Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Carboxylic Azo Monomer and its Homopolymer: Synthesis, Self-organization and Fluorescence Behavior in Solution

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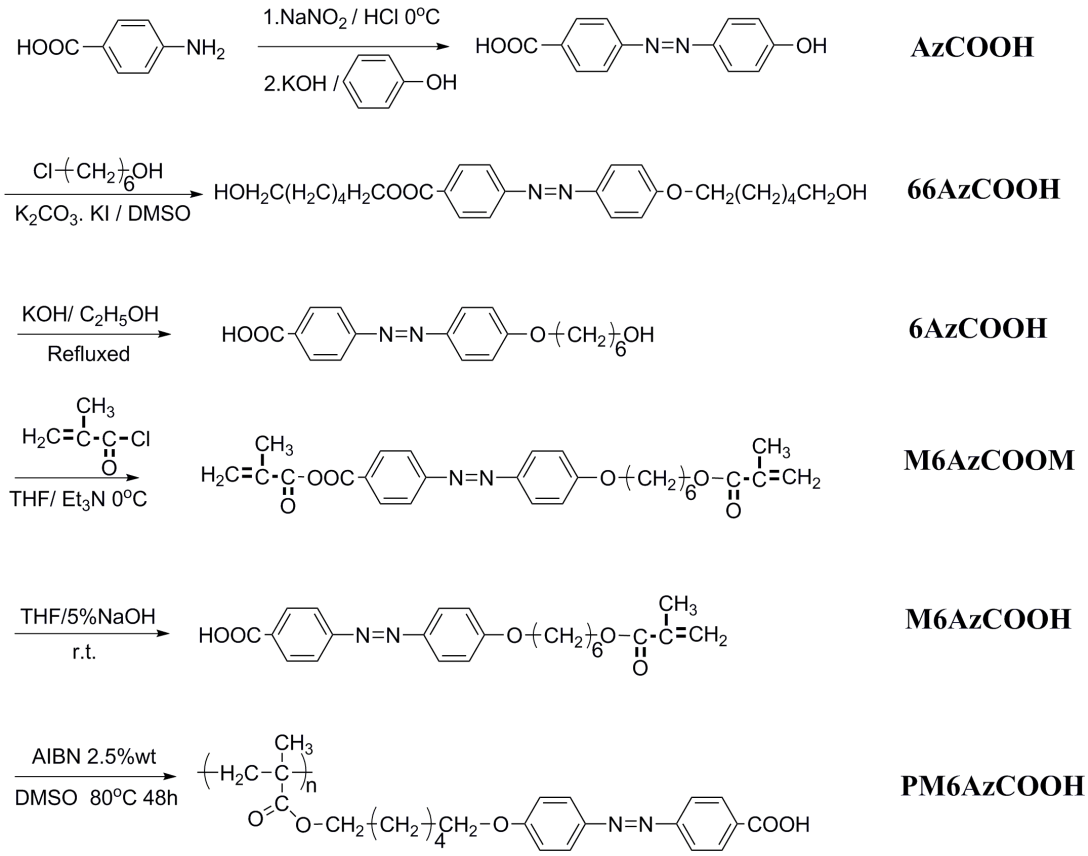
1. Synthesis of M6AzCOOH and PM6AzCOOH

The synthetic route for the monomer M6AzCOOH and the homopolymer PM6AzCOOH is given in Scheme 1.



Scheme S1. Synthetic route for M6AzCOOH and PM6AzCOOH.

4-[(4'-Hydroxy)phenylazo]benzoic acid (AzCOOH)

A solution of $NaNO_2$ (4.14 g, 60 mmol) in 60 cm^3 H_2O was added to a solution of 4-aminobenzoic acid (8.23 g, 60 mmol) in 24 cm^3 HCl (37 %) at 0 °C. The mixed solution was stirred for 30 min and diluted with 300 cm^3 ice water. Then phenol (5.92 g, 63 mmol) and NaOH (2.52 g, 63 mmol) in 30 cm^3 of H_2O was added dropwise at 0-5 °C. The mixture was stirred for 2 h and NaOH was added to precipitate the product. 15.0 g Orange product was obtained with a yield of 95%. ^{1}H NMR (DMSO-

6d,400MHz):δ_H(ppm)=7.98(d,*J*=8.0Hz,2H),7.78(d,*J*=8.0Hz,2H),7.69(d,*J*=8.0Hz,2H), 6.94(d,*J*=8.0Hz,2H).

4-(6-Hydroxyhexyloxy)carboxy-4'-(6'-hydroxyhexyloxy) azobenzene (66 AzCOOH)

A mixture of AzCOOH (3.63 g, 15 mmol), 6-chloro-1-hexanol (4.37 g, 32 mmol), K_2CO_3 (4.42 g, 32 mmol), KI (0.2 g), and dry dimethylsulfoxide (DMSO) (50 cm^3) was heated at 140 °C for 8 h. Then reaction mixture was cooled to room temperature and poured into water (200 cm^3). The obtained red-yellow precipitate was filtered off and dried under vacuum at 50 °C to get 5.3 g red orange solids (yield: 80 %).^{1}H NMR (DMSO-6d,400MHz):δ_H(ppm)=8.14(d,*J*=8.0Hz,2H),7.94(d,*J*=1.6Hz,2H),7.92(d,*J*=2.0Hz,2H), 7.15(d,*J*=8.4Hz,2H),4.30(t,*J*=6.4,2H),4.09(t,*J*=6.2,2H),3.40(t,*J*=6.12,4H),1.70-1.80(m,4H),1.26-1.55(m,12H).

