

Supporting information

**Mechanically self-locked gemini-[1]rotaxane-assembled microsphere
and its properties on L-Arg controlled reversible morphology and
fluorescent changes**

Yun-Fei Zhang, Ying-Jie Li, Zhong-Hui Wang, Xiao-Wen Sun, Qing-Yu Yang, Hong-Qiang Dong, You-Ming Zhang, Tai-Bao Wei, Hong Yao and Qi Lin*

Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China; Research Center of Gansu Military and Civilian Integration Advanced Structural Materials; College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, 730070, China; E-mail: linqi2004@126.com.

Contents

Scheme S1 Synthetic route to related compounds.

Scheme S2 Synthetic route of the **4**.

Figure S1 ^1H NMR spectrum (600 MHz, CDCl_3 , 298 K) of **1**.

Figure S2 ^{13}C NMR spectrum (600 MHz, CDCl_3 , 298 K) of **1**.

Figure S3 The HR-MS spectrum of **1**.

Figure S4 ^1H NMR spectrum (600 MHz, CDCl_3 , 298 K) of **2**.

Figure S5 ^{13}C NMR spectrum (400 MHz, CDCl_3 , 298 K) of **2**.

Figure S6 The HR-MS spectrum of **2**.

Figure S7 ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **3**.

Figure S8 ^{13}C NMR spectrum (400 MHz, CDCl_3 , 298 K) of **3**.

Figure S9 The HR-MS spectrum of **3**.

Figure S10 2D NOESY spectrum of compound **3**. (600 MHz, $\text{DMSO-}d_6$, 298 K)

Figure S11 ^1H - ^1H COSY spectrum of compound **3**. (600 MHz, $\text{DMSO-}d_6$, 298 K)

Figure S12 ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **DEP5**.

Figure S13 ^{13}C NMR spectrum (600 MHz, CDCl_3 , 298 K) of **DEP5**.

Figure S14 2D NOESY spectrum (600 MHz, $\text{DMSO-}d_6$, 298 K) of compound **DEP5**.

Figure S15 ^1H - ^1H COSY spectrum of compound **3**. (600 MHz, $\text{DMSO-}d_6$, 298 K)

Figure S16 The HR-MS spectrum of compound **DEP5**.

Figure S17 ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **4**.

Figure S18 Partial ^1H NMR spectra (600 MHz, $\text{DMSO-}d_6$, 298 K) of the **2**, **4** and **2+4**.

Figure S19 The photograph shown the fluorescence color changes of **DEP5** after added the 60 equiv. of various amino acids.

Figure S20 Photos showing the Tyndall effect of (a) **DEP5** and (b) **DEP5-L-Arg**.

Figure S21 Selectivity of the **DEP5** for **L-Arg** in the presence of different interfering substances. (1: **DEP5**; 2: L-Phe, 3: L-Gln, 4: L-Ile, 5: L-Thr, 6: L-Glu, 7: L-Ala, 8: L-Ser, 9: L-Met, 10: L-Val, 11: L-Tyr, 12: L-Arg, 13: L-Asp, 14: L-Pro, 15: L-His, 16: L-Leu, 17: L-Gly, 18: L-Trp, 19: L-Asn, and 20: L-Cys)

Figure S22 Fluorescence linear ranges of **DEP5** for L-Arg (LOD= 1.43×10^{-7} M).

Table S1 Comparison on the detection limit (LOD) of L-Arg with other different sensors.

Figure S23 Effect of pH on the fluorescence spectra for **DEP5** in response to L-Arg from 3 to 10 in $\text{DMSO}/\text{H}_2\text{O}$ (v/v, 7: 3) HEPES buffered solution. ($c = 1 \times 10^{-4}$ M, $\lambda_{\text{ex}} = 295$ nm, $\lambda_{\text{em}} = 325$ nm)

Figure S24 Fluorescence intensity of **DEP5** (1×10^{-4} M) and after the addition of 60 equiv. L-Arg and 20 equiv. TFA. ($\lambda_{\text{ex}} = 295$ nm)

Figure S25 Fluorescence intensity of **DEP5** (1×10^{-4} M) and after the addition of 60 equiv. L-Arg and 20 equiv. (a) HCl; (b) HClO_4 ; (c) CH_3COOH ; (d) HCOOH . ($\lambda_{\text{ex}} = 295$ nm)

Figure S26 TEM image of (a) **DEP5**; (b) **DEP5+L-Arg** and (c) **DEP5+L-Arg+TFA**.

Figure S27 The MSD curves of (a) **DEP5** and (b) **DEP5+L-Arg**.

Figure S28 Partial ^1H NMR spectra (400 MHz, 298 K) of **DEP5** in $\text{DMSO-}d_6$ at different equivalent of L-Arg: (a) **DEP5**; (b) **DEP5** + 0.5 equiv. L-Arg; (c) **DEP5** + 1.0 equiv. L-Arg.

Figure S29 IR spectra of **DEP5** and **DEP5+L-Arg**.

Figure S30 The HR-MS of **DEP5+L-Arg** complexion.

1. Experiment section

1.1 Materials and methods

Materials: ethyl chloroacetate, 1, 4-dimethoxybenzene, paraformaldehyde, *p*-methoxyphenol, boron trifluoride diethyl etherate, PEG-400, K₂CO₃, KI, decanediamine, 1, 4-benzoyl chloride, and all other reagents and solvents were commercially available at analytical grade used without further purification.

Instruments: Melting point were measured on X-4 digital melting point instrument. Fluorescence spectrum data were measured by Shimadzu RF-5310 spectrometer. The NMR spectra were obtained on a MercuryPlus-400/DD2-600 spectrometer with tetramethyl silane (TMS, δ scale with solvent resonances as internal standards). High-resolution MS was conducted on a Bruker Esquire 3000 Plus spectrometer (Bruker-Franzen Analytic GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. Scanning electron microscopy (SEM) images of the xerogels were investigated using ULTRA plus (5kV) instrument. TEM images were investigated Tecnai G2 F20 Field emission transmission electron microscope (FEI, American).

1.2 General procedure

1.2.1 Fluorescence spectra experiments

All the fluorescence spectroscopy was carried out in DMSO/H₂O (v/v, 7: 3) **DEP5** solution on a Shimadzu RF-5301 spectrometer. Any fluorescence spectra change of the synthesized compound were recorded on addition of amino acids while keeping the concentration constant (1.0×10^{-4} M) in all experiments. Twenty different amino acids (L-Phe, L-Gln, L-Ile, L-Thr, L-Glu, L-Ala, L-Ser, L-Met, L-Val, L-Tyr, L-Arg, L-Asp, L-Pro, L-His, L-Leu, L-Gly, L-Trp, L-Asn, and L-Cys, $c=0.1$ M) were used for the fluorescence experiments. The all experiments were carried out at room temperature.

1.2.2 General procedure for pH control experiments

The pH control experiments were carried out at room temperature by using a Sartorius PB-10 acidometer. The pH was adjusted by addition of TBAOH and HClO₄ to the HEPES buffered system (5 mmol/ L). The fluorescence emission spectra were recorded in 10 mm quartz cuvettes after equilibration.

1.2.3 ¹H NMR experiments

For ¹H NMR titrations, the solution of **DEP5** were prepared in DMSO-*d*₆ (400 MHz, 298K) and the appropriate concentrated solution of L-Arg was prepared in distilled water.

1.2.4 SEM method

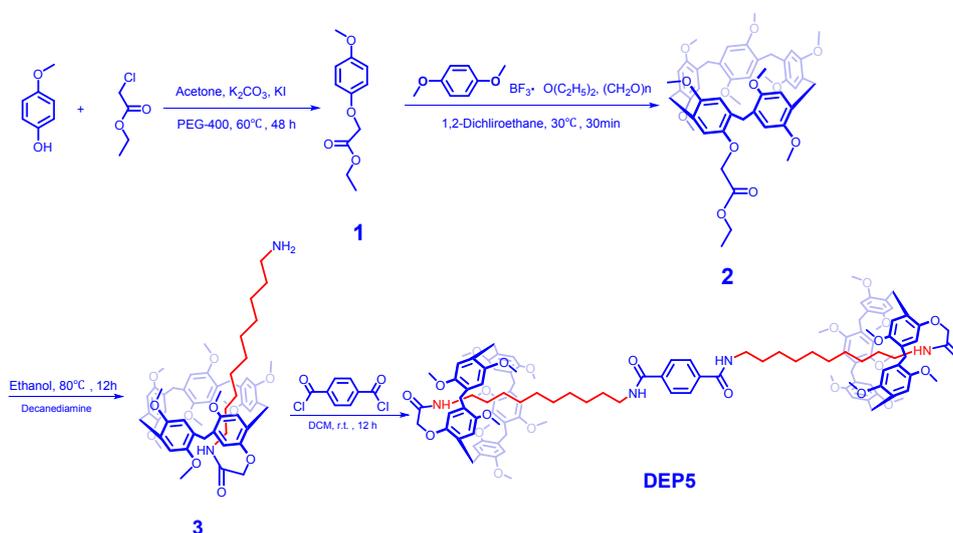
The SEM experiments were investigated on JSM-6701F instrument. The **DEP5** solution were prepared in DMSO/H₂O (v/ v, 7: 3) binary solution (0.1 M; 2 mL); the **DEP5**-L-Arg solution were prepared upon the addition L-Arg (60 equiv.) into the above **DEP5** solution; the **DEP5**-L-Arg-TFA solution were prepared upon the addition TFA

(20 equiv.) into the above **DEP5**-L-Arg solution.

