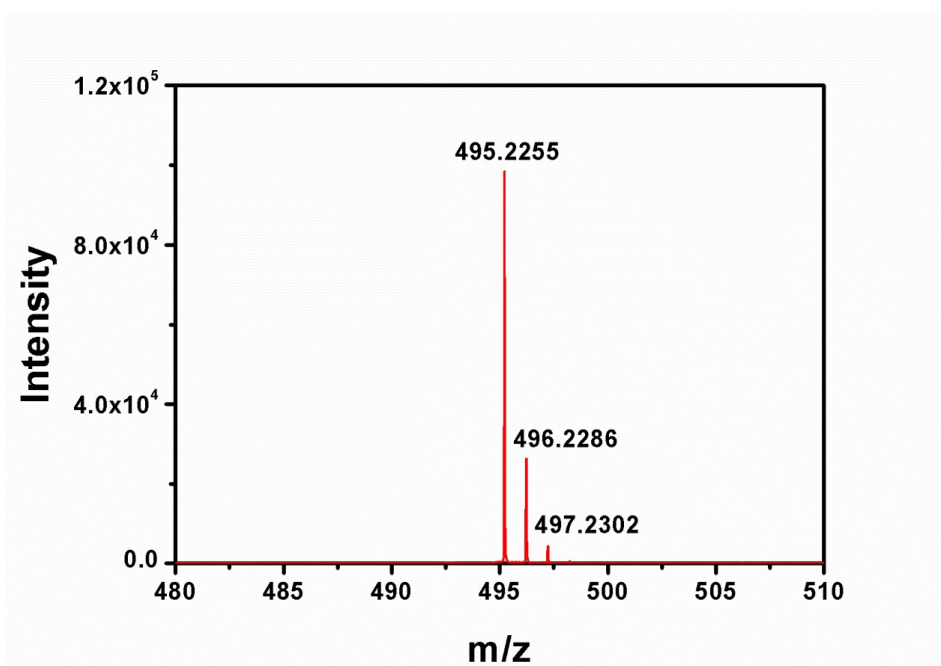


Figure S31. ESI-MS spectrum of 1, 4-(phosphonate)butoxybenzene (M2).

