Electronic Supplementary Information

Synthesis and Multimodal Responsiveness of Poly(α-Amino Acid)s Bearing OEGylated Azobenzene Side-Chains

Wei Xiong,[†] Xiaohui Fu,[¶] Yaoming Wan,[‡] Yunlong Sun,[†] Zhibo Li,*[, ¶] and Hua Lu*[, †]

EMAIL: chemhualu@pku.edu.cn (H.L.); zbli@qust.edu.cn (Z.B.L.)

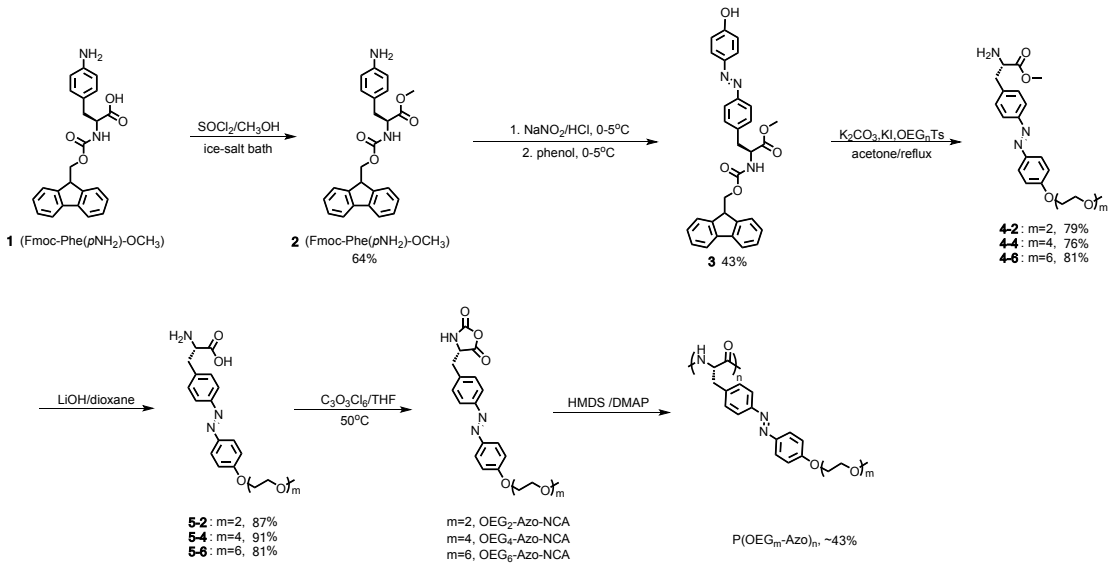
[†]Beijing National Laboratory for Molecular Sciences, Center for Soft Matter Science and Engineering, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

[‡]Beijing National Laboratory for Molecular Sciences, Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

[¶]School of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

Materials: All chemicals were purchased from commercial sources and used as received unless otherwise specified. Anhydrous dichloromethane (DCM), hexane, and tetrahydrofuran (THF) were obtained by passing regular solvents through columns packed with neutral alumina or activated 4Å molecular sieves. Anhydrous *N,N*-dimethylformaide was purchased from Sigma-Aldrich and treated with methyl isocyanate bounded polystyrene beads prior to polymerization. Dry $CDCl_3$ was prepared by treating commercial $CDCl_3$ with $CaSO_4$ overnight and filtered in a dry box. Fmoc-Phe(*p*NH_2)-OH (**1**) was purchased from Beijing HWRK Chem Co. LTD (Beijing China).

Instrumentations: NMR spectra were recorded on a 400MHz Bruker ARX400FT-NMR spectrometer. FT-IR spectroscopy was performed on a Bruker Vector 22 FT-IR spectrometer. Circular dichroism (CD) spectra were recorded on a Jasco J810 CD Spectrometer with a 0.1 cm path length quartz cell. Fluorescence spectra were recorded on a Hitachi F7000 Fluorescence Spectrometer. The transmittance of samples were measured on a Shimadzu UV-Vis spectrometer. UV irradiation was performed by a Vilber VL-215.L photochemical reactor (30 W) or a Rayolet photochemical reactor (400 W). Tandem gel permeation chromatography was performed at 150 ^{o}C on a PL-GPC 220 High Temperature GPC/SEC System (Agilent Inc.) equipped with a refractive index (RI) and a two-angle (15 and 90) light scattering detector. Separation was realized by two sequentially connected PLgel Olexis columns (10 μm, 300 × 7.5 mm) in 1,2,4-trichlorobenzene at a flow rate of 1.0 mL/min. The system was calibrated with polystyrene standards for molecular weight calculation.



Synthesis of Fmoc-Phe(pNH$_2$)-OCH$_3$ (2)

A methanol solution (5 mL) of Fmoc-Phe(pNH$_2$)-OH (**1,** 1.0 g, 4.76 mmol) in a 25-mL round-bottom flask was cooled to -15 ^{o}C with an ice-salt bath, to which was added thionyl chloride (1.34 mL, 18.5 mmol) dropwise. The reaction mixture was stirred at -15 ^{o}C for another 2 h before it was concentrated by rotary evaporation. The crude product was washed by petroleum ether, filtered and dried by rotary evaporation to afford a grey solid (4.5 g, yield: 64%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.41 (broad, 2H), 7.90 (m, 3H), 7.66 (m, 2H), 7.42 (t, J = 7.0 Hz, 2H), 7.38 – 7.25 (m, 6H), 4.37 – 4.13 (m, 4H), 3.66 (s, 3H), 3.13-3.02 (m, 1H), 2.98-2.86 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.6, 156.4, 144.2, 141.2, 137.8, 131.1, 130.8, 128.2, 127.6, 125.7, 123.5, 120.6, 66.1, 55.8, 52.5, 47.1, 36.2. ESI-MS: calc. MS = 416.17; observed MS = 417.25 (M + H$^+$), 439.24 (M + Na$^+$).

Synthesis of 3

Fmoc-Phe(pNH$_2$)-OCH$_3$ (**2**, 1.80 g, 4.0 mmol) and HCl (1N × 9.7 mL) were placed in a 50-mL round-bottom flask and stirred vigorously at 0 ^{o}C, to which was slowly added a

sodium nitrite solution (177 mg/mL, 1.8 mL) and stirred for another 10 min (solution I). In parallel, a potassium phenoxide solution in methanol (15 mL) was prepared *in situ* by mixing phenol (443 mg, 4.5 mmol) and KOH (527 mg, 8.94 mmol) in another 50-mL round-bottom flask, which was cooled to 0 ^{o}C in ice bath and used without further purification (solution II). The solution I was added to the solution II dropwise at pH 8.0, and the resulting mixture was stirred at room temperature for 1.5 h, filtered and concentrated by rotary evaporation. Purification of the crude product by column chromatography (DCM/methanol = 80:1) afforded an orange solid (0.93 g, yield: 43%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.28 (b, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 7.4 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H), 7.68 – 7.60 (m, 2H), 7.47 – 7.35 (m, 4H), 7.30 (dd, J = 16.8, 7.7 Hz, 3H), 6.96 (d, J = 8.6 Hz, 2H), 4.39 – 4.29 (m, 1H), 4.25 (dd, J = 13.2, 7.2 Hz, 2H), 4.19 (dd, J = 13.2, 6.5 Hz, 2H), 3.65 (s, 3H), 3.16 (dd, J = 13.6, 4.5 Hz, 1H), 3.06 – 2.94 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.7, 161.3, 156.4, 151.3, 145.7, 144.2, 141.2, 140.8, 130.6, 128.1, 127.5, 125.6, 125.2, 122.5, 120.6, 116.4, 66.1, 55.7, 52.5, 47.0, 36.7. ESI-MS: calc. MS = 521.20; observed MS = 522.15 ($M + H^+$), 544.13 ($M + Na^+$), 560.02 ($M + K^+$).

General Protocol for the Synthesis of 4-m (m =2, 4, and 6)

Taking **4-6** as an example, **3** (1.00 g, 1.92 mmol) and mOEG$_6$-OTs (0.95 g, 2.11 mmol) were dissolved in acetone (130 mL), to which was added potassium carbonate (523 mg, 4.22 mmol) at room temperature. The mixture was refluxed at 56 ^{o}C for 48 h, filtered and the solvent was rotary evaporated. Purification of the crude product by column chromatography (DCM/methanol = 80:1) afforded a brown oil (800 mg, yield: 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.8 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 4.22 (t, J = 4.8 Hz, 2H), 3.90 (t, J = 4.6 Hz, 2H), 3.78- 3.59 (m, 19H), 3.54 (t, J = 4.6 Hz, 2H), 3.39 (s, 3H), 3.16 (dd, J = 13.5, 5.1 Hz, 1H),

2.98 (dd, J = 13.5, 7.7 Hz, 1H), 2.06 (broad, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 161.5, 152.3, 151.7, 147.0, 136.2, 130.1, 124.9, 123.3, 114.9, 71.9, 70.9, 70.7, 70.7, 70.6, 70.5, 69.7, 67.9, 59.1, 58.8, 37.8. ESI-MS: calc. MS = 577.30; observed MS = 289.85 ((M + $2H^+$)/2), 298.46 ((M + H^+ + NH_4^+) /2), 300.82 ((M +H^+ + Na^+)/2), 578.58 (M + H^+), 600.48 (M + Na^+).

4-2 and **4-4** were prepared by following the same protocol as described above.

4-2 (694 mg, 79 % yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 4.22 (t, J = 4.7 Hz, 2H), 3.90 (t, J = 4.7 Hz, 2H), 3.82 (t, J = 6.4 Hz, 1H),3.78-3.67 (m, 5H), 3.59 (t, J = 4.6 Hz, 2H), 3.40 (s, 3H), 3.16 (dd, J = 13.5, 5.3 Hz, 1H), 2.97 (dd, J = 13.5, 7.7 Hz, 1H), 2.25 (broad, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 161.3, 151.8, 147.1, 139.7, 130.0, 124.7, 122.8, 114.9, 72.0, 70.8, 69.7, 67.7, 59.1, 55.7, 52.1, 40.6. ESI-MS: calc. MS = 401.20; observed. MS=402.63 (M+H^+) 424.36 (M+Na^+) 440.24 (M+K^+).

4-4 (680 mg, 76 % yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.9 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.01 (d, J = 8.9 Hz, 2H), 4.21 (t, J = 4.8 Hz, 2H), 3.90 (t, J = 4.8 Hz, 2H), 3.78- 3.59 (m, 14H), 3.54 (t, J = 4.6 Hz, 2H), 3.37 (s, 3H), 3.19 (dd, J = 13.5, 5.3 Hz, 1H), 3.05 (dd, J = 13.5, 7.7 Hz, 1H), 2.73 (broad, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 161.3, 151.7, 147.0, 139.9, 130.0, 124.7, 122.7, 114.8, 71.9, 70.9, 70.7-70.5 (m), 70.5, 69.6, 67.7, 59.0, 55.7, 52.0, 40.9. ESI-MS: calc. MS = 489.25; observed. MS = 490.58 (M+H^+).

General Protocol for the Synthesis of 5

Synthesis of 5-6: To a solution of **4-6** (500 mg, 0.85 mmol) in dioxane (25 mL) was added LiOH (83 mg, 33 mg/mL, H_2O) in one portion. The mixture was stirred at room temperature for 4 h. Upon completion of the reaction as monitored by TLC, 1 M HCl was added to the solution to adjust pH to ~7.0. The mixture was extracted with DCM and the organic layer was concentrated under vacuum to afford a brown oil (396 mg, yield: 81%). ^{1}H NMR (400 MHz, D_2O) δ 7.03 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 8.3 Hz, 2H), 6.68 (d, *J* = 8.3 Hz, 2H), 6.32 (d, *J* = 9.0 Hz, 2H), 3.53 (m, 1H), 3.38 (m, 2H), 3.04 (m, 2H), 2.93-2.56 (m, 20H), 2.47 (s, 3H), 2.31 (dd, *J* = 14.3, 7.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.1, 161.7, 152.1, 146.7, 138.4, 131.1, 124.9, 122.6, 115.5, 71.8, 70.5, 70.3, 70.1, 69.3, 68.2, 58.6, 58.4, 36.6.
ESI(-)-MS: calc. MS = 563.28; observed MS = 562.59 ($M - H^+$).

5-2, 5-4 were synthesized by following the same protocol as described above.

5-2 (400 mg, 87 % yield): ^{1}H NMR (400 MHz, D_2O) δ 7.18 (d, *J* = 9.1 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.41 (d, *J* = 9.1 Hz, 2H), 3.71-3.64 (m, 1H), 3.56 (t, *J* = 4.3 Hz, 2H), 3.22-3.15 (m, 2H), 2.99-3.03 (m, 2H), 2.87-2.91 (m, 2H), 2.72 (dd, *J* = 14.4, 5.6 Hz, 1H), 2.63 (s, 3H), 2.59 (dd, *J* = 14.4, 8.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.2, 161.8, 152.1, 151.6, 146.7, 138.4, 131.2, 125.0, 122.7, 115.6, 71.8, 70.2, 69.3, 68.2, 58.6, 36.6. ESI(-)-MS: calc. MS = 387.18; observed MS = 386.42 ($M - H^+$).