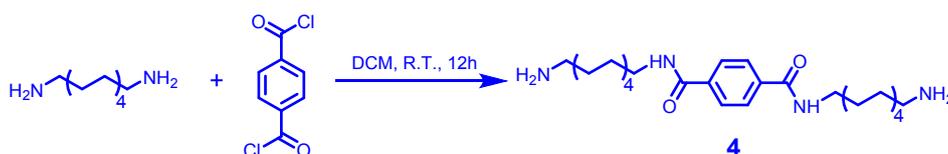
1.2.5 TEM method

The TEM experiments were investigated on Tecnai G2 F20 instrument. The **DEP5** solution were prepared in distilled water (0.1 M; 2 mL); the **DEP5**-L-Arg solution were prepared upon the addition L-Arg (60 equiv.) into the above **DEP5** solution; the **DEP5**-L-Arg-TFA solution were prepared upon the addition TFA (20 equiv.) into the above **DEP5**-L-Arg solution.

2. Synthesis and characterization of related compounds



Scheme S1 Synthetic route to related compounds.

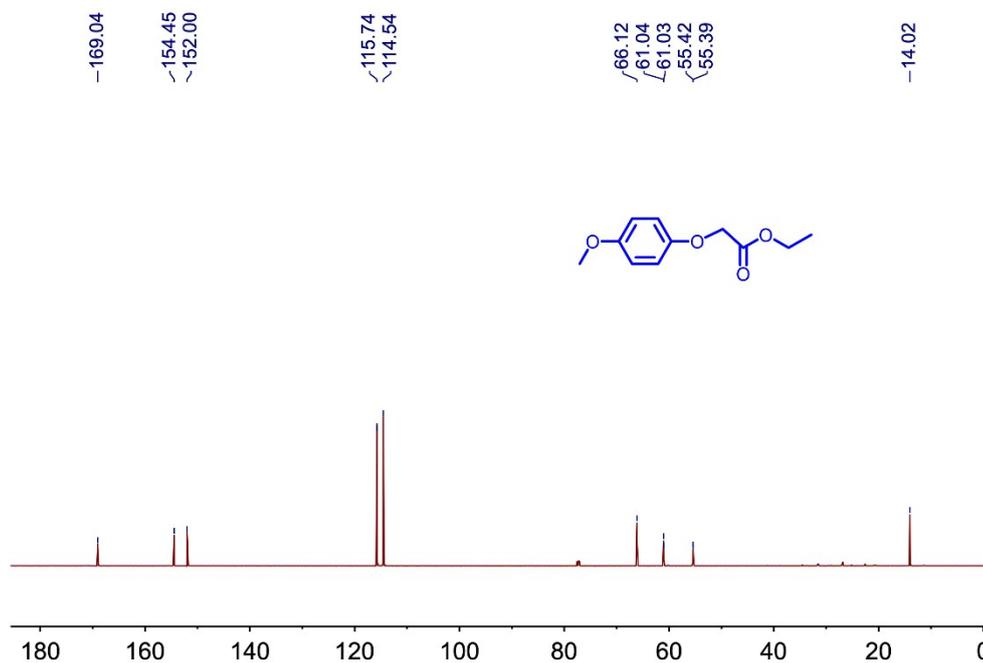
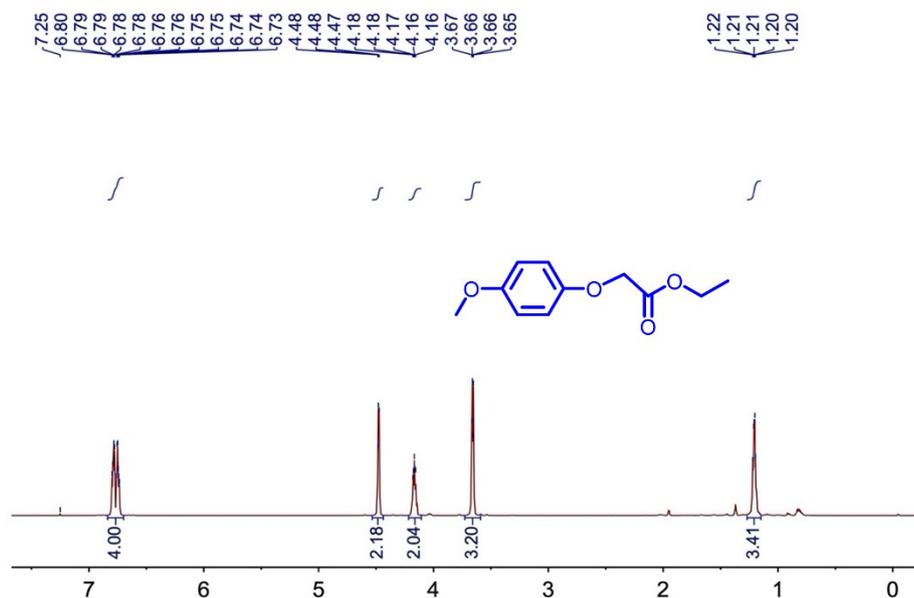


Scheme S2 Synthetic route of the **4**.

2.1 Compound 1

In a 500 mL round-bottom flask, 4-methoxyphenol (10 mmol, 12.40 g), ethyl chloroacetate (10 mmol, 13.00 g), K_2CO_3 (8.28 g), KI (9.96 g), and acetonitrile (400 mL) were mixture. The reaction was stirred at $60^\circ C$ refluxing for 72 h. When the reaction is over, a suitable amount of silica gel was added to the mixture and dried in vacuum, and separated by column chromatography (PE: EA=20:1), we can get yellow liquid **1** (20.30 g, 96.5%). The 1H NMR spectrum of **1** shown in Figure S1 (600 MHz, $CDCl_3$, room temperature) δ (ppm): 6.73–7.26 (m, $J = 9$ Hz, 4 H), 4.47–

4.48 (s, 2H), 4.16-4.48 (t, $J = 7.72$ Hz, 2H), 3.65-3.67 (s, 3H), 1.20-1.22 (t, $J = 7.2$ Hz, 3H). The ^{13}C NMR spectrum of **1** shown in Figure S2 (600 MHz, CDCl_3 , room temperature) δ (ppm): 169.04, 154.45, 152.00, 115.74, 114.54, 66.12, 61.04, 61.03, 55.42, 55.39, 14.02. HR-MS: m/z calcd for $[\mathbf{1} + \text{Na}]^+ \text{C}_{11}\text{H}_{14}\text{O}_4^+$, 233.0784; found 233.0782. (Figure S3)



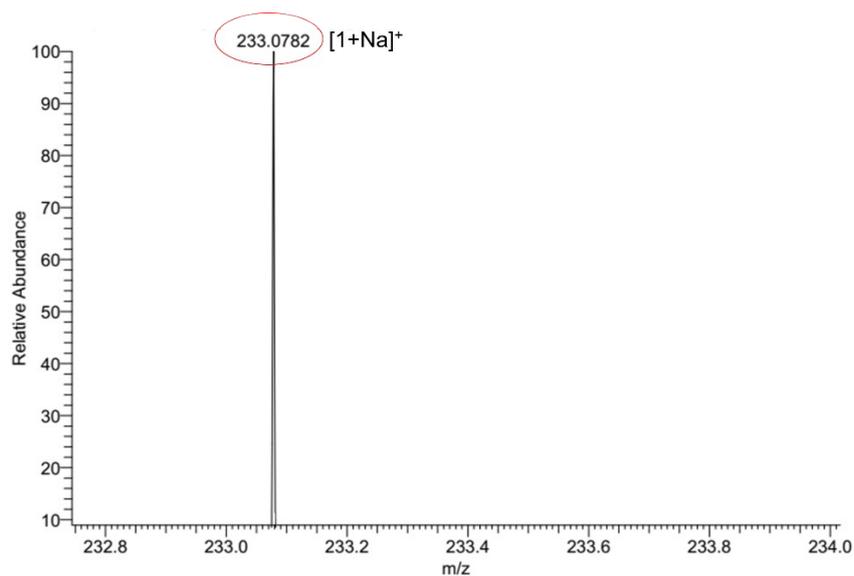


Figure S3 The HR-MS spectrum of **1**.

2.2 Compound 2

In a 250 mL round-bottom flask, we add 1,2-dichloroethane (200 mL), and then we add 1,4-dimethoxyphenol (60 mmol, 7.0 g), **1** (10 mmol, 2.1 g), paraformaldehyde (2.5 g), $\text{BF}_3 \cdot \text{OC}_2\text{H}_5$ (5 mL) one by one, stirring at 30 °C for half an hour. After the end of the reaction, 20 mL of deionized water was added to quench the reaction. The suspension was washed with methanol and extract it three times with deionized water. The organic layer is dried with Na_2SO_4 and filtered. After that we add suitable amount of silica gel to the solution and separated by column chromatography (PE: DCM = 20: 1), we can get white powder **2** (2.93 g, 35.3%). M. P.: 210 - 212 °C. The ^1H NMR spectrum of **2** shown in Figure S3 (600 MHz, CDCl_3 , room temperature) δ (ppm): 6.57-7.25 (m, 10 H), 4.5 (s, 2 H), 3.60-3.79 (m, 37 H), 2.17-2.21 (m, $J = 6.6$ Hz, 2 H), -1.44--1.47 (t, $J = 7.0$ Hz, 3 H). The ^{13}C NMR spectrum of **2** shown in Figure S4 (600 MHz, CDCl_3 , room temperature) δ (ppm): 169.34, 151.44, 150.98, 150.93, 150.62, 150.33, 150.12, 150.10, 129.47, 129.36, 129.18, 128.83, 128.73, 1228.60, 128.22, 127.92, 127.34, 115.41, 115.33, 114.30, 114.16, 114.03, 113.59, 113.54, 113.25, 112.84, 112.54, 65.00, 60.80, 56.67, 56.23, 56.16, 56.08, 56.04, 55.94, 55.91, 55.78, 55.69, 55.40, 32.00, 31.18, 30.54, 29.19, 28.92, 27.47, 11.07. HR-MS: m/z calcd for $[\mathbf{1} + \text{Na}]^+$ $\text{C}_{48}\text{H}_{54}\text{O}_{12}^+$, 845.3507; found 845.3507. (Figure S6)