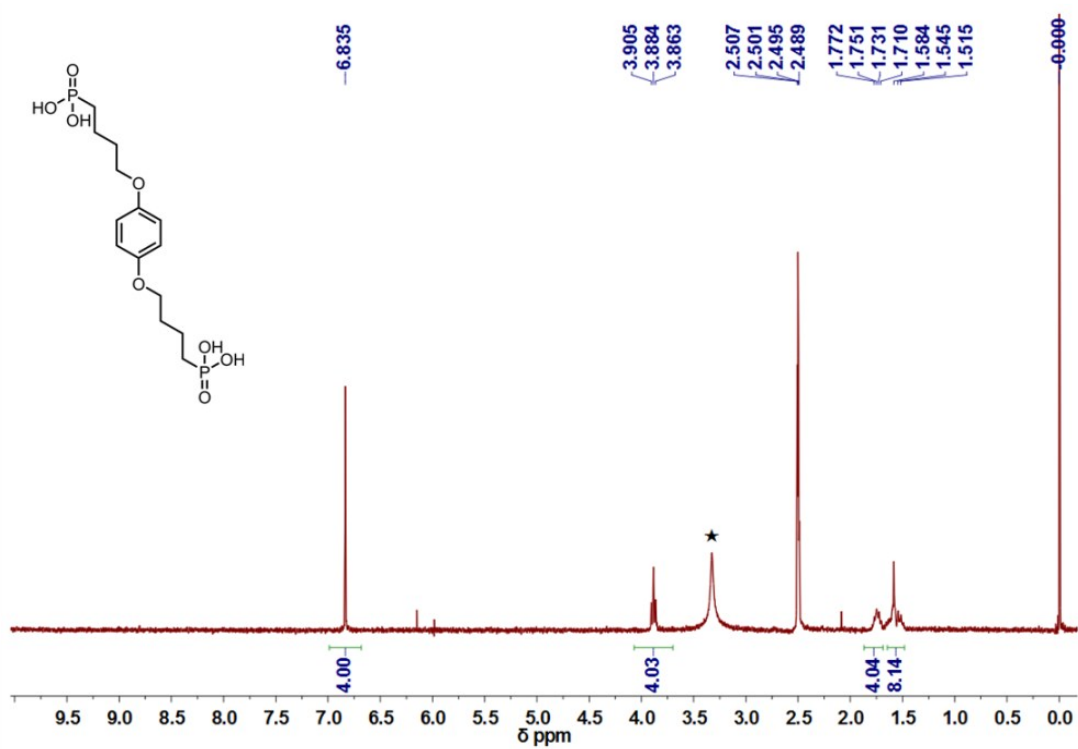


Figure S32. ¹H NMR spectrum of 1, 4-(phosphonic acid)butoxybenzene (M3) in DMSO-*d*₆.

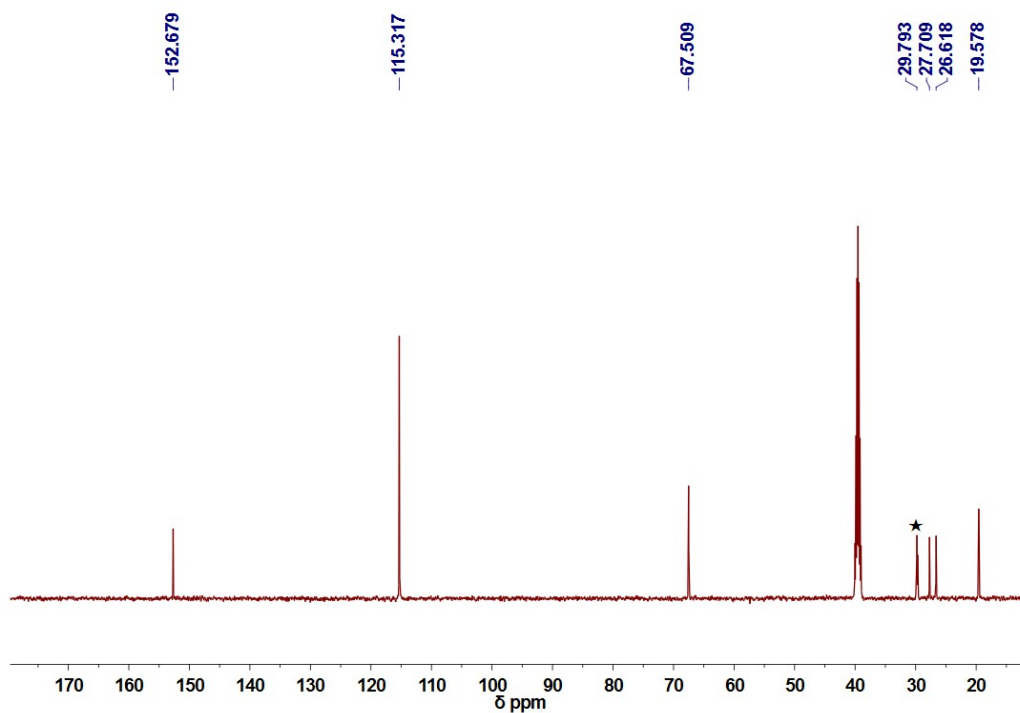


Figure S33. ^{13}C NMR spectrum of **1, 4-(phosphonic acid)butoxybenzene (M3)** (acetone solvent peaks are marked with asterisks) in $\text{DMSO-}d_6$.