5-4 (538 mg, 91 % yield): ^{1}H NMR (400 MHz, D_2O) δ 7.67 (d, *J* = 8.9 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 4.24 (t, *J* = 5.7 Hz, 1H), 4.07-4.15 (m, 2H), 3.70- 3.78 (m, 2H), 3.55-3.62 (m, 2H), 3.40-3.55 (m, 8H), 3.33-3.40 (m, 2H), 3.24 (dd, *J* = 14.8, 6.0 Hz, 1H), 3.13 (s, 3H). ^{13}C NMR (101 MHz, DMSO-

d$_6$) δ 171.2, 161.8, 152.1, 151.6, 146.7, 138.4, 131.1, 125.0, 122.7, 115.6, 71.8, 70.4, 70.3, 70.3, 70.1, 69.3, 68.2, 58.5, 36.6.

ESI(–)-MS: calc. MS=475.23; observed. MS=474.54 ($M - H^+$).

General Protocol for the Synthesis of OEG$_m$-AzoNCA

Synthesis of OEG$_6$-AzoNCA: In an oven-dried 100-mL round-bottom flask, **5-6** (480 mg, 0.86 mmol) was placed under high vacuum for 0.5 h before dissolved in dry THF (30 mL) under a nitrogen atmosphere. To the solution was added triphosgene (47 mg, 0.38 mmol) in one portion under vigorous stirring. The mixture was stirred at 50 ^oC for another 4 h before concentrated under vacuum and the residue was further dried overnight under high vacuum. Purification of the crude product by column chromatography (EA) afforded a brown solid (211 mg, yield: 43%). ^1H NMR (400 MHz, DMSO-*d*$_6$) δ 9.14 (s, 1H), 7.87 (d, *J* = 8.9 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.9 Hz, 2H), 4.85 (t, *J* = 5.5 Hz, 1H), 4.22 (t, *J* = 4.5 Hz, 2H), 3.80 (t, *J* = 4.5 Hz, 2H), 3.62 (m, 2H), 3.53 (m, 19H), 3.45-3.38 (m, 2H), 3.23 (s, 3H), 3.15 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 161.5, 152.0, 151.7, 147.0, 136.4, 130.2, 124.9, 123.2, 114.9, 71.9, 70.9, 70.6, 69.7, 67.9, 59.1, 58.8, 37.7. ESI-MS: calc. MS = 589.26; observed. MS = 612.25 ($M + Na^+$), 628.23 ($M + K^+$). FT-IR (4000-400 cm^{-1}): 3056 (ν N-H), 1851 and 1786 (ν anhydride).

OEG$_2$-AzoNCA , OEG$_4$-AzoNCA were synthesized by following the same protocol as described above.

OEG$_2$-AzoNCA (410 mg, yield: 53%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 5.65 (s, 1H), 4.58 (dd, *J* = 8.8, 4.4 Hz, 1H), 4.24 (t, *J* = 5.0 Hz, 2H), 3.91 (t, *J* = 5.0 Hz, 2H), 3.74

(t, J = 4.8 Hz, 2H), 3.60 (t, J = 4.8 Hz, 2H), 3.40 (s, 3H),3.39 (dd, J = 14.1, 4.4 Hz, 1H) 3.06 (dd, J = 14.1, 8.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 161.5, 152.3, 151.7, 147.0, 136.2, 130.1, 124.9, 123.3, 114.9, 71.9, 70.9, 70.7, 70.7, 70.6, 70.5, 69.7, 67.9, 59.1, 58.8, 37.8. ESI-MS: calc. MS = 413.16; observed. MS = 414.17 ($M + H^+$) 436.15 ($M + Na^+$). FT-IR (4000-400 cm^{-1}): 2927 (ν N-H), 1852 and 1787 (ν anhydride).

OEG_4-AzoNCA (300 mg, yield: 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 7.08 (d, J = 8.8 Hz, 2H), 6.28 (s, 1H), 4.58 (dd, J = 7.7, 4.3 Hz, 1H), 4.11 (t, J = 4.8 Hz, 2H), 3.80 (t, J = 4.8 Hz, 2H), 3.64-3.81 (m, 10H), 3.60 (dd, J = 5.6, 3.7 Hz, 2H), 3.28 (s, 3H), 3.21 (dd, J = 14.2, 4.3 Hz, 1H), 2.99 (dd, J = 14.2, 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 160.4, 151.1, 150.9, 145.9, 135.4, 129.1, 123.8, 122.1, 113.9, 70.9, 69.8, 69.5, 69.4, 68.6, 66.7, 57.9, 57.6, 36.4. ESI-MS: calc. MS = 501.21; observed. MS = 502.22 ($M+H^+$) 524.20 ($M+Na^+$). FT-IR (4000-400 cm^{-1}): 2923 (ν N-H), 1850 and 1783 (ν anhydride).

General Procedure for the ROP of NCAs

In a dry glove-box, OEG_6-AzoNCA (**6-3**, 100 mg, 0.167 mmol) was dissolved in anhydrous THF (500 μL) under stirring. To the solution was added stock solutions of hexamethyldisilazane (HMDS, 500 mM) and dimethylaminopyridine (DMAP, 200 mM) in appropriate volumes at room temperature. Upon the full conversion of the NCA as monitored by FT-IR, the polymer, denoted as $P(OEG_6\text{-}Azo)_n$ (n = feeding M/I ratio), was precipitated and washed by diethyl ether twice (20 mL). The residue was dried under vacuum to afford an orange solid in ~50% yield.

TEM Studies: Sample Preparation and Imaging

The solution of $P(OEG_6\text{-}Azo)_n$ in Milli-Q water (20 μL of 10 μM) was deposited on plasma treated carbon-coated hydrophilic grids for 2 min and then rinsed with Milli-Q water. Samples were stained with uranyl acetate solution for 1 min and imaged using a JEM-2100 Transmission electron microscope.

Determination of the Critical Micelle Concentrations (CMC) of $P(OEG_6\text{-}Azo)_{50}$

A stock solution of Nile Red in DCM (24 μL × 0.05 mg/mL) was added to a series of empty vials, which were then placed under vacuum for at least 2 h to ensure complete solvent removal. To the vials were added a stock solution of $P(OEG_6\text{-}Azo)_{50}$ in 10 mM aqueous phosphate buffer at pH 7.4 (4.0 mg/mL) at varying volumes. More buffer was added to bring the total volume of each solution up to 4.0 mL. These solutions were shaken vigorously and then allowed to equilibrate at room temperature for at least 2 h. Fluorescence measurements were taken at the excitation wavelength of 550 nm and the emission was monitored from 560 to 700 nm. The relative fluorescent intensity against the concentration of $P(OEG_6\text{-}Azo)_{50}$ in log was plotted to calculate the CMC value.

Supporting Figures and Tables

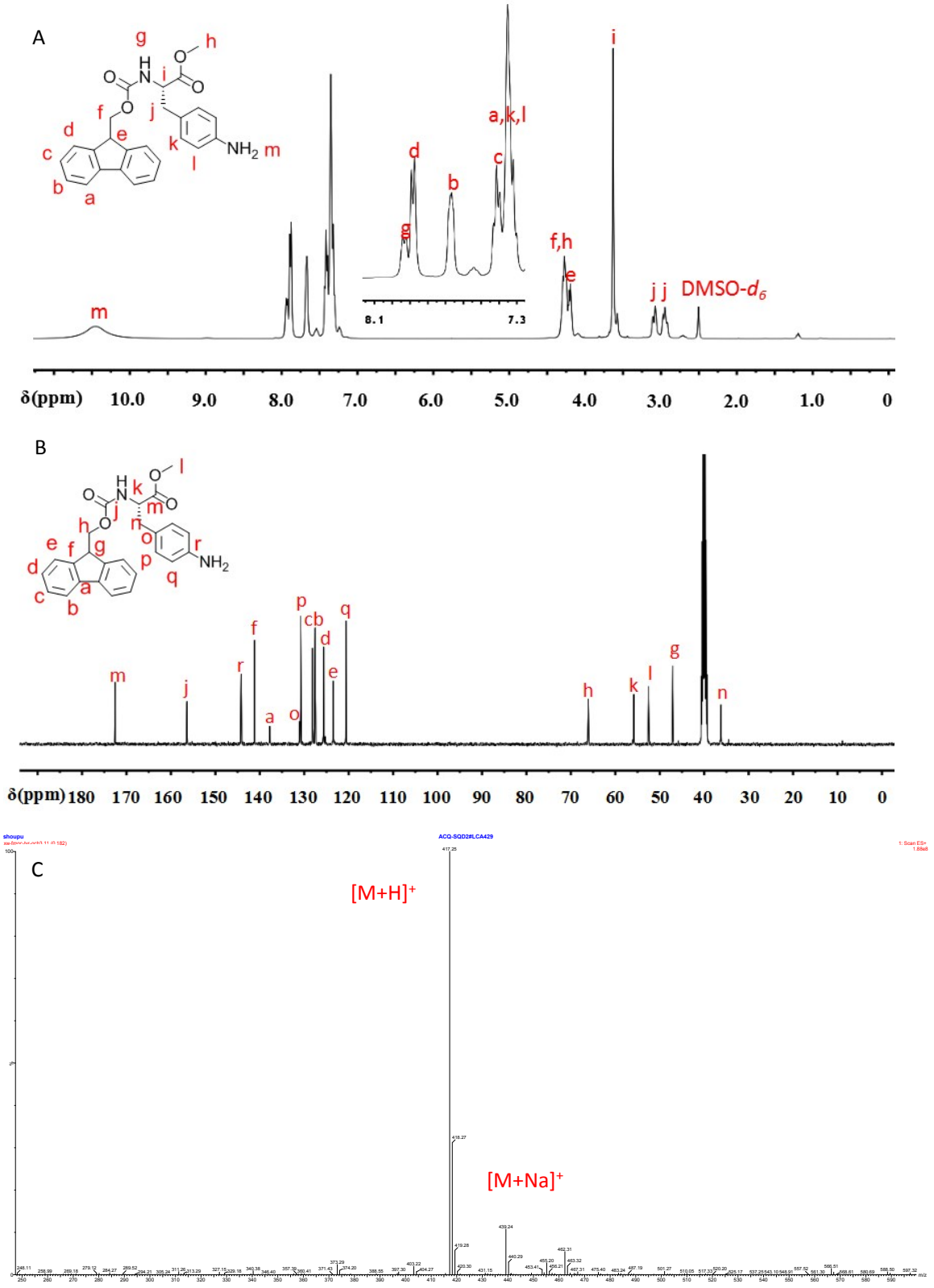


Figure S1. ^{1}H NMR (**A**), ^{13}C NMR (**B**), and ESI-MS (**C**) spectra of **2**.