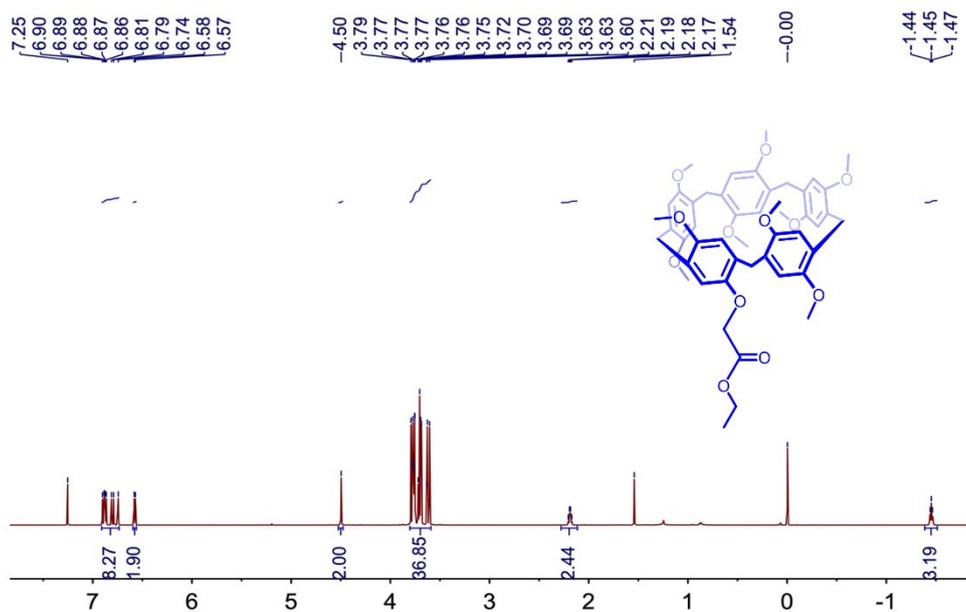


Figure S4 ^1H NMR spectrum (600 MHz, CDCl_3 , 298 K) of **2**.

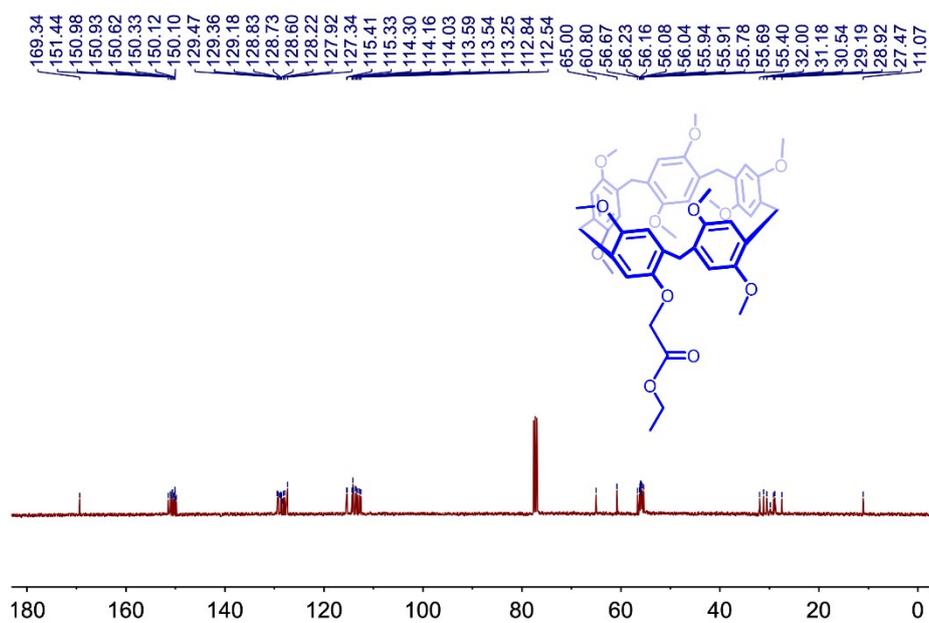


Figure S5 ^{13}C NMR spectrum (400 MHz, CDCl_3 , 298 K) of **2**.

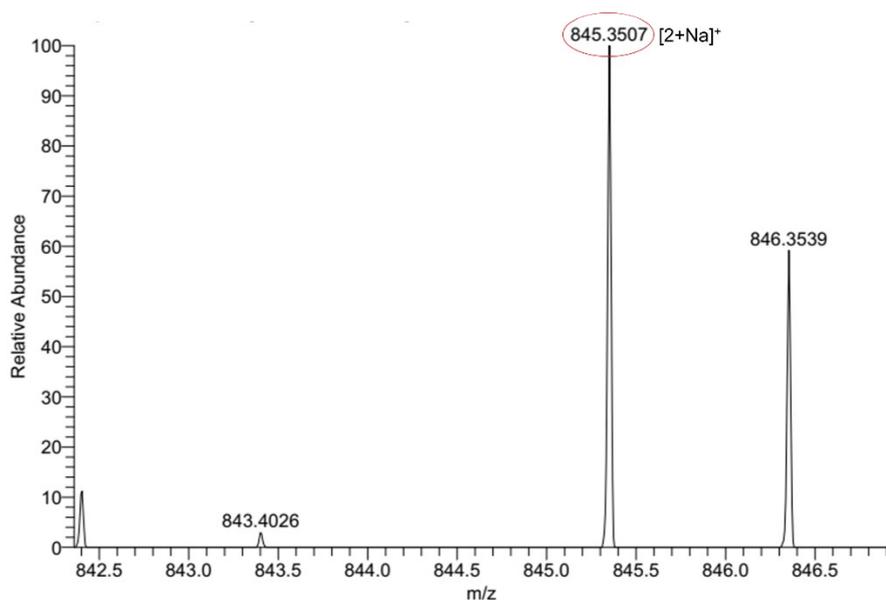
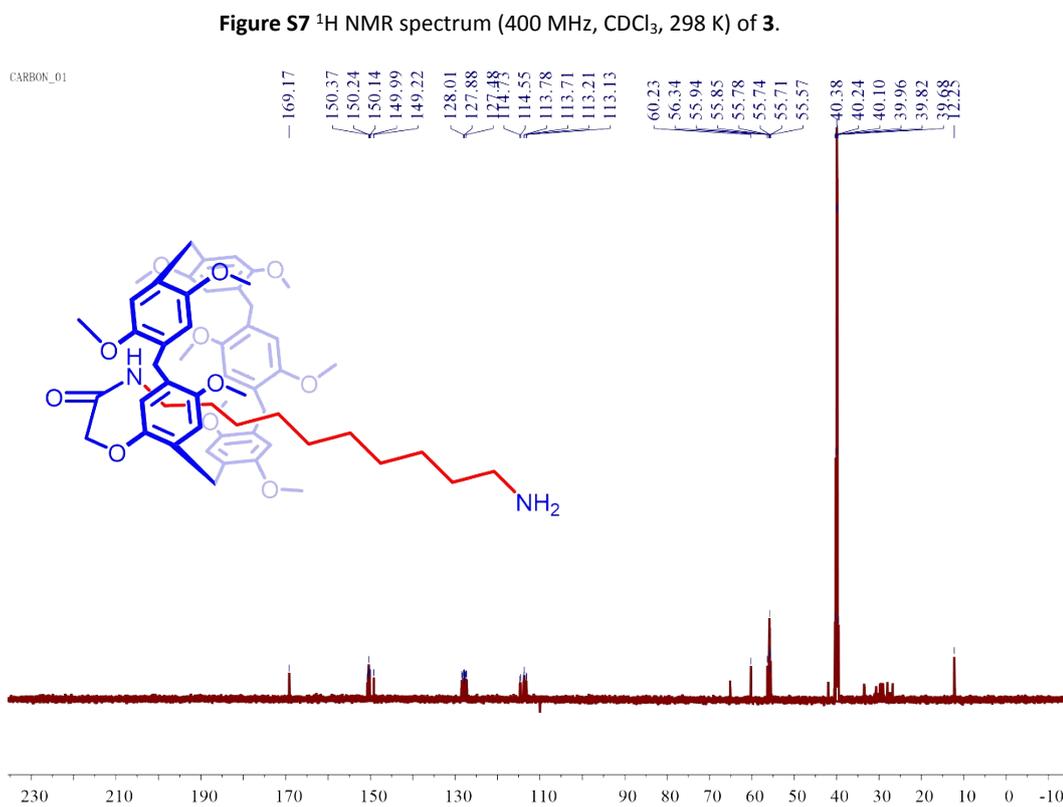
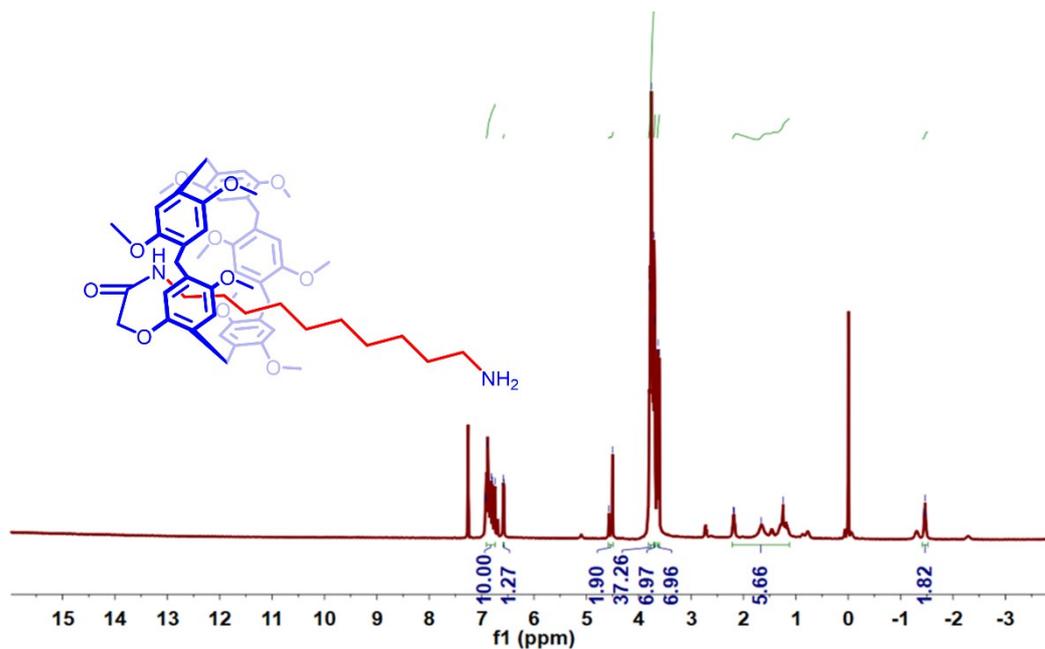