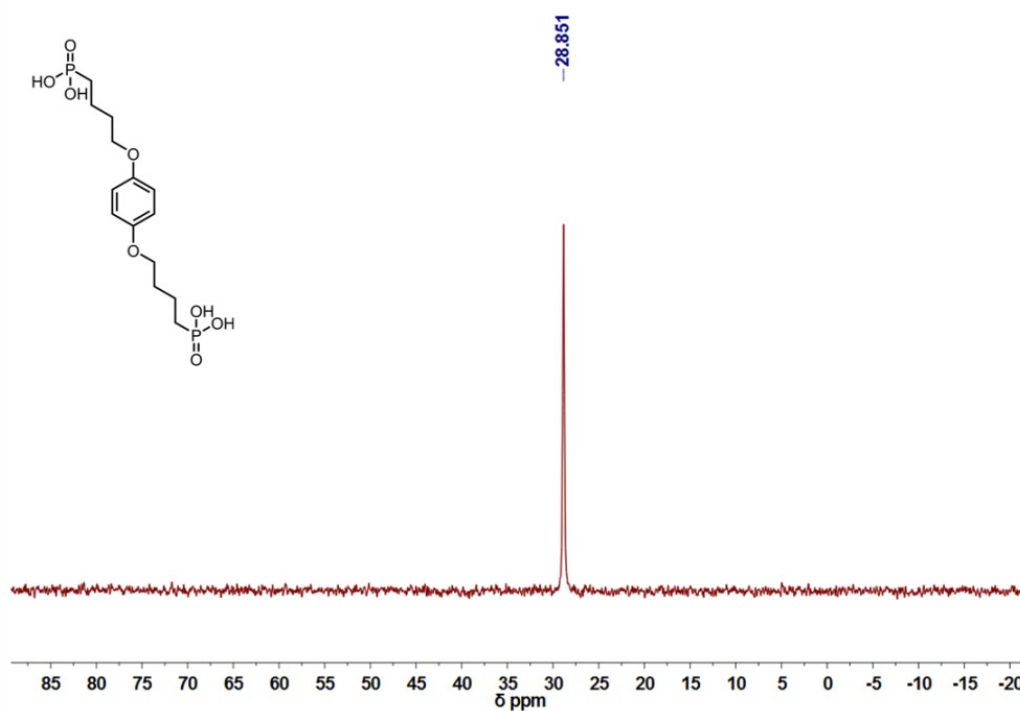


Figure S34. ^{31}P NMR spectrum of **1, 4-(phosphonic acid)butoxybenzene (M3)** in $\text{DMSO-}d_6$.

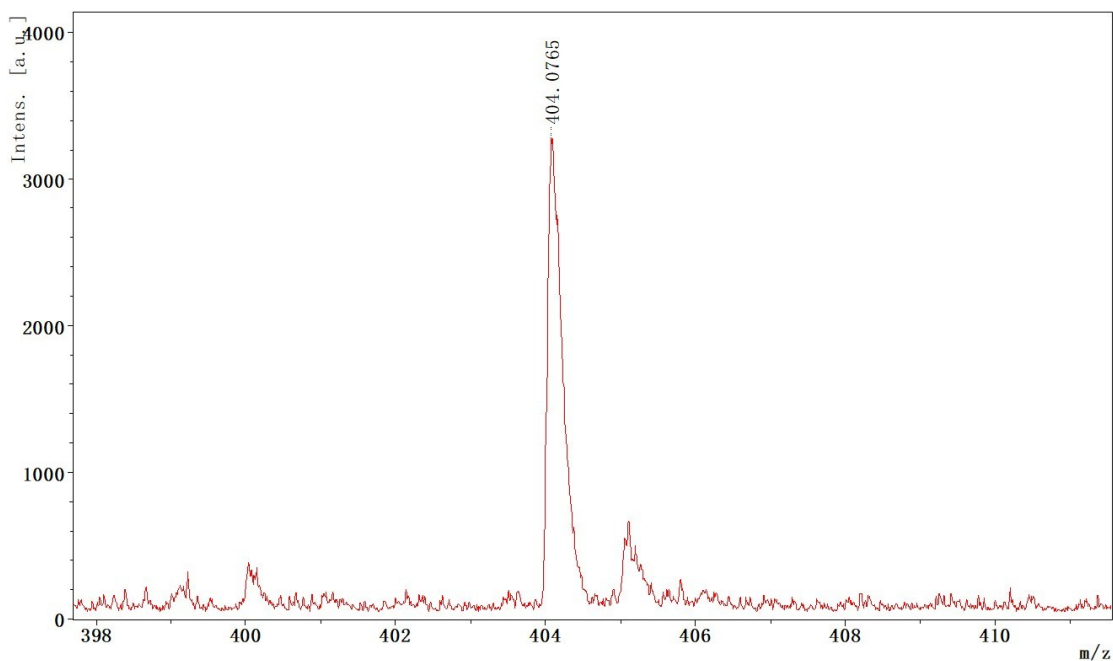


Figure S35. MALDI-TOF spectrum of **1, 4-(phosphonic acid)butoxybenzene (M3)**.

15. References

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