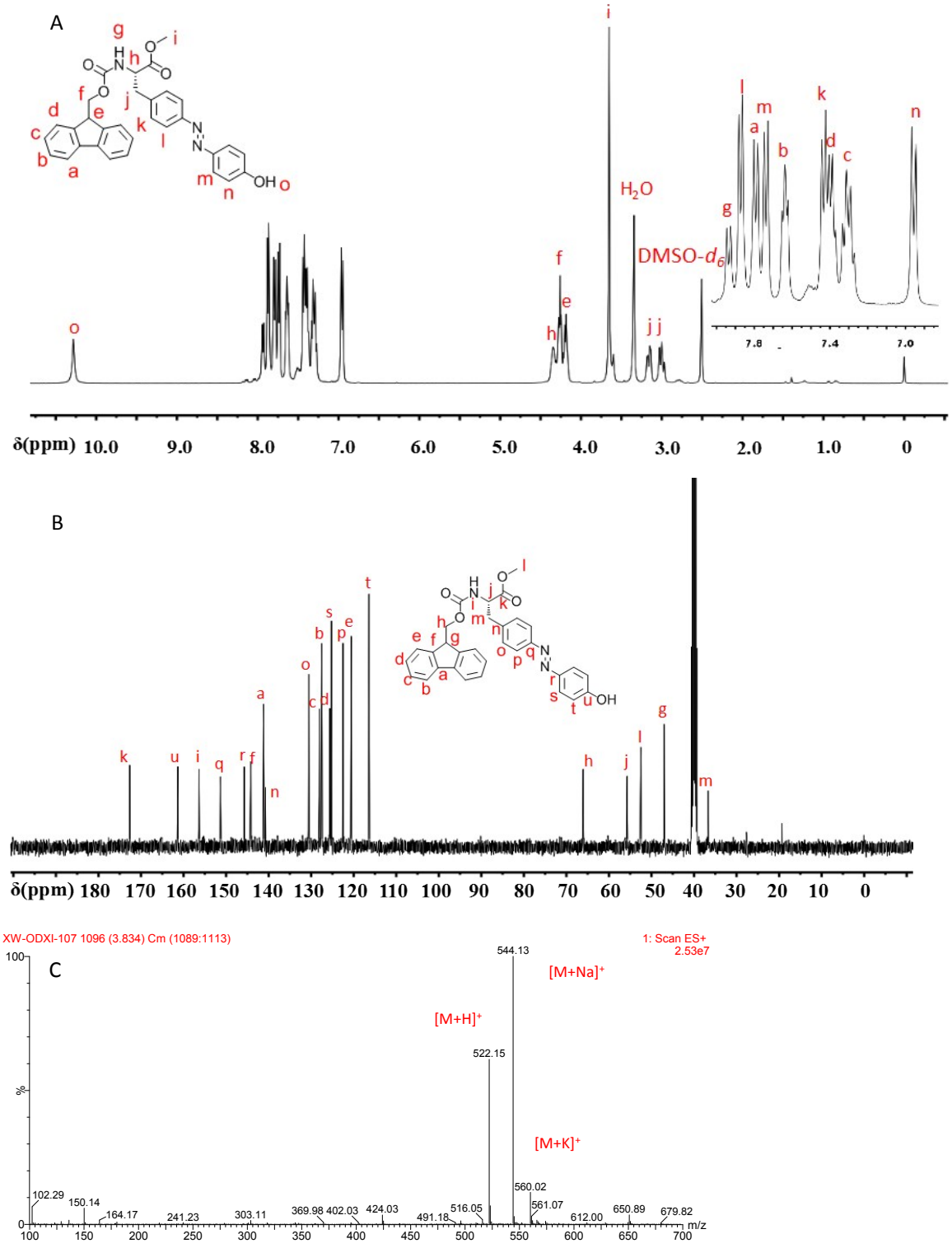
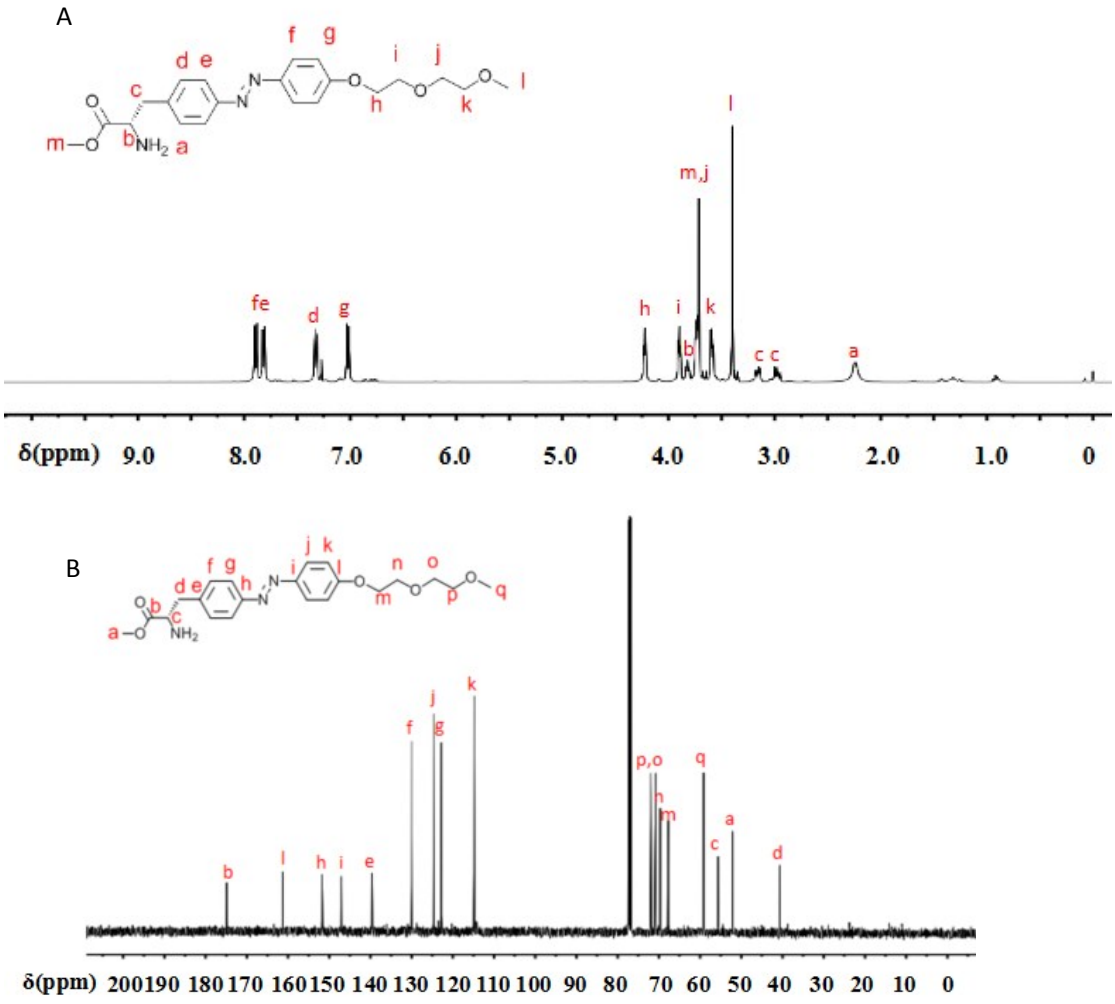


Figure S2. ^{1}H NMR (**A**), ^{13}C NMR (**B**), and ESI-MS(**C**) spectra of **3**.



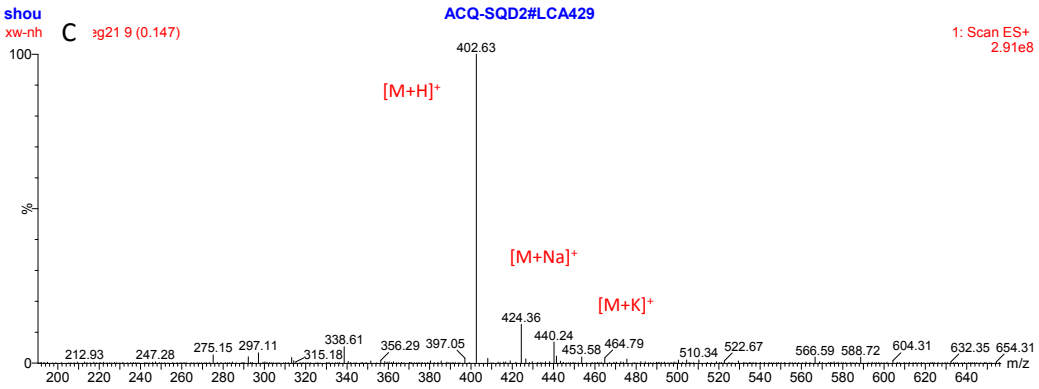


Figure S3. ^{1}H NMR (**A**), ^{13}C NMR (**B**), and ESI-MS (**C**) spectra of **4-2**.

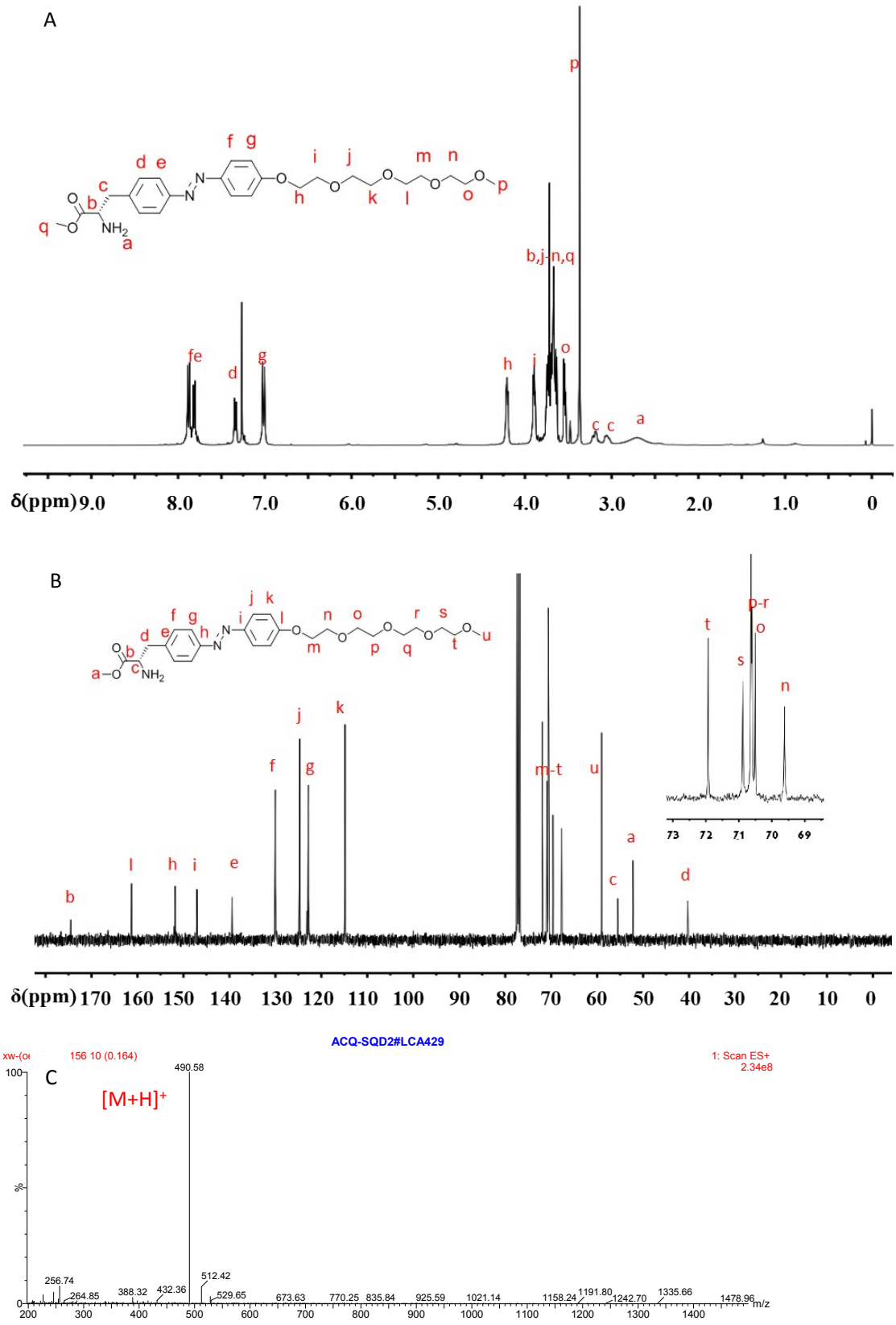


Figure S4. ^{1}H NMR (**A**), ^{13}C NMR (**B**), and ESI-MS (**C**) spectra of **4-4**.

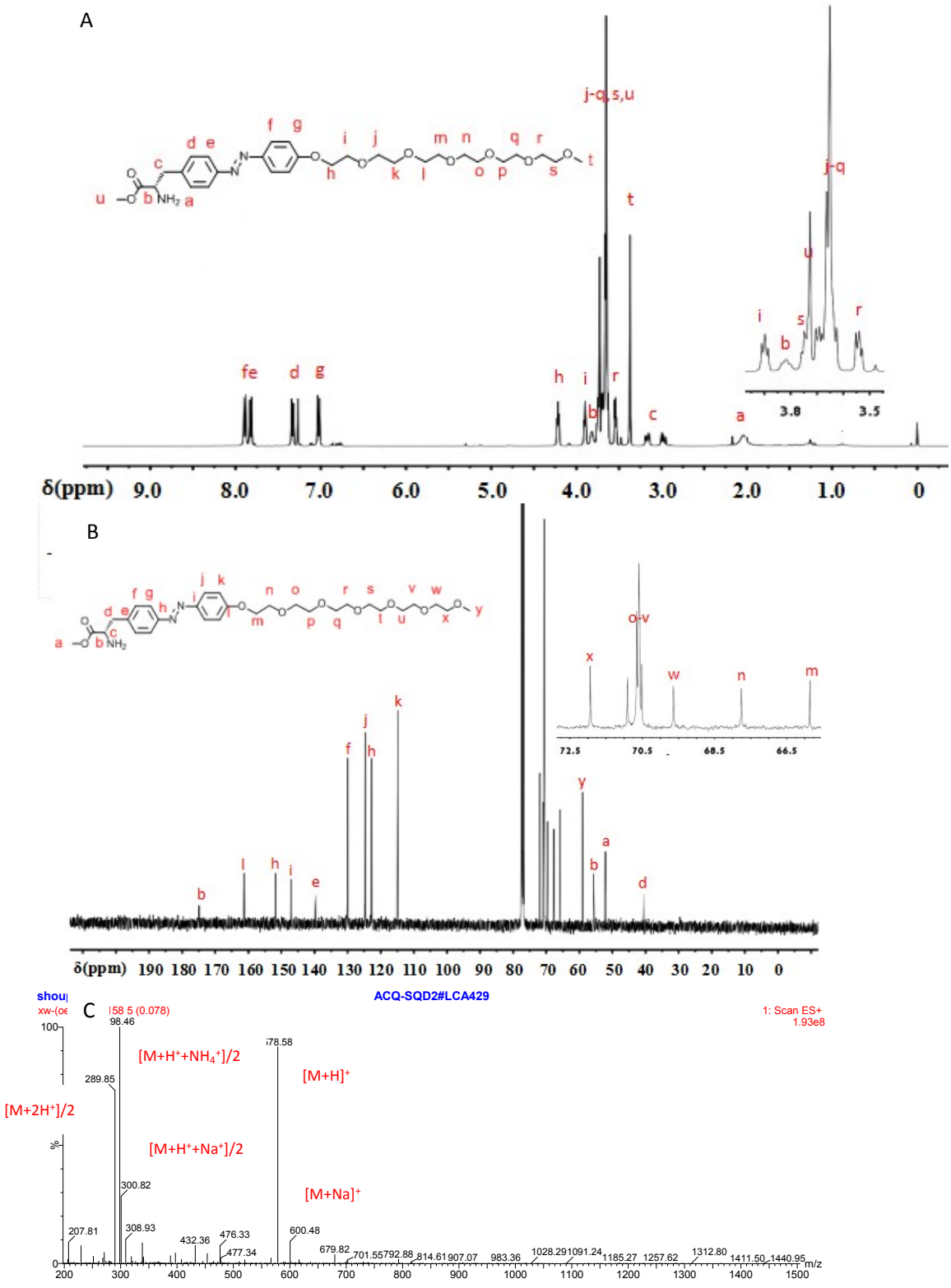


Figure S5. ^{1}H NMR (**A**), ^{13}C NMR (**B**), and ESI-MS (**C**) spectra of **4-6**.