Figure S6 The HR-MS spectrum of **2**.

2.3 Compound 3

In a 100 mL round-bottom flask, we add ethanol (50 mL), and then we add **2** (0.1 mmol, 0.082 g), decanediamine (0.1 mmol, 0.017 g) one by one, stirring at 80 °C for 24 h. After the end of the reaction, then removing the solvents and washed by deionized water and methanol. We could obtain the white powder compound **3** (0.0759 g, 93.1%). The ¹H NMR spectrum of **3** shown in Figure S5 (400 MHz, CDCl₃, room temperature) δ (ppm): 6.75-6.91 (m, 10 H), 6.49 (s, 1 H), 4.48-4.63(m, 2 H), 3.21-3.78 (m, 51 H), 1.08-2.09 (m, 6 H), -1.14 (s, 2 H). The ¹³C NMR spectrum of **3** shown in Figure S6 (400 MHz, CDCl₃, room temperature) δ (ppm):169.17, 150.37, 150.24, 150.14, 149.99, 149.22, 128.01, 127.88, 114.73, 113.78, 113.13, 60.23, 56.34, 55.85, 40.38, 39.82, 12.25. HR-MS: m/z calcd for [**3** + H]⁺ C₅₆H₇₂N₂O₁₁⁺, 949.5208; found 949.5208. (Figure S9)



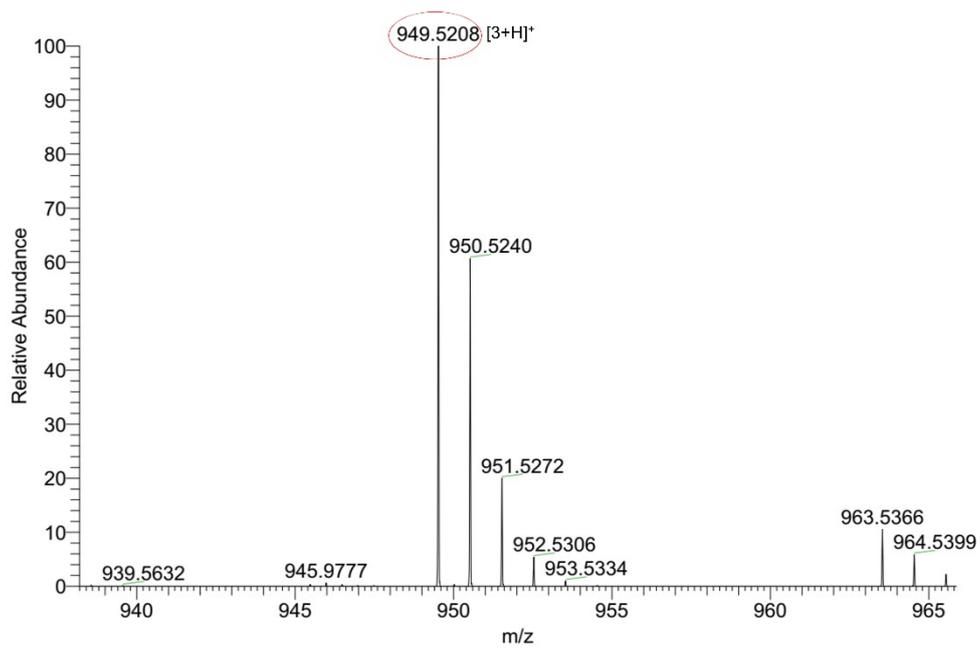


Figure S9 The HR-MS of compound 3.

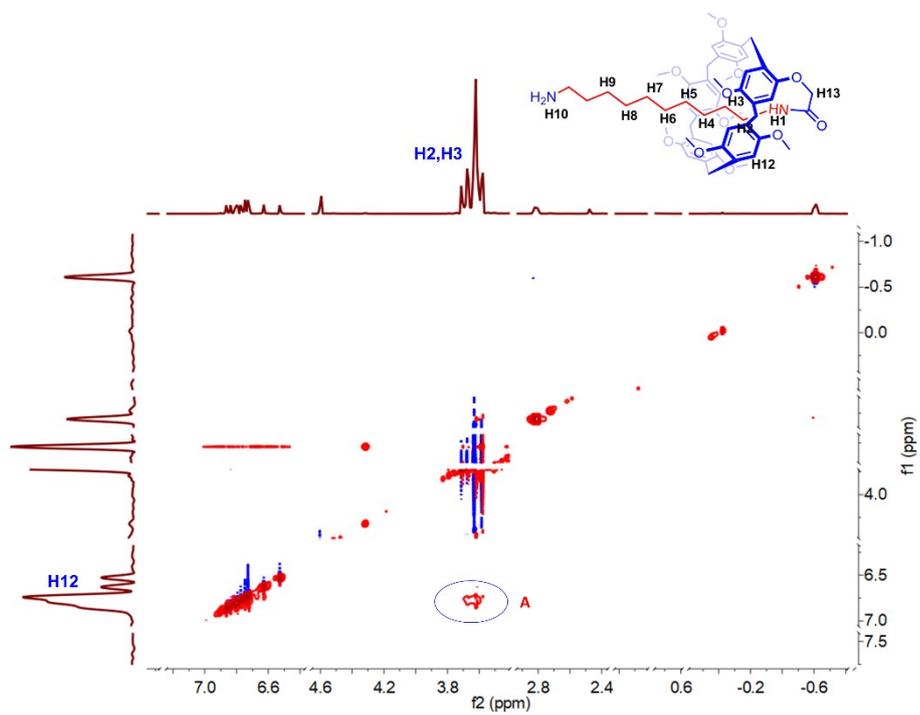


Figure S10 2D NOESY spectrum of compound 3. (600 MHz, DMSO- d_6 , 298 K)

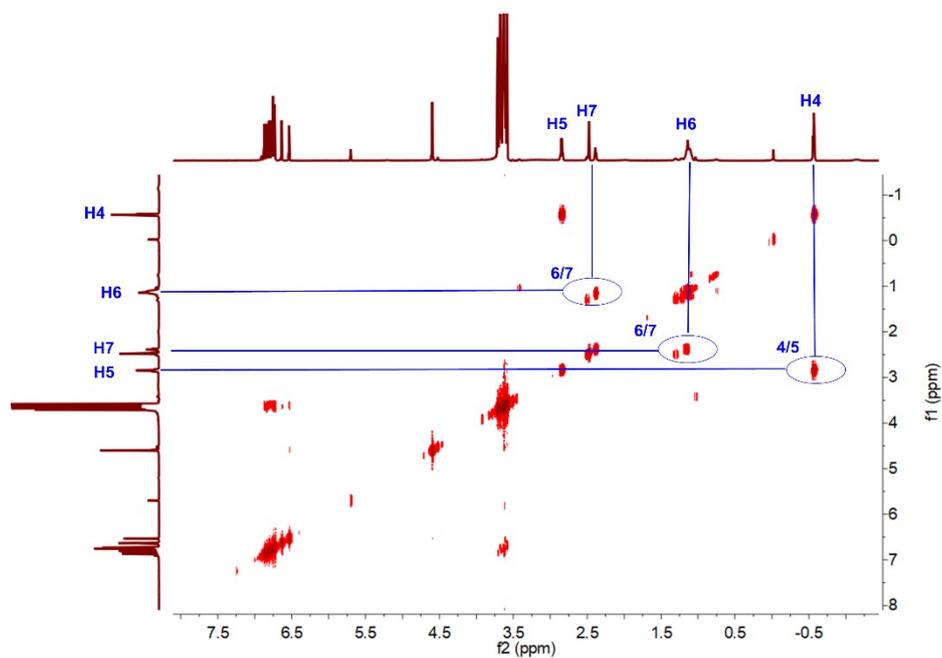


Figure S11 ^1H - ^1H COSY spectrum of compound **3**. (600 MHz, $\text{DMSO-}d_6$, 298 K)

2.4 Compound DEP5

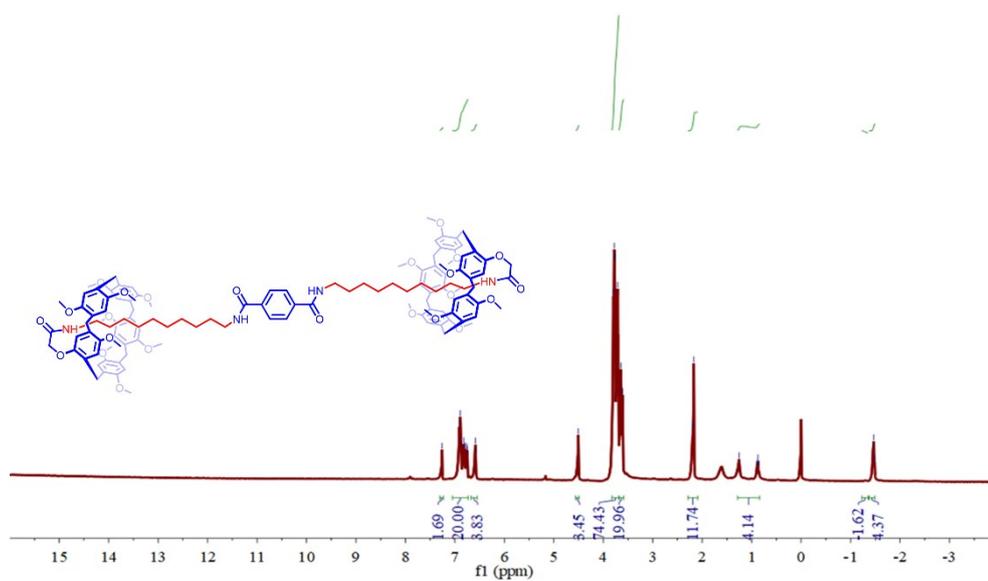


Figure S12 ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **DEP5**.

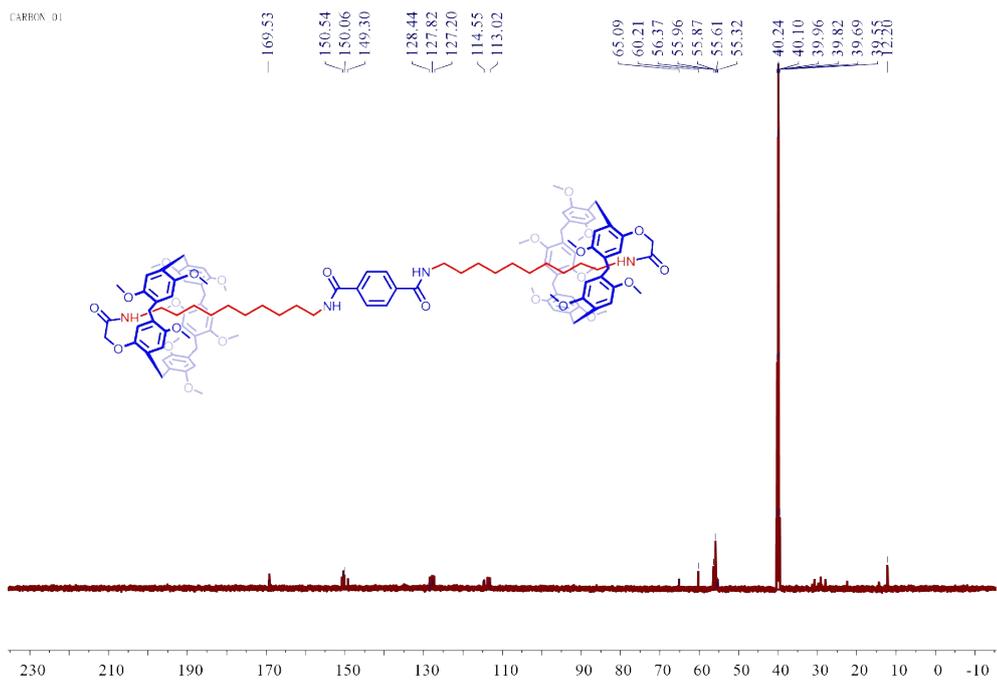


Figure S13 ^{13}C NMR spectrum (600 MHz, CDCl_3 , 298 K) of DEP5.

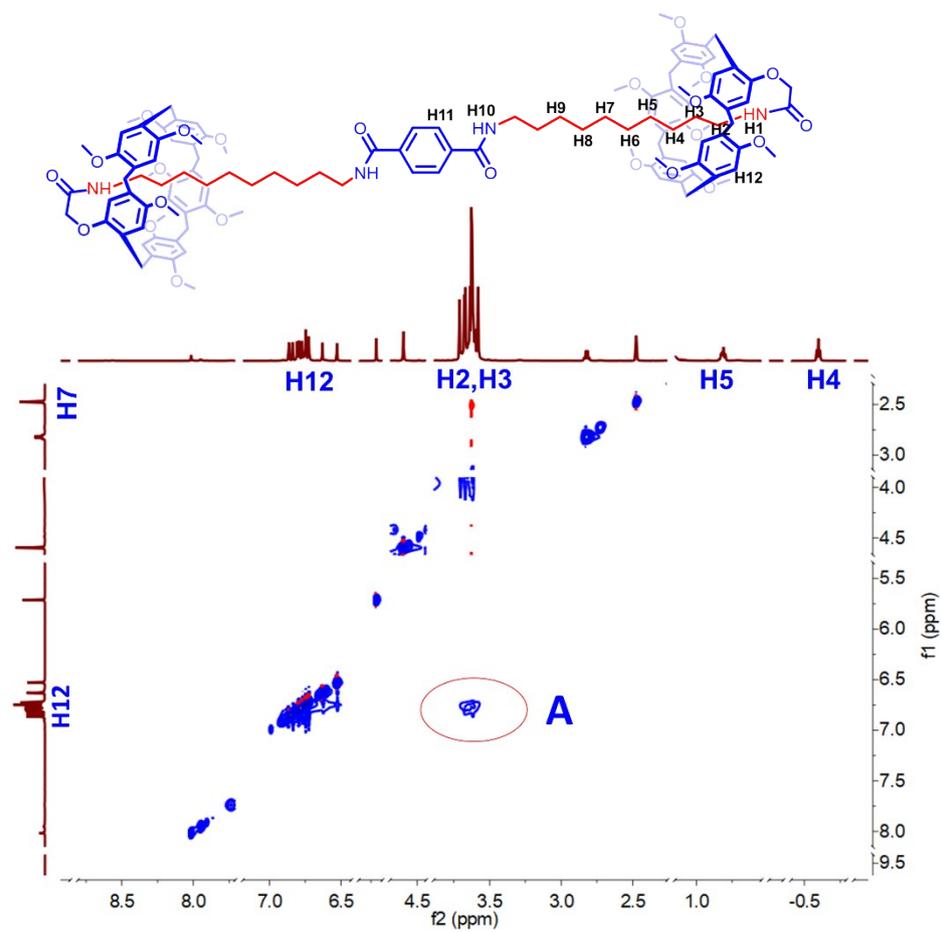


Figure S14 2D NOESY spectrum of compound DEP5. (600 MHz, $\text{DMSO}-d_6$, 298 K)

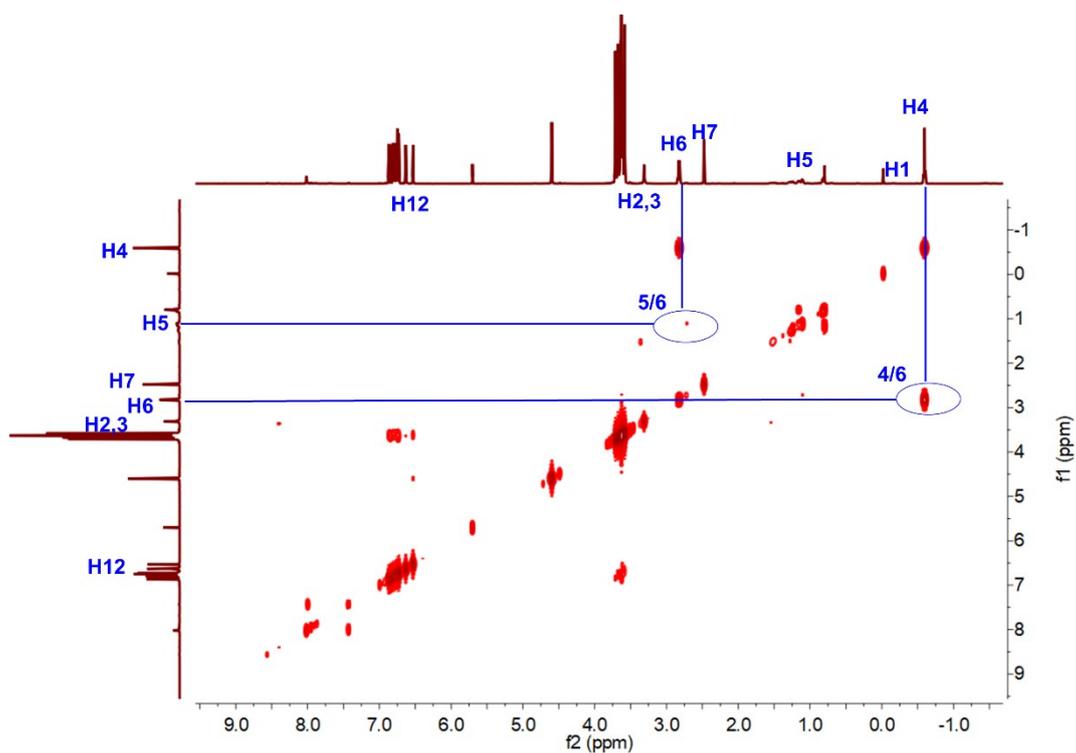


Figure S15 ^1H - ^1H COSY spectrum of compound DEP5. (600 MHz, $\text{DMSO}-d_6$, 298 K)