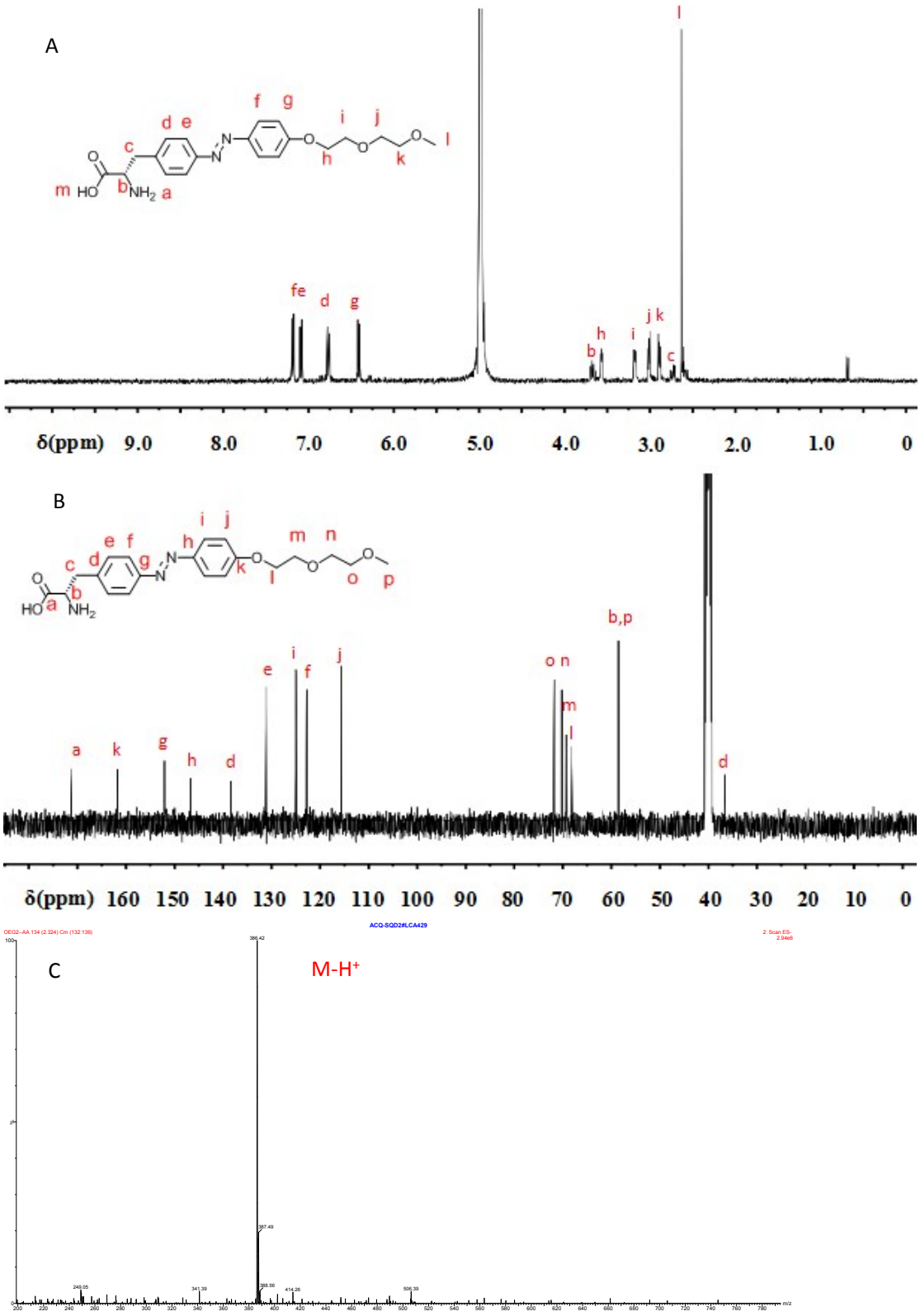


Figure S6. ^{1}H NMR (**A**), ^{13}C NMR (**B**), and ESI-MS (**C**) spectra of **5-2.**

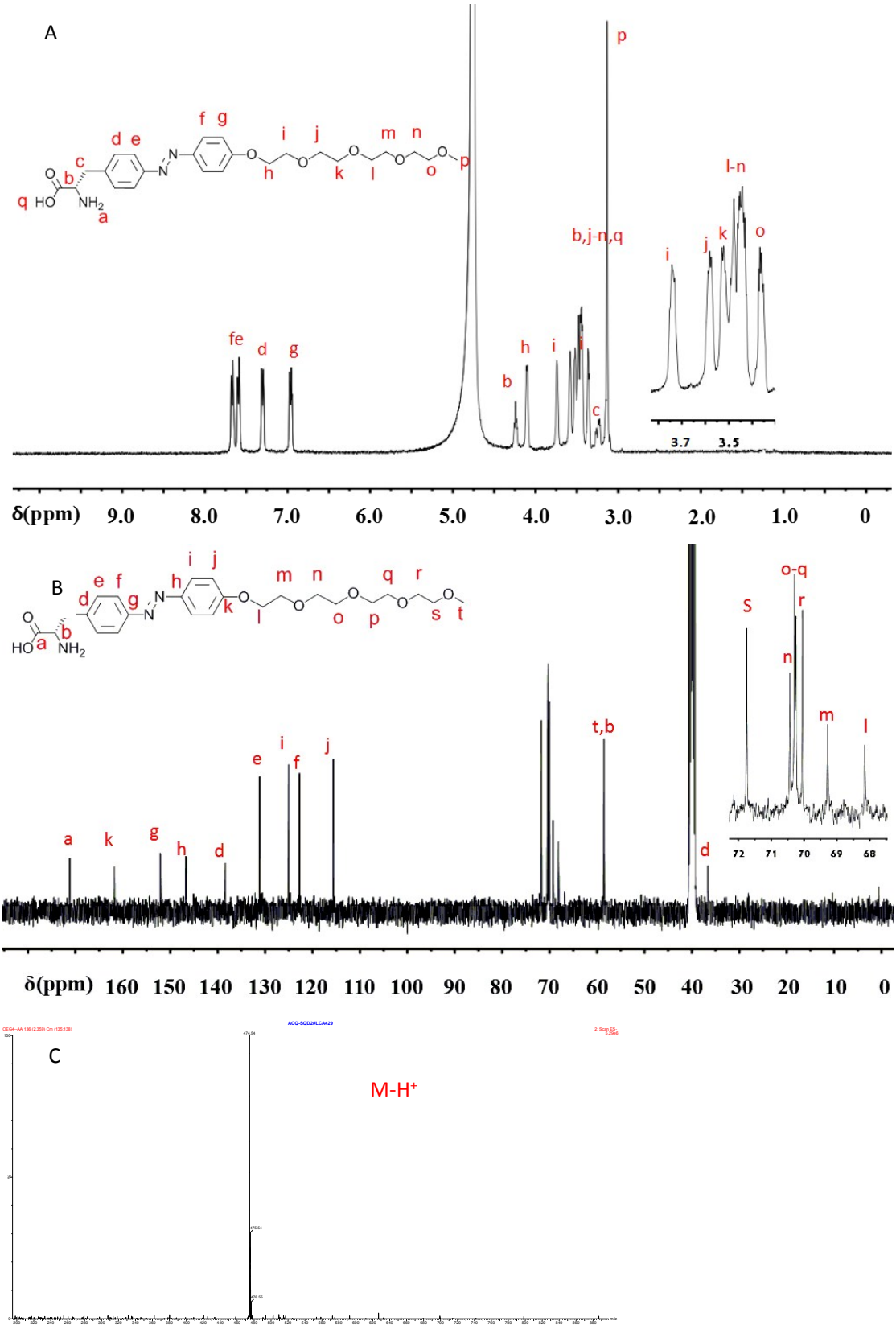


Figure S7. ^{1}H NMR (**A**), ^{13}C NMR (**B**), and ESI-MS (**C**) spectra of **5-4.**

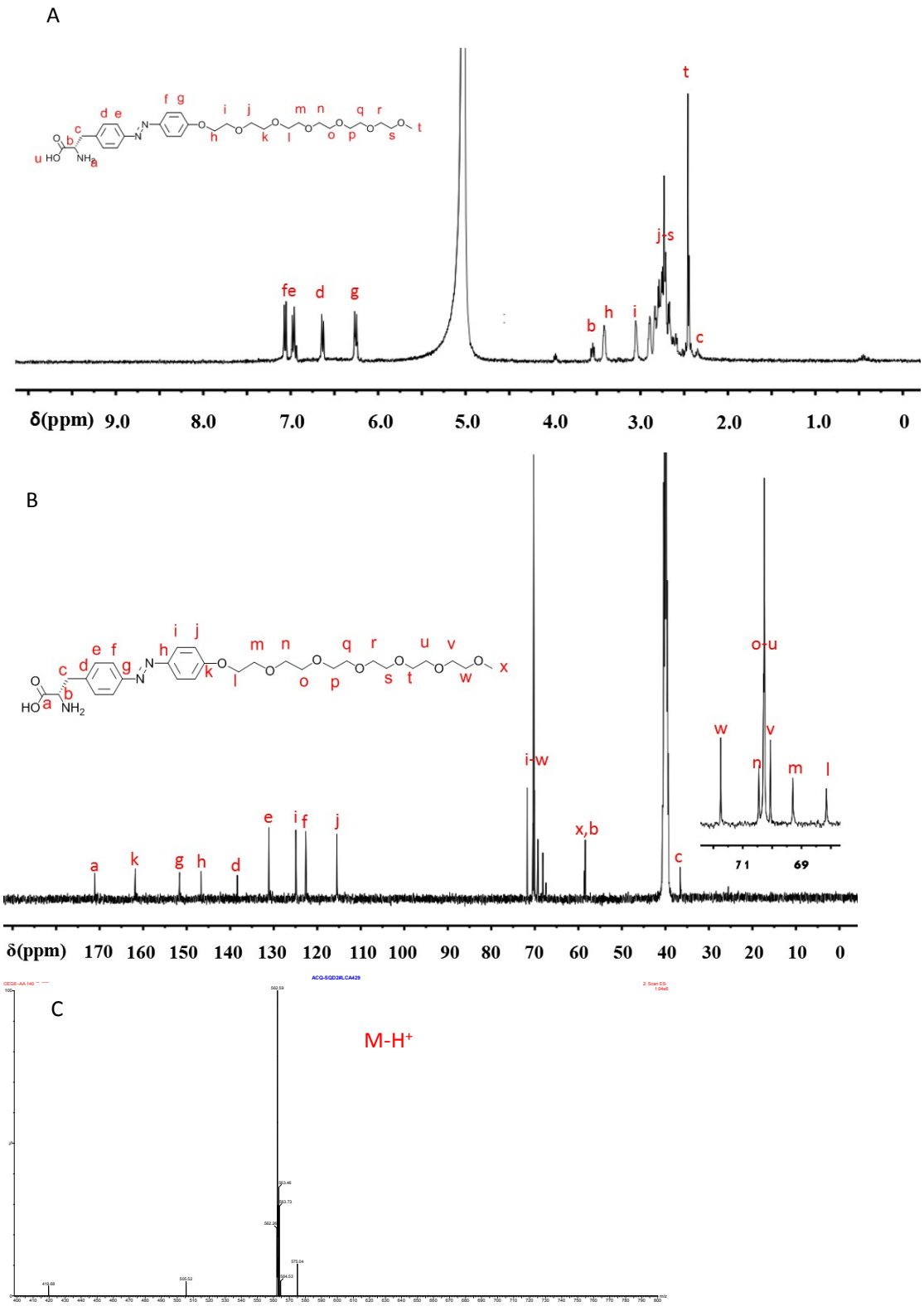
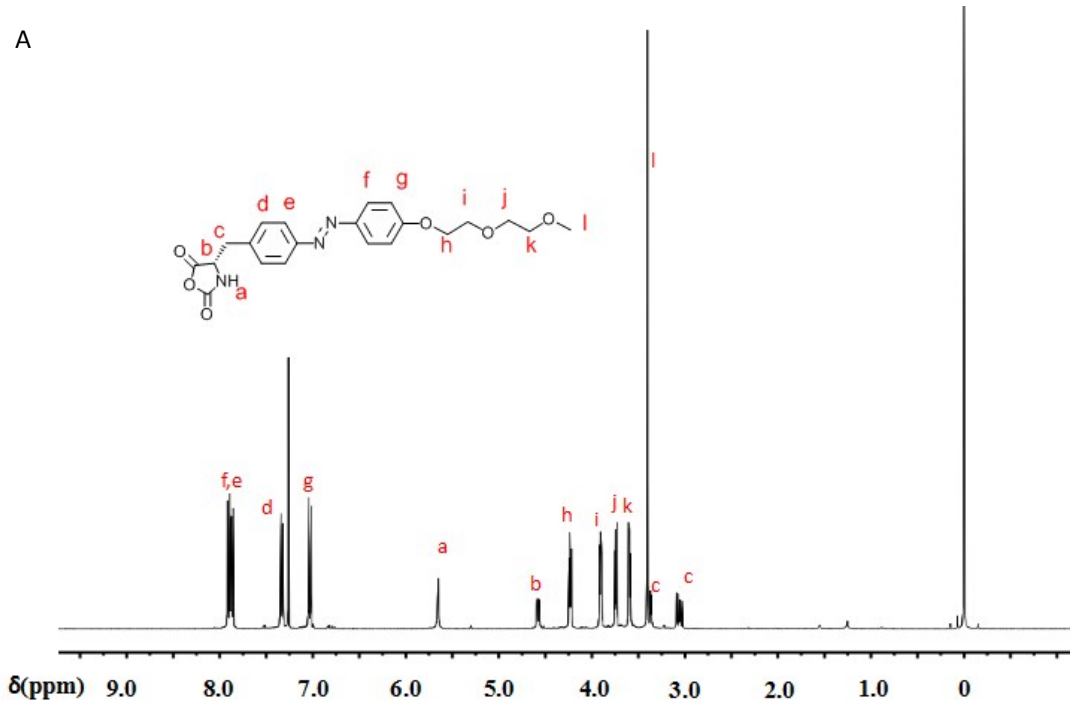
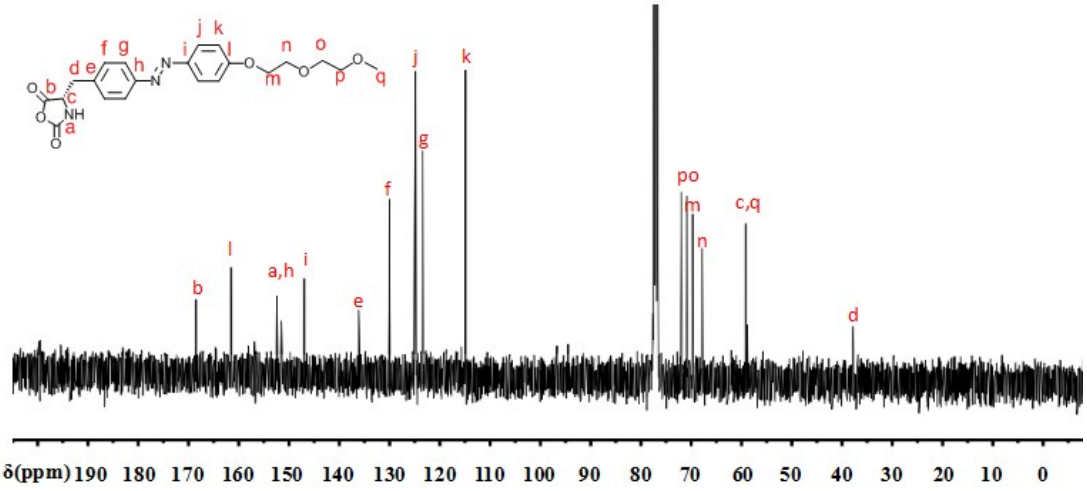


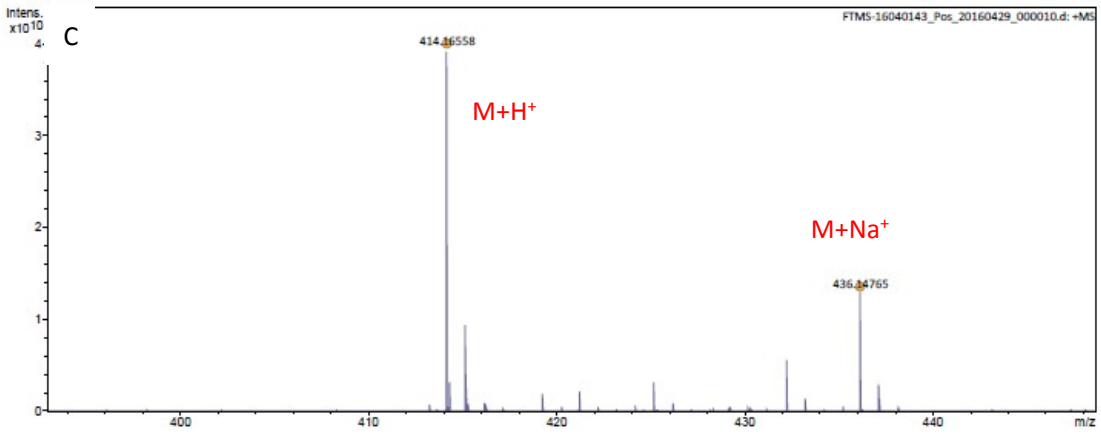
Figure S8. ^{1}H NMR (**A**), ^{13}C NMR (**B**), and ESI-MS (**C**) spectra of **5-6.**

A


f g
d e
i j
l
c
b
h
k
NH
a
f,e
d
g
a
h
i
j k
b
c
c
δ(ppm) 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

B


j k
f g
i
l
n o
d e
h
m
p
q
b
c
NH
a
j
k
g
f
po
m
c,q
n
l
a,h
i
b
e
d
δ(ppm) 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



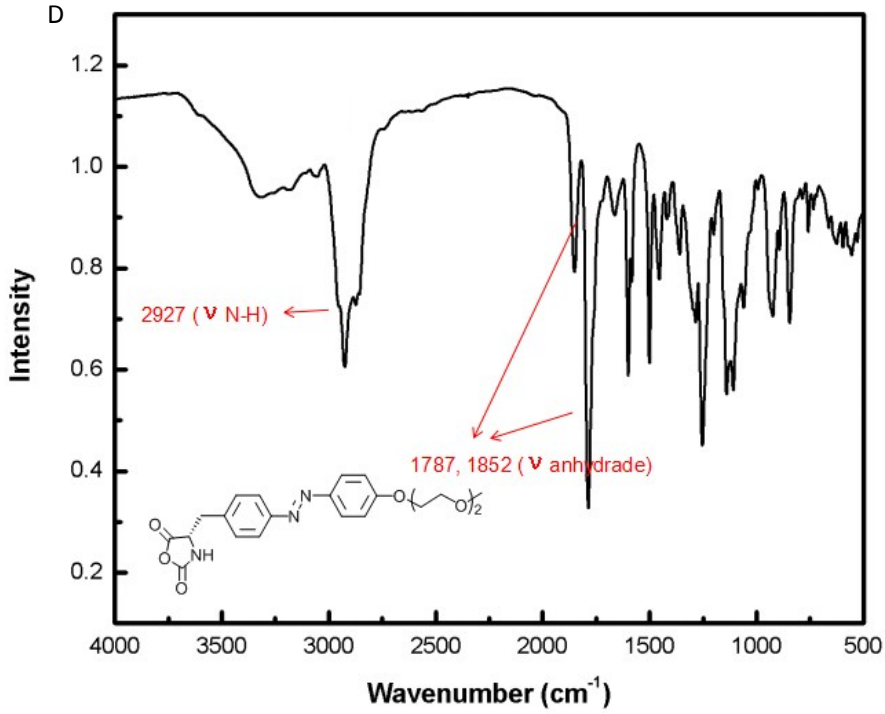
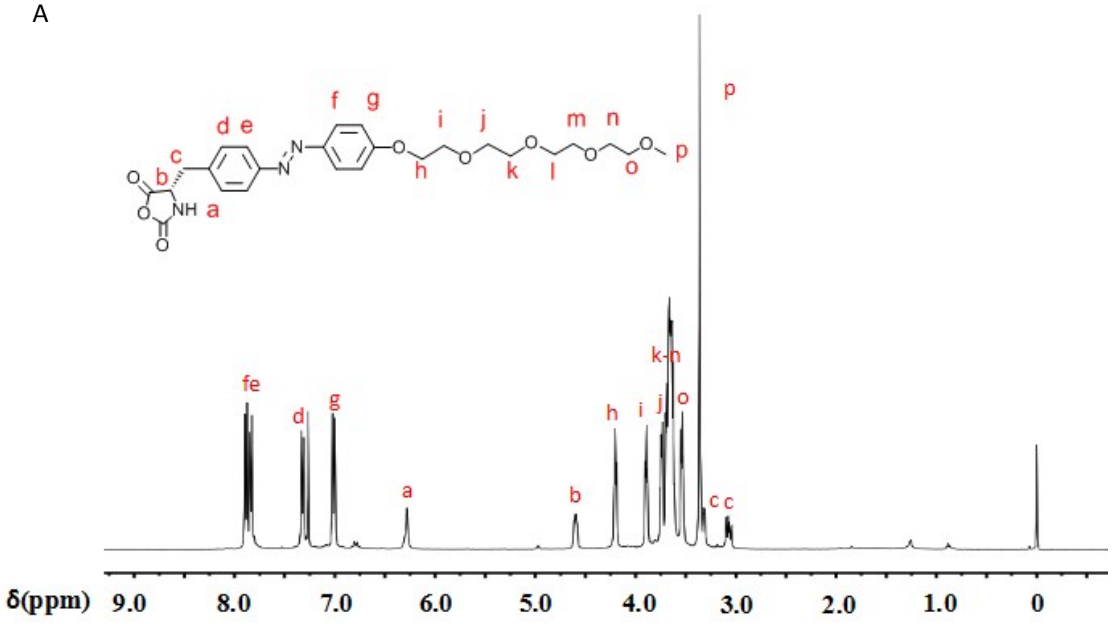
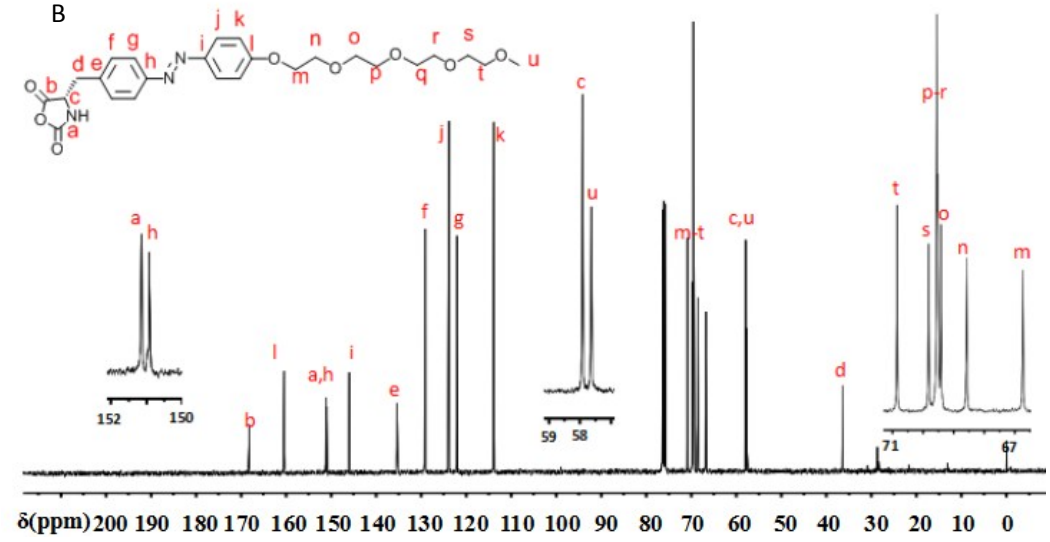


Figure S9. ^{1}H NMR (**A**), ^{13}C NMR (**B**), ESI-MS (**C**) and FT-IR (**D**) spectra of OEG_2-AzoNCA**.**