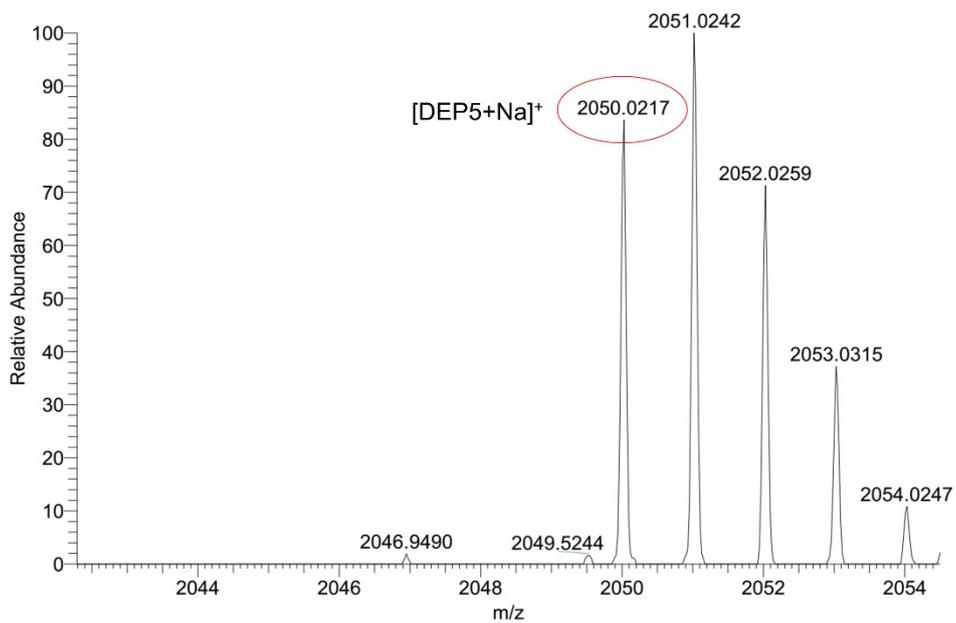


Figure S16 The HR-MS of compound DEP5.

2.5 Compound 4

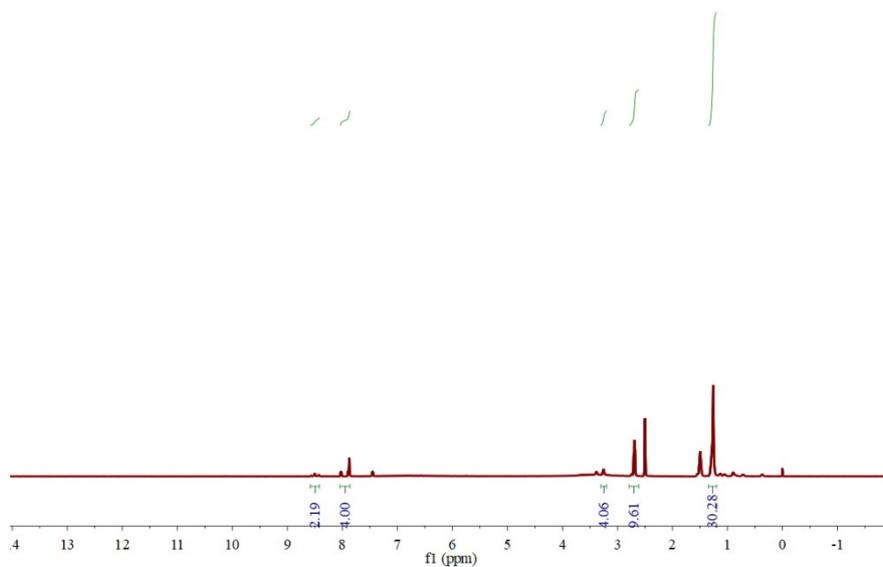


Figure S17 ^1H NMR spectrum (400 MHz, CDCl_3 , 298 K) of **4**.

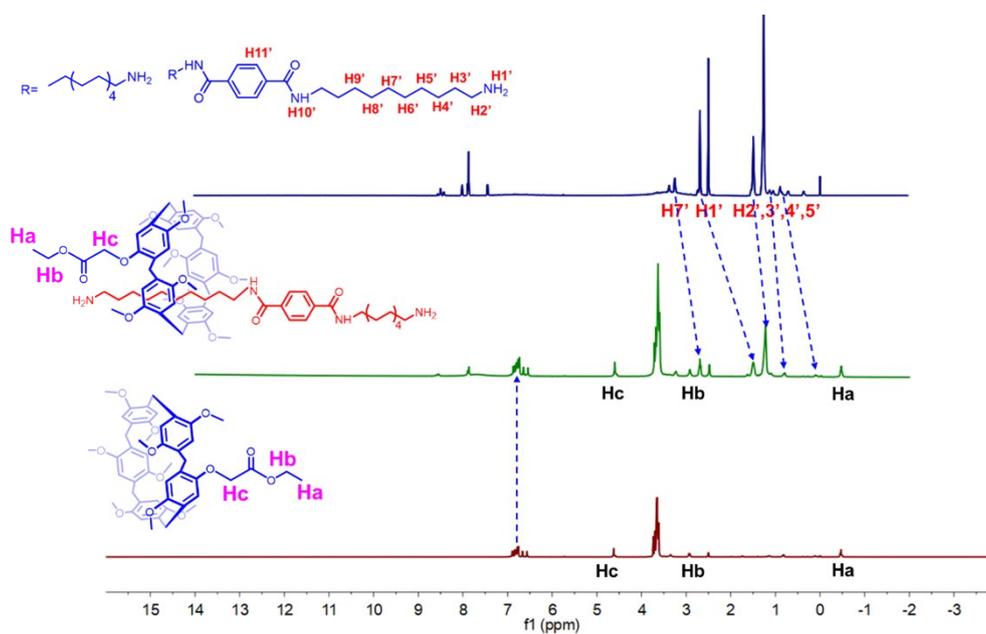


Figure S18 Partial ^1H NMR spectra (600 MHz, $\text{DMSO}-d_6$, 298 K) of the **2**, **4** and **2+4**.



Figure S19 The photograph shown the fluorescence color changes of DEP5 after added the 60 equiv. of various amino acids.

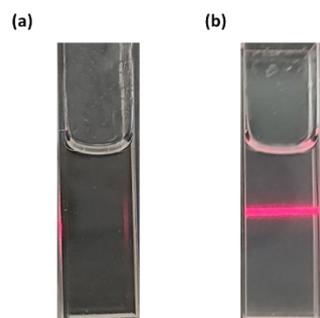


Figure S20 Photos showing the Tyndall effect of (a) DEP5 and (b) DEP5-L-Arg.

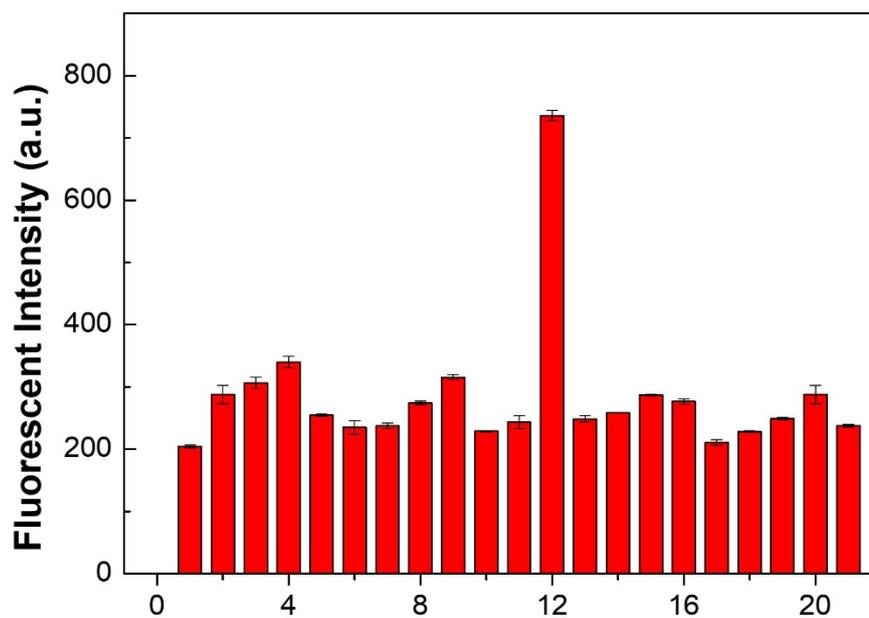


Figure S21 Selectivity of the DEP5 for L-Arg in the presence of different interfering substances. (1: DEP5; 2: L-Phe, 3: L-Gln, 4: L-Ile, 5: L-Thr, 6: L-Glu, 7: L-Ala, 8: L-Ser, 9: L-Met, 10: L-Val, 11: L-Tyr, 12: L-Arg, 13: L-Asp, 14: L-Pro, 15: L-His, 16: L-Leu, 17: L-Gly, 18: L-Trp, 19: L-Asn, and 20: L-Cys)

The lowest of detection limit of DEP5

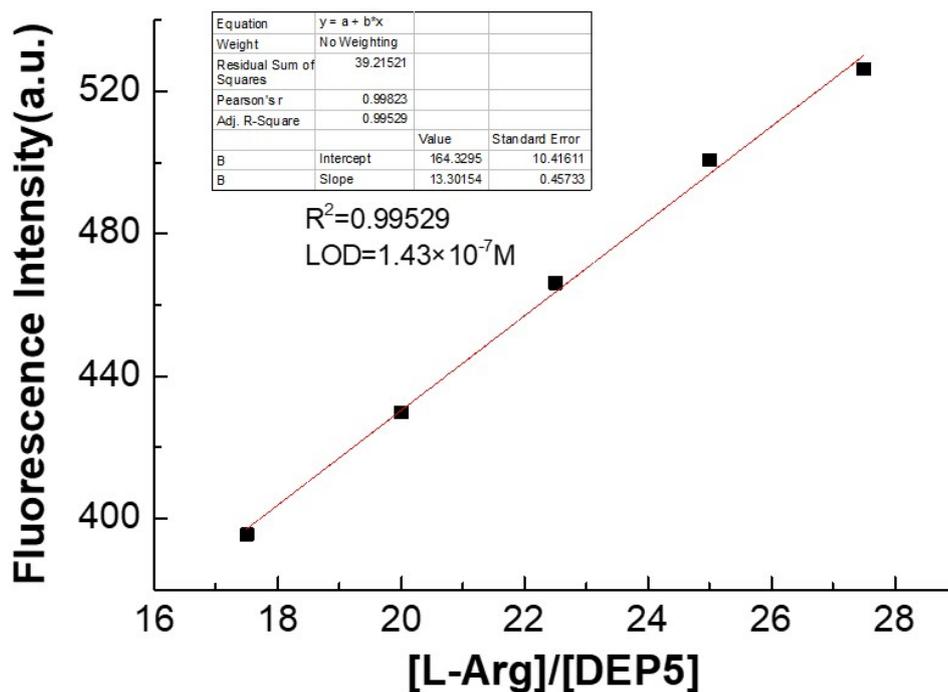


Figure S22 Fluorescence linear ranges of **DEP5** for L-Arg (LOD= 1.43×10^{-7} M).

The lowest of detection limit (LOD) was determined from the equation: $LOD = K \times \sigma/S$, where $K = 3$, S is the slope of the calibration curve (Figure S22).

The result of the analysis as follows:

Linear Equation: $Y = 13.30154X + 164.3295$

$R^2 = 0.99529$; $S = 13.30154$

$\delta = \sqrt{\frac{\sum (F_i - \bar{F})^2}{N - 1}} = 0.53404$ ($N = 20$)

$LOD = K \times 10^{-6} \times \delta/S = 1.43 \times 10^{-7}$ M ($K = 3$)

Table S1 Comparison on the detection limit (LOD) of L-Arg with other different sensors.

Sensors	Detection limit (μM)	References
Thiol functionalized AuNPs	4	[1]
Zn (II)-terpyridine complex	2	[2]
Au/CODs composite	45	[3]
Citrate-capped AuNPs	0.016	[4]
Plumbagin	1	[5]
This work (DEP5)	0.143	

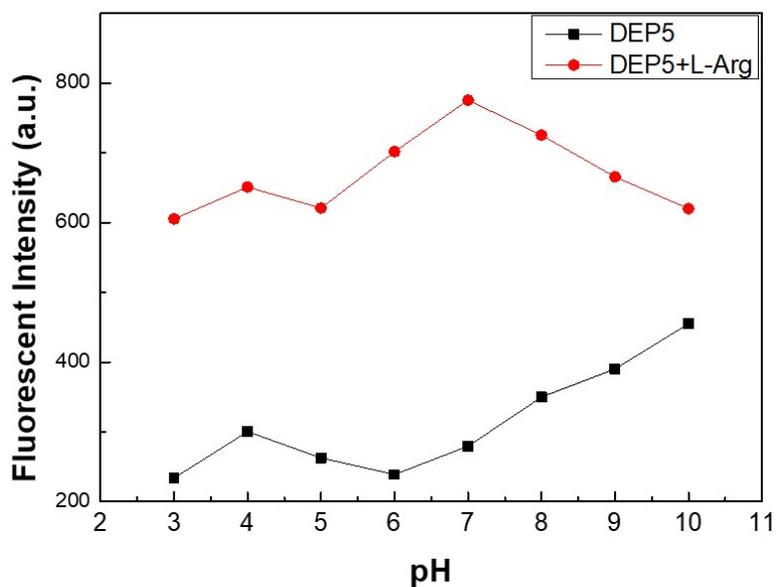


Figure S23 Effect of pH on the fluorescence spectra for **DEP5** in response to L-Arg from 3 to 10 in DMSO/H₂O (v/v, 7: 3) HEPES buffered solution. ($c = 1 \times 10^{-4}$ M, $\lambda_{ex} = 295$ nm, $\lambda_{em} = 325$ nm)

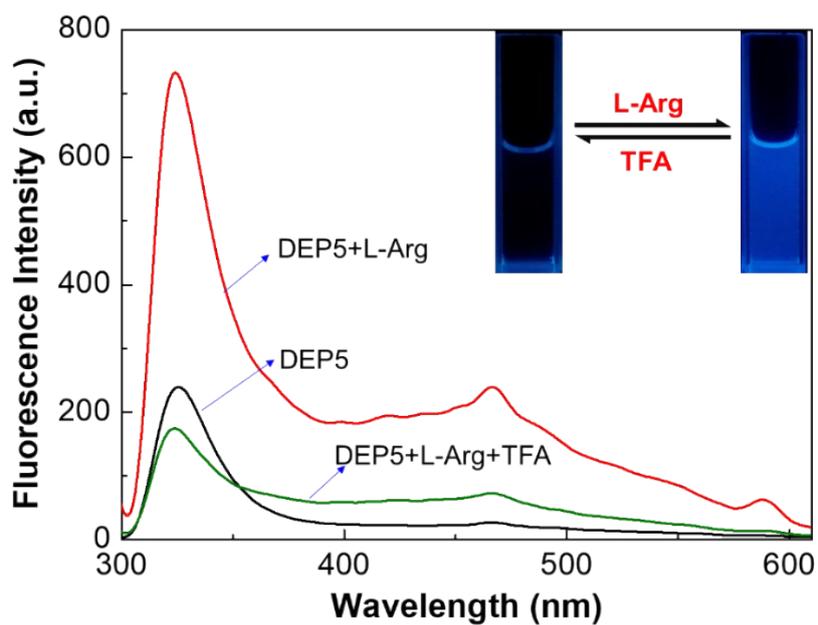


Figure S24 Fluorescence intensity of **DEP5** (1×10^{-4} M) and after the addition of 60 equiv. L-Arg and 20 equiv. TFA. ($\lambda_{ex} = 295$ nm)

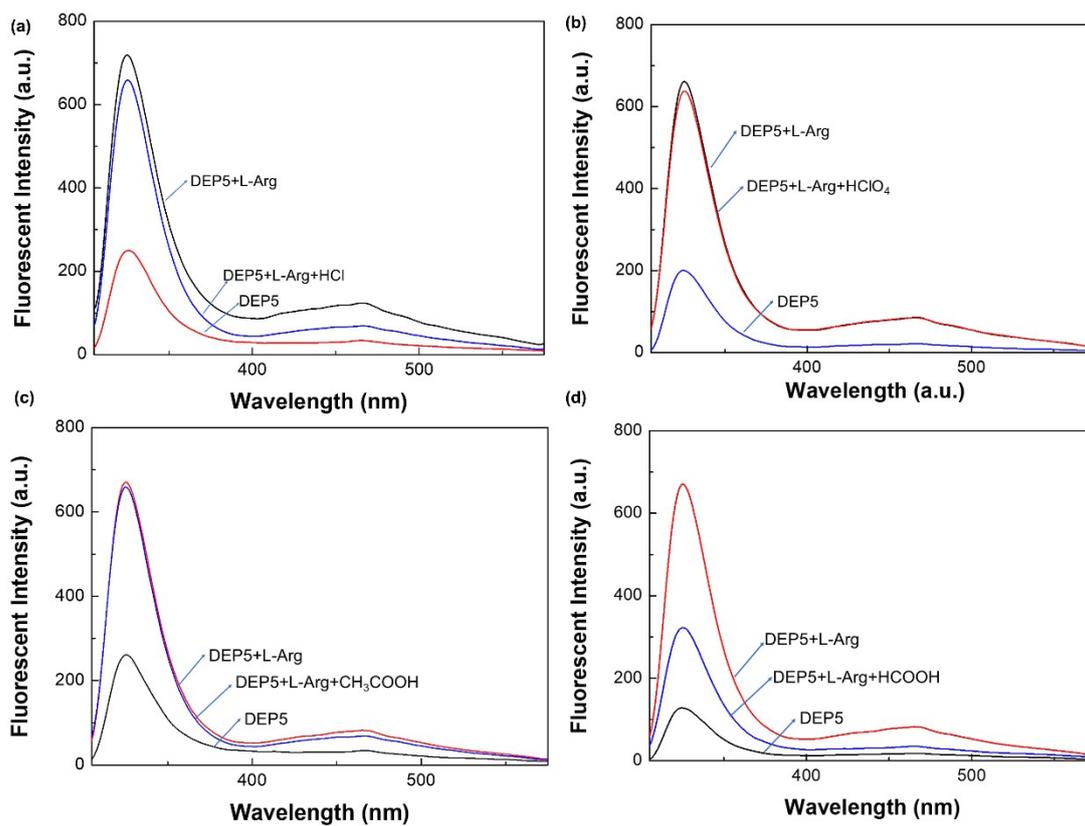


Figure S25 Fluorescence intensity of DEP5 (1×10^{-4} M) and after the addition of 60 equiv. L-Arg and 20 equiv. (a)