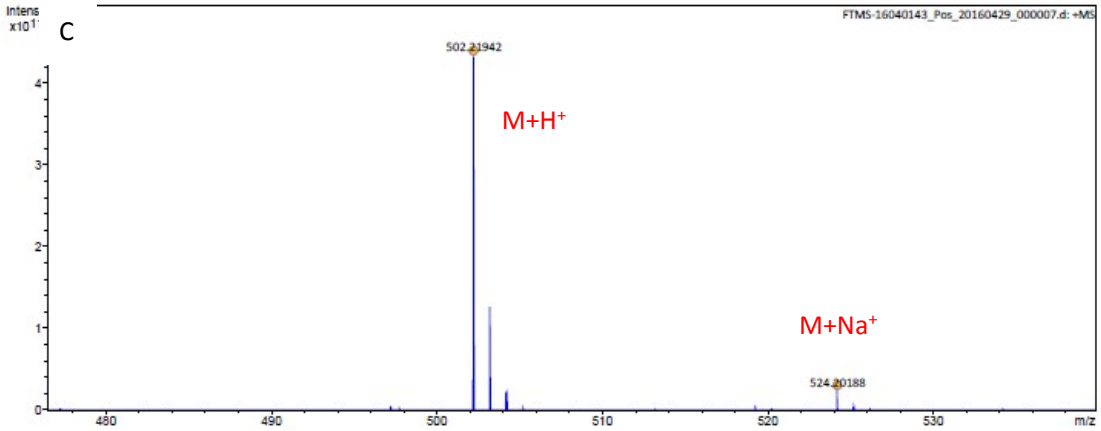
A


δ(ppm) 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

B


δ(ppm) 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

C


FTMS-16040143_Pos_20160429_000007.d: +MS
502.21942
M+H+
M+Na+
524.20188
m/z

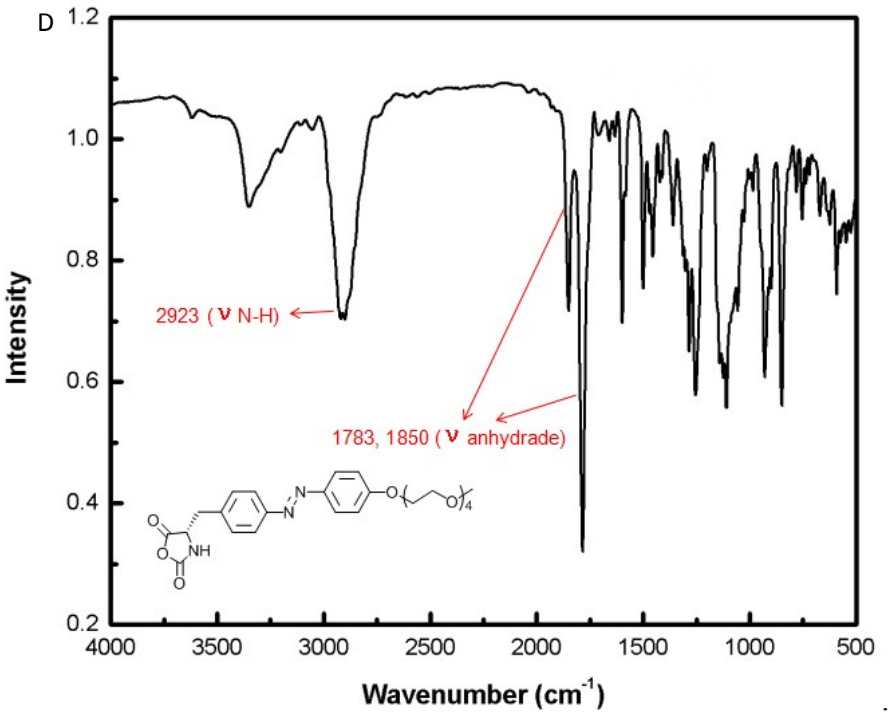
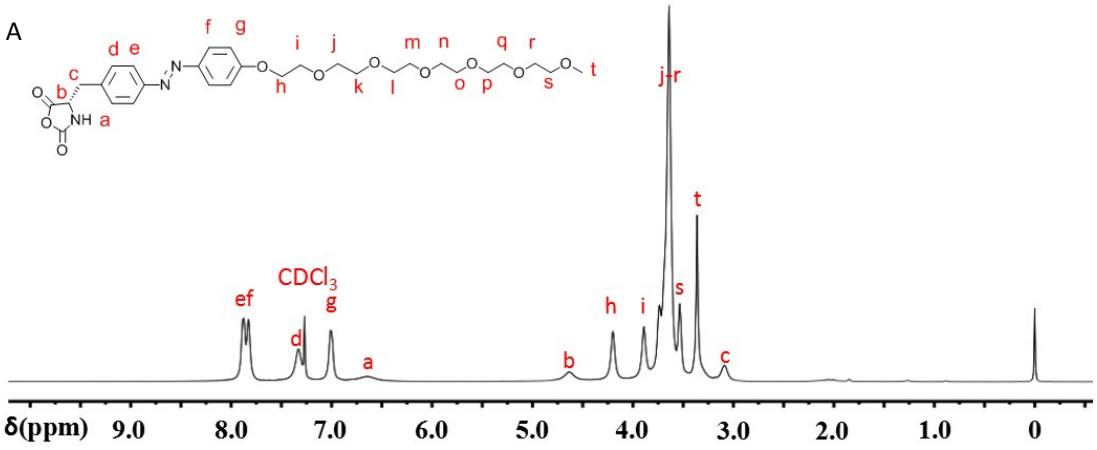
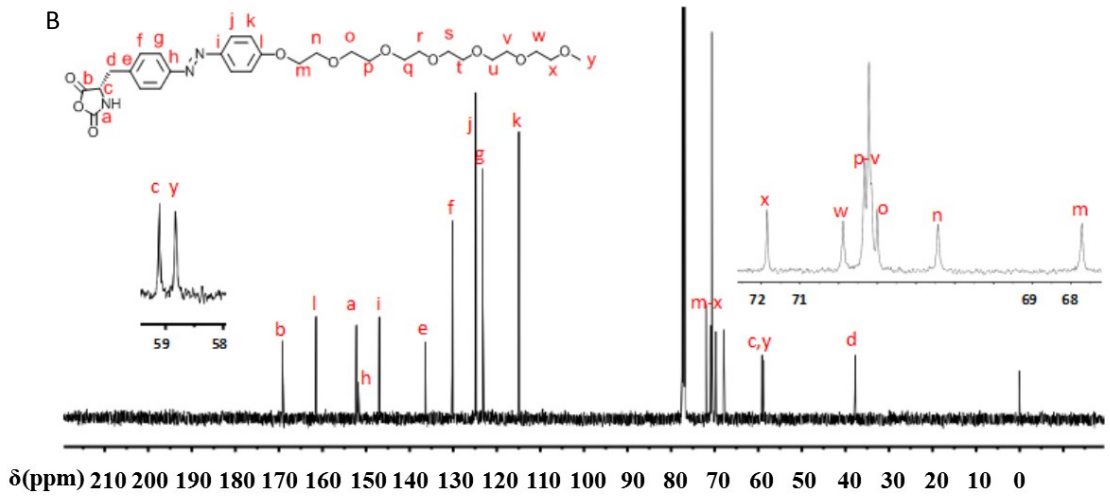
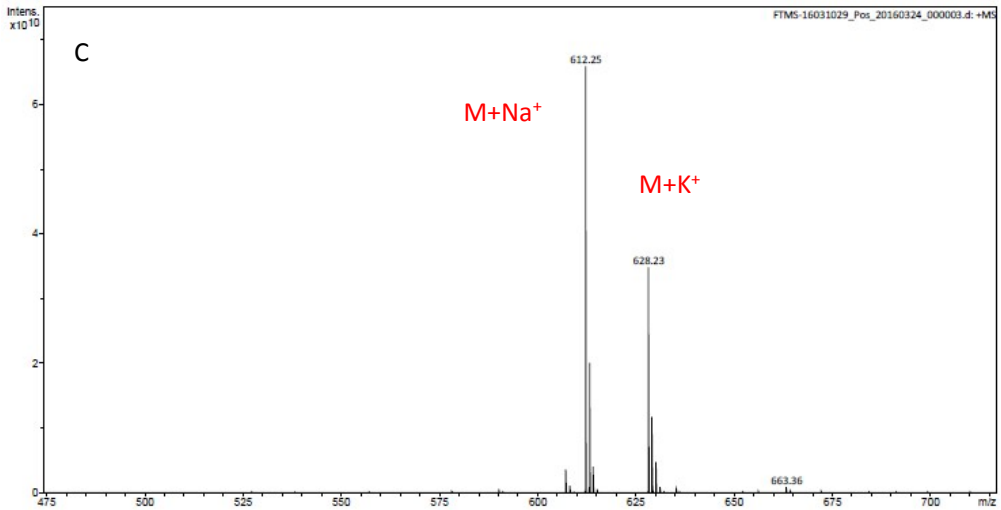


Figure S10. ^{1}H (**A**), ^{13}C (**B**) NMR in $CDCl_3$, ESI-MS (**C**) and FT-IR (**D**) spectra of OEG_4-AzoNCA.


A
CDCl3
δ(ppm) 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0


B
δ(ppm) 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


C
FTMS-16031029_Pos_20160324_000003.d: +MS
612.25
M+Na+
M+K+
628.23
663.36
m/z

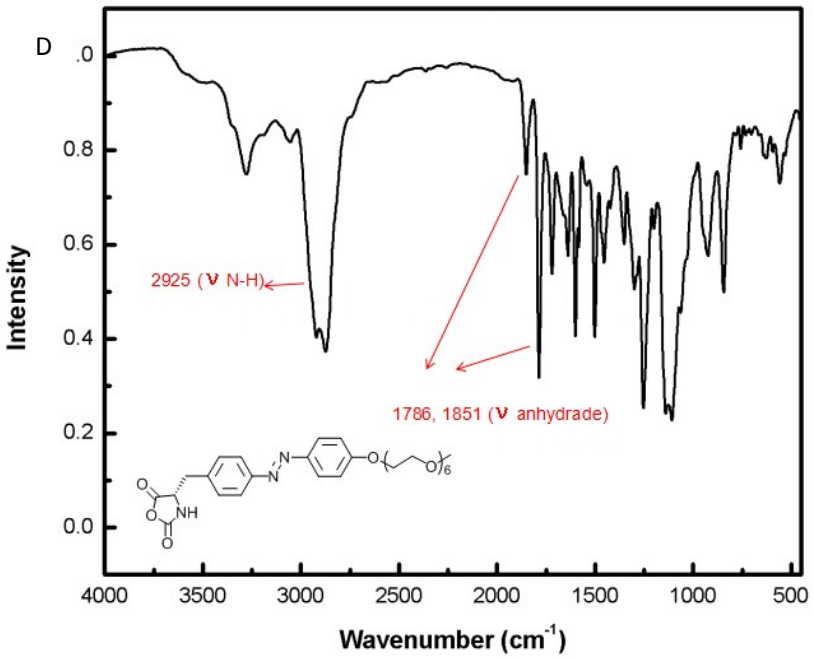


Figure S11. ^{1}H (**A**), ^{13}C (**B**) NMR in $CDCl_3$, ESI-MS (**C**) and FT-IR (D) spectra of OEG_6-AzoNCA.

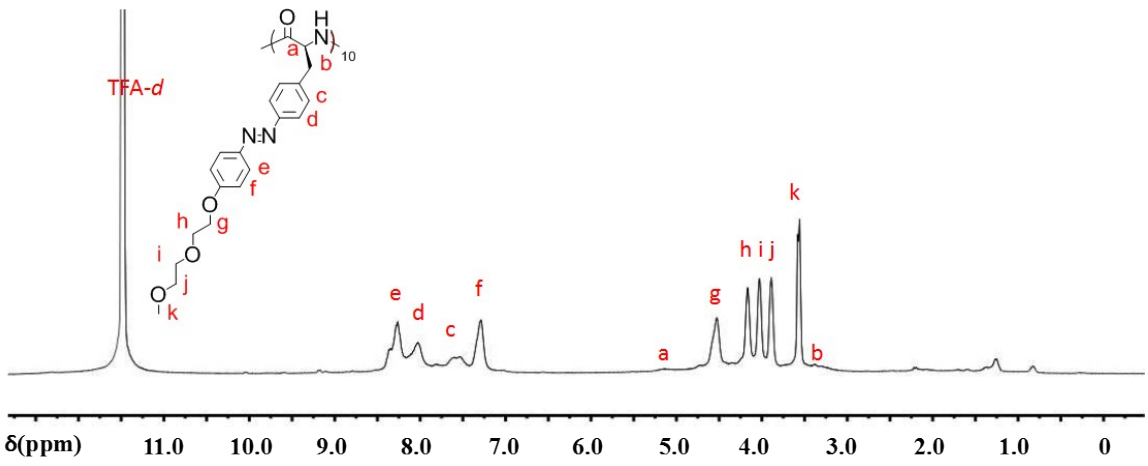


Figure S12. ^{1}H NMR of P(OEG$_2$-Azo)$_{10}$ in TFA-*d*.