HCl; (b) HClO₄; (c) CH₃COOH; (d) HCOOH. ($\lambda_{\text{exc}} = 295$ nm)

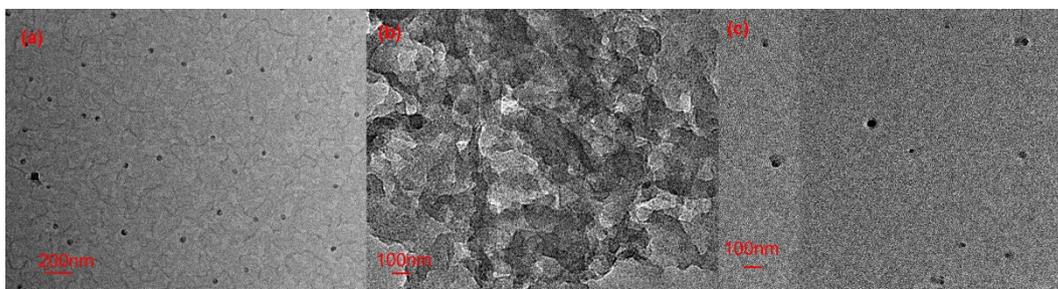


Figure S26 TEM image of (a) DEP5; (b) DEP5+L-Arg and (c) DEP5+L-Arg+TFA.

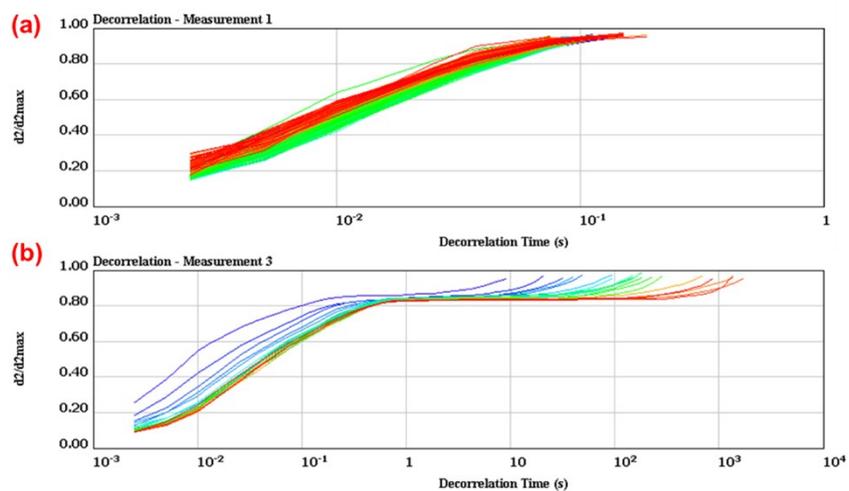


Figure S27 The MSD curves of (a) DEP5 and (b) DEP5+L-Arg.

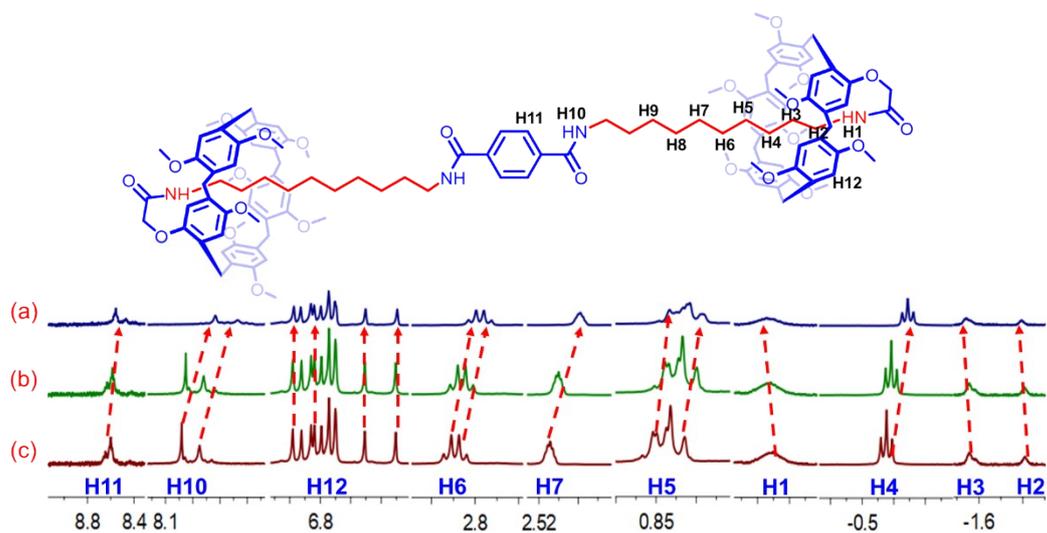


Figure S28 Partial ^1H NMR spectra (400 MHz, 298 K) of DEP5 in $\text{DMSO-}d_6$ at different equivalent of L-Arg: (a) DEP5;

(b) DEP5 + 0.5 equiv. L-Arg; (c) DEP5 + 1.0 equiv. L-Arg.

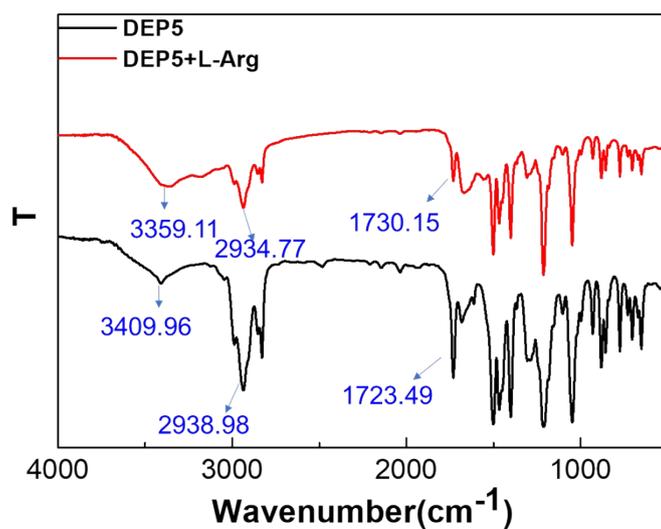


Figure S29 IR spectra of DEP5 and DEP5+L-Arg.

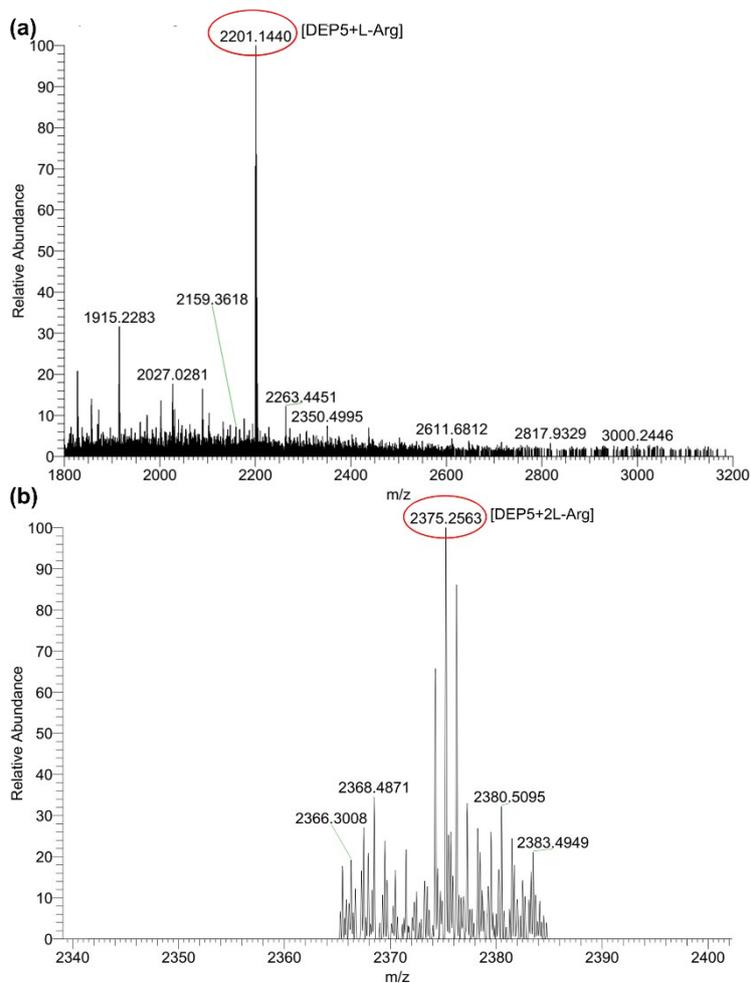


Figure S30 The HR-MS of DEP5+L-Arg complexion.

Notes and references

- [1] G. Patel, S. Menon, *Chem. Commun.*, 2009, **24**, 3563-3565.
- [2] X. Zhou, X. Jin, D. Li, X. Wu, *Chem. Commun.*, 2011, **47**, 3921-3923.
- [3] T. Liu, N. Li, J. X. Dong, Y. Zhang, Y. Z. Fan, S. M. Lin, H. Q. Luo, N. B. Li, *Biosens. Bioelectron.*, 2017, **87**, 772-778.
- [4] W. Pu, H. Zhao, C. Huang, L. Wu, D. Xu, *Anal. Chim. Acta*, 2013, **764**, 78-83.
- [5] S. D. Parveen, A. Affrose, K. Pitchumani, *Sens. Actua. B: Chem.*, 2015, **31**, 521-527.