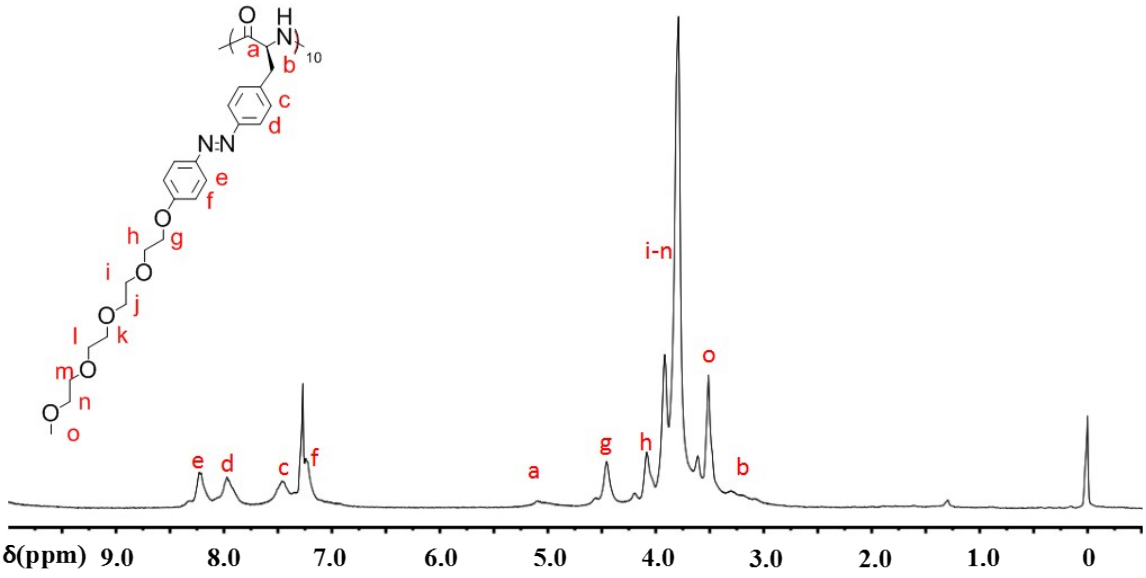


Figure S13. ^{1}H NMR of P(OEG$_4$-Azo)$_{10}$ in $CDCl_3$ /TFA-*d*.DCl_3.

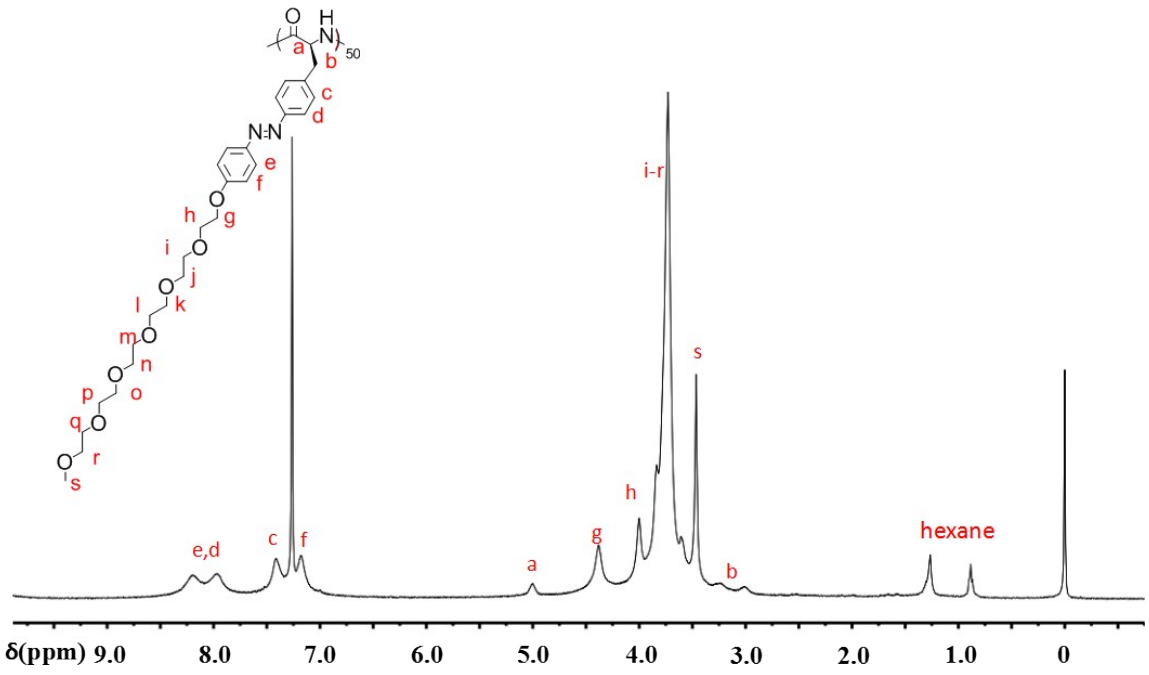


Figure S14. ^{1}H NMR of P(OEG$_6$-Azo)$_{10}$ in $CDCl_3$ /TFA-*d*.

Table S1. Sizes and PDIs of $P(OEG_m\text{-}Azo)_n$s in ethanol and water as measured by DLS.

		$P(OEG_2\text{-}Azo)_{10}$	$P(OEG_2\text{-}Azo)_{50}$	$P(OEG_4\text{-}Azo)_{10}$	$P(OEG_4\text{-}Azo)_{50}$	$P(OEG_6\text{-}Azo)_{50}$
Ethanol	**Size** **PDI**	244.13 nm 0.329	675.95 nm 0.323	206.18 nm 0.335	240.19 nm 0.475	174.84 nm 0.306
Water	**Size** **PDI**	insoluble	insoluble	insoluble	insoluble	209.17 nm 0.359

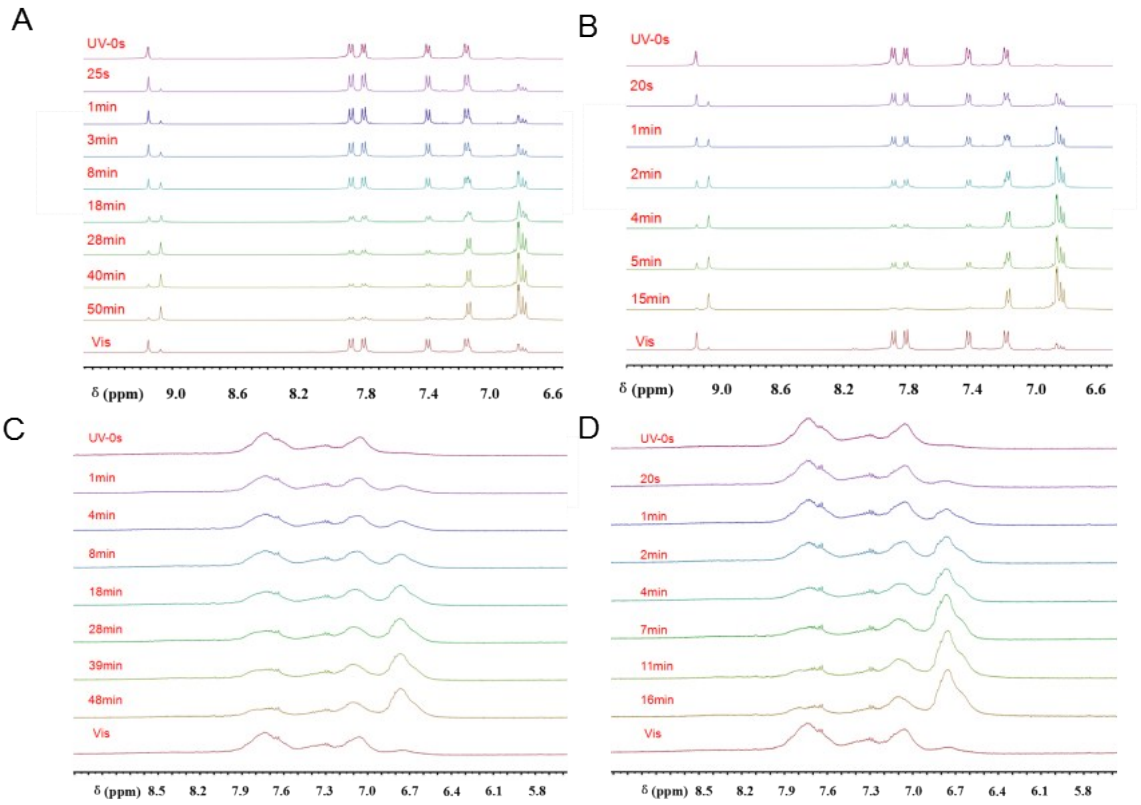


Figure S15. Photo reversibility of OEG_6-AzoNCA and $P(OEG_6Azo)_{10}$ as determined by ^1H NMR in DMSO-d_6.

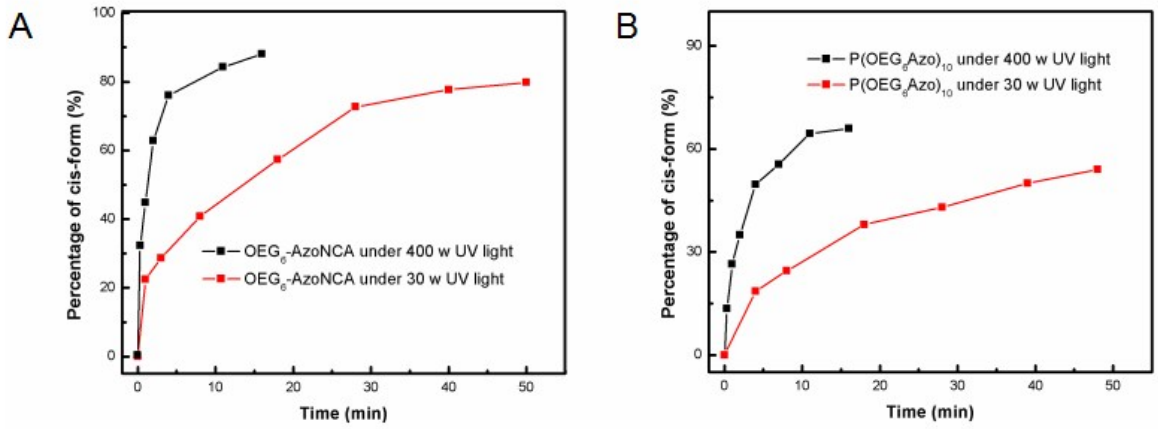


Figure S16. Plot of UV-triggered *trans-cis* isomerization of OEG_6-AzoNCA (**A**) and $P(OEG_6Azo)_{10}$ (**B**) at two different lamp powers.

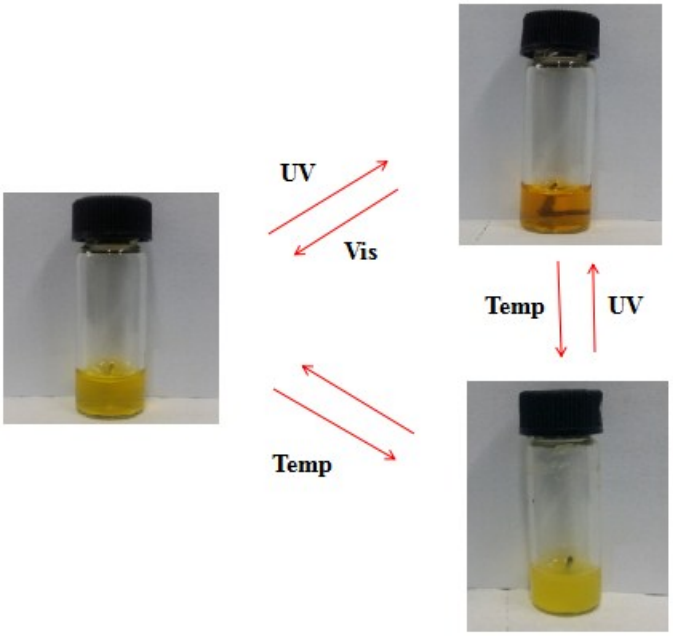


Figure S17. Photographs of 2.5 mg/mL P(OEG_6-Azo)$_{50}$ aqueous solutions under various environmental conditions.

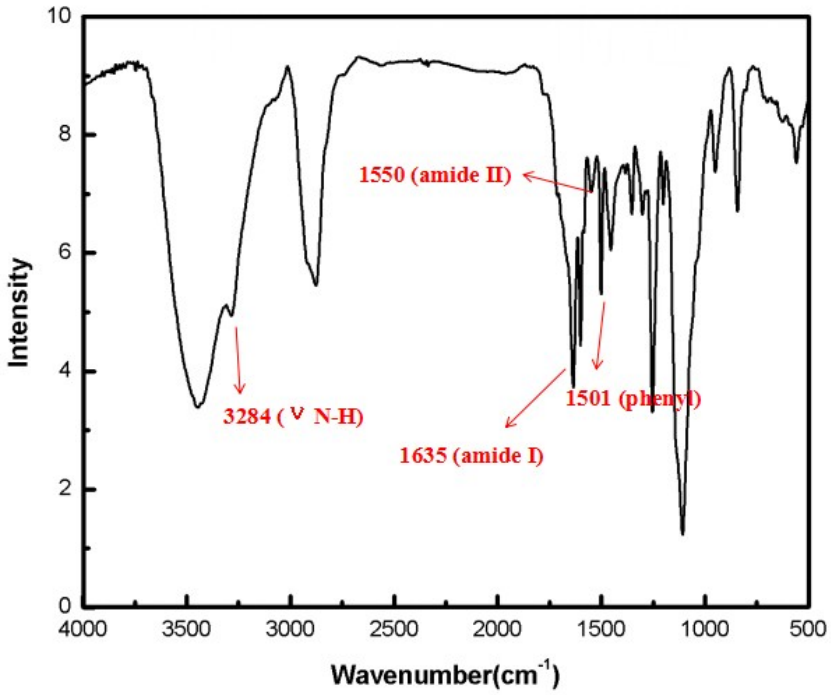


Figure S18. FT-IR spectrum of $P(OEG_2\text{-}Azo)_{10}$ in DCM.

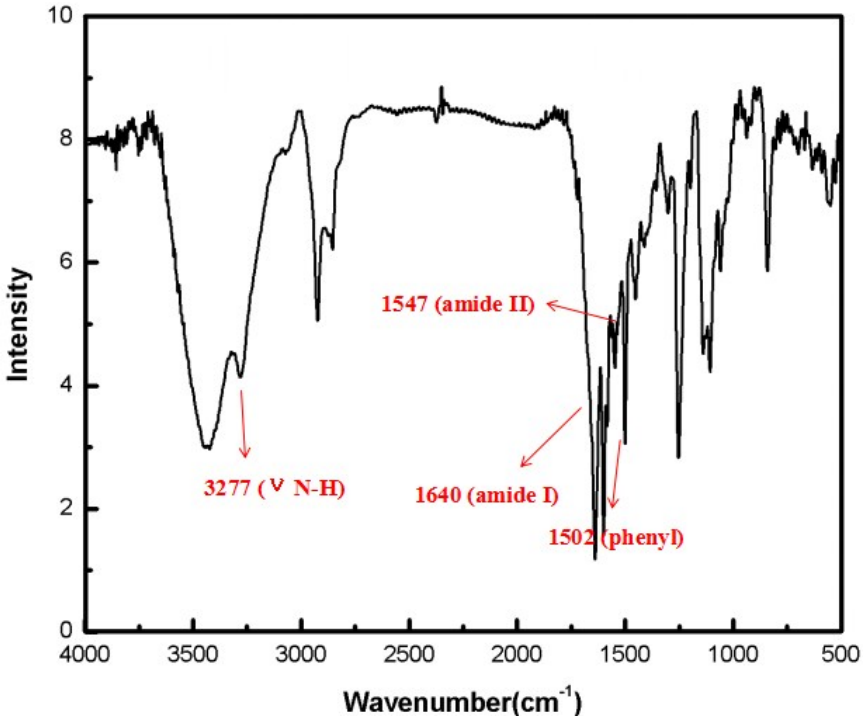


Figure S19. FT-IR spectrum of $P(OEG_2\text{-}Azo)_{50}$ in DCM.

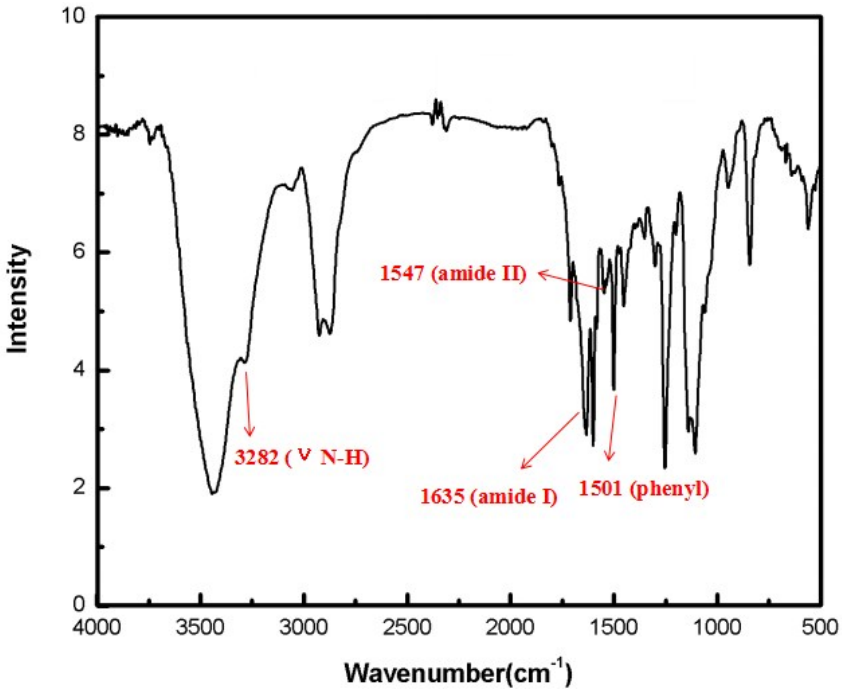


Figure S20. FT-IR spectrum of $P(OEG_4\text{-}Azo)_{10}$ in DCM.

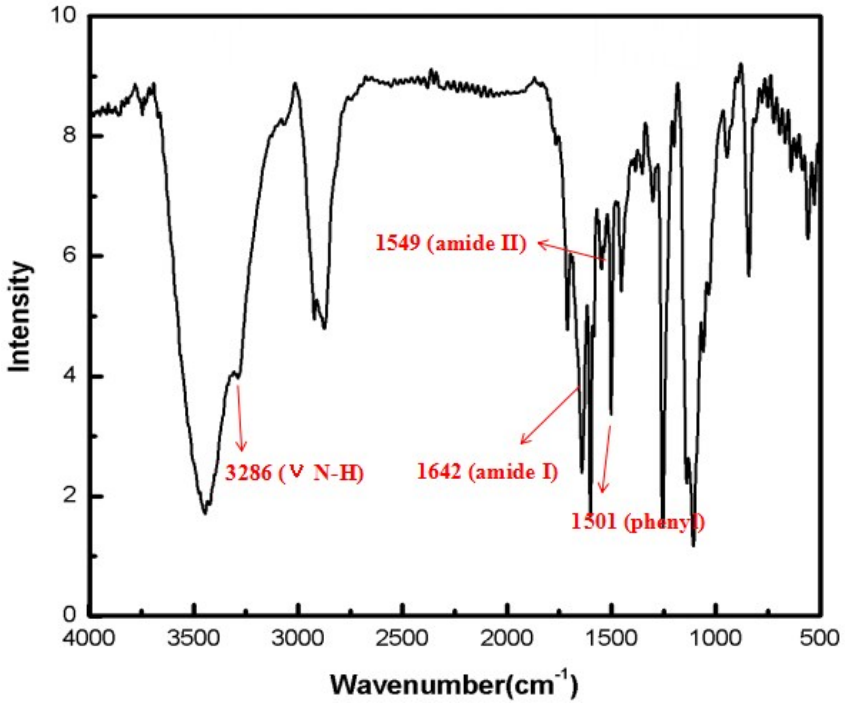


Figure S21. FT-IR spectrum of $P(OEG_4\text{-}Azo)_{50}$ in DCM.

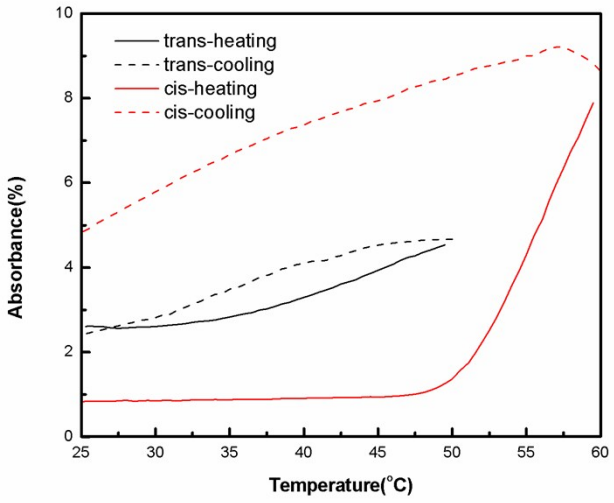


Figure S22. Temperature dependence of the transmittance at 500 nm of 0.2 mg/mL *trans*- and *cis*-P(OEG$_6$-Azo)$_{50}$ aqueous solutions before and after UV irradiation.

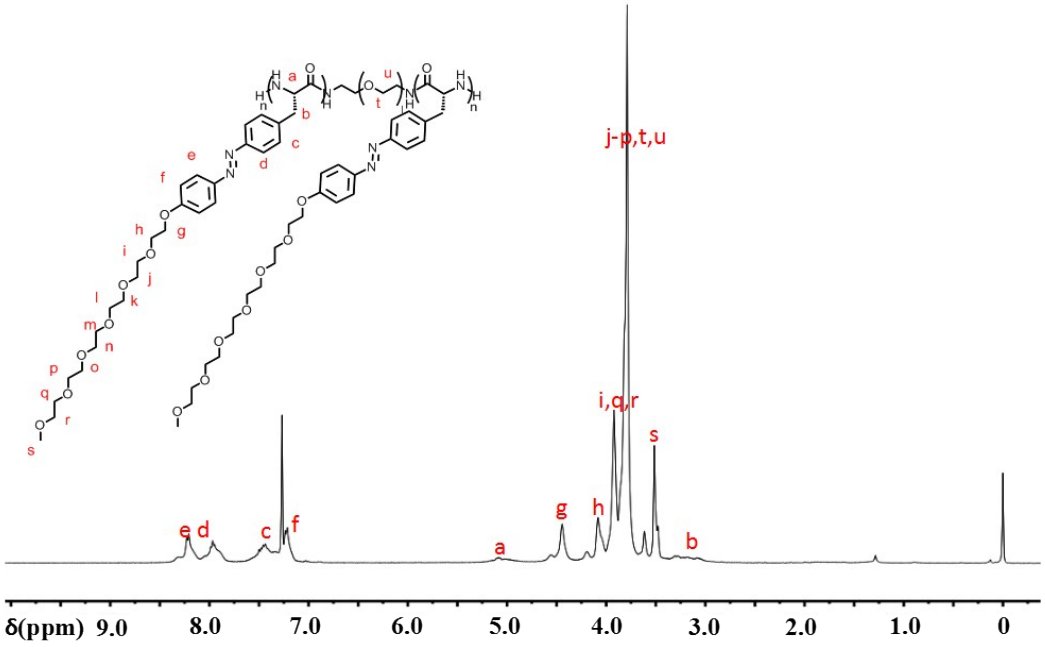


Figure S23. ^{1}H NMR of P(OEG$_6$-Azo)$_7$-PEG-P(OEG$_6$-Azo)$_7$ in $CDCl_3$/TFA-*d*.

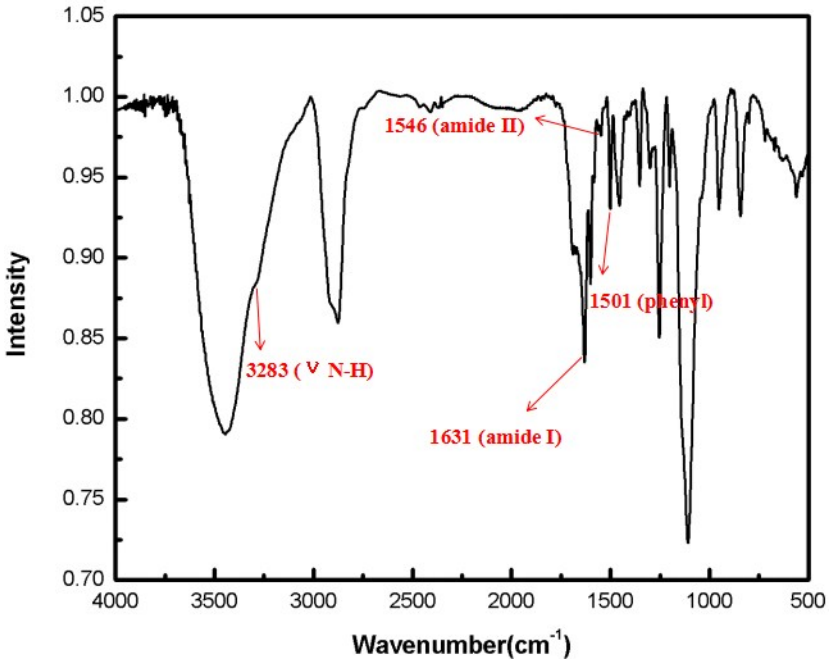


Figure S24. FT-IR spectrum of $P(OEG_6\text{-}Azo)_7$ -PEG-$P(OEG_6\text{-}Azo)_7$.

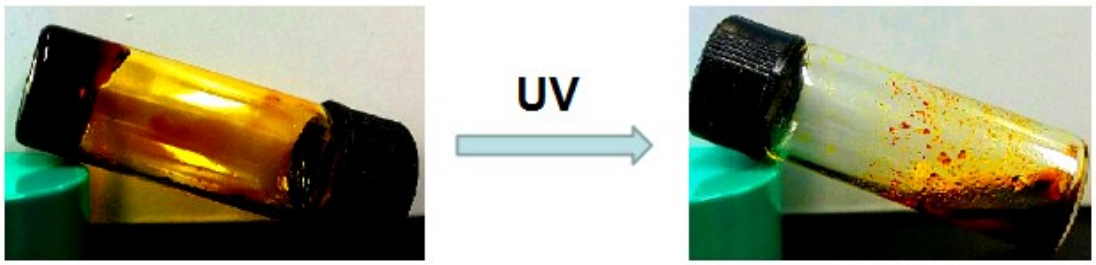


Figure S25. UV induced gel-sol transition of $P(OEG_4\text{-}Azo)_{10}$-PEG-$P(OEG_4\text{-}Azo)_{10}$ in THF.