4-[4'-(6-Hydroxyhexyloxy)phenylazo]benzoic acid (6AzCOOH)

A mixture of 66AzCOOH (6.63 g, 15 mmol), KOH (1.68 g, 30 mmol), C_2H_5OH 225 cm^3, and H_2O 60 cm^3 was refluxed for 12 h. Then the reaction mixture was cooled down to room temperature, the obtained yellow crystals was filtered off washed with C_2H_5OH, and dried under vacuum at 50 °C to yield 4.06 g red orange solids (80 %). ^{1}H NMR (DMSO-6d): δ_H(ppm)= 8.12 (d, *J*=8.2Hz,2H), 7.93 (d,*J*=5.6, 2H), 7.91 (d, *J*=4.8,2H), 7.14 (d,*J*=8.0,2H), 4.09 (t,*J*=6.4,2H) 3.42 (t, *J*=6.4,2H), 1.70–1.85 (m, 2H),1.27–1.57 (m, 6H).

6-[4-(4- methacrylic carboxyl anhydride phenylazo)phenoxyl]hexyl methacrylate (M6AzCOOM)

M6AzCOOM was prepared by methacryloyl chloride and 6AzCOOH. 6AzCOOH (5.13 g, 15 mmol) and triethylamine (5.06 g, 50 mmol) were dissolved in dry tetrahydrofuran (THF) (50 cm^3), and cooled in an ice-water bath. A solution of methacryloyl chloride (5.23 g, 50 mmol) in dry THF (15 cm^3) was added over 2 hours, and the mixture was stirred for 48 hours. After filtration, the mixture was concentrated and then poured into methanol; yellow precipitate 3.1 g yellow solid was obtained (50 %).^{1}H NMR (DMSO-6d): δ_H(ppm)=8.24(d,*J*=8.8,2H), 7.99(d,*J*=8.4,2H),7.95(d,*J*=8.8,2H),7.16(d,*J*=8.8,2H),6.41(s,1H),6.11(s,1H), 6.02(s,1H),5.66(s,1H),4.11(t,*J*=6.4,4H),2.02(s,3H),1.87(s,3H),1.77(m,2H), 1.65(m,2H),1.36-1.55(m,4H).

6-[4-(4-carboxyl phenylazo)phenoxyl]hexyl methacrylate (M6AzCOOH)

M6AzCOOM(3.1g) was dissolved in tetrahydrofuran THF(50 cm^3), using 5% NaOHaq solution to adjust pH=7, after stirring for 24 hours, the pH was adjusted to pH=3-5 by 1 mol/L HCl solution. The obtained yellow solid was filtered off washed with distilled water until a neutral aqueous solution was obtained. The product was obtained in a 80% yield. ^{1}H NMR (DMSO-6d): δ_H(ppm)=8.12(d,*J*=8.8,2H), 7.93(d,*J*=5.6,2H),7.91(d,*J*=4.8,2H),7.14(d,*J*=9.2,2H),6.02(s,1H),5.66(t,*J*=1.2,1H),4.12(m,4H), 1.87(s,3H), 1.77(m,2H), 1.65(m,2H),1.35-1.55(m,4H).

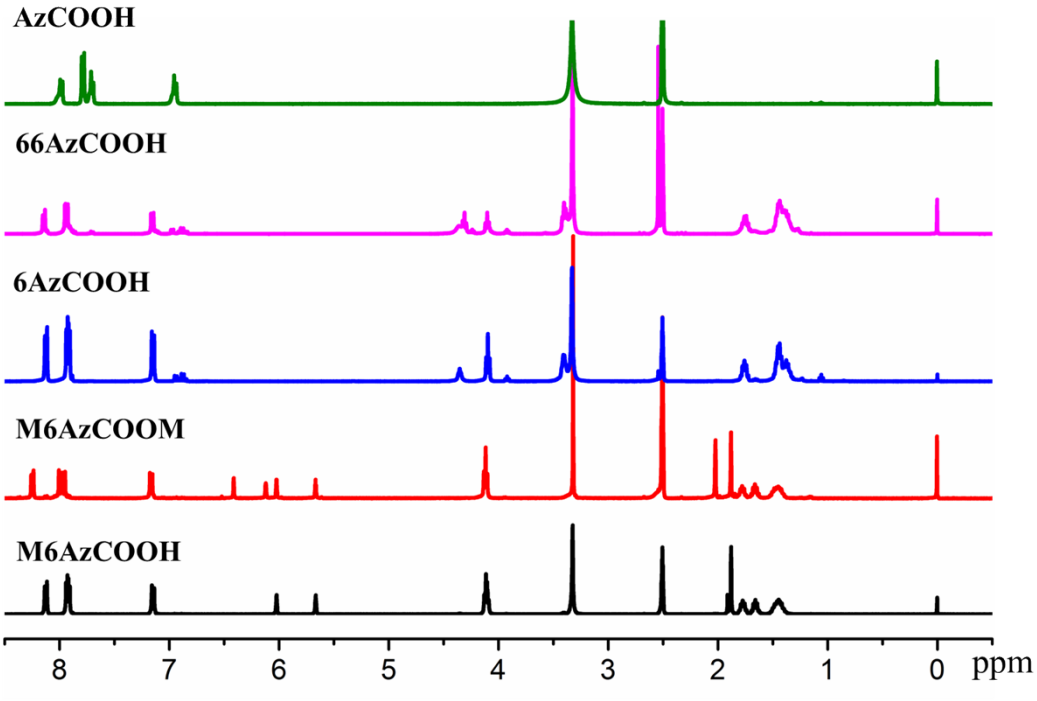


Fig. S1 ^{1}H NMR spectra of the monomer and intermediates.

Synthesis of PM6AzCOOH

The carboxylic azo polymer PM6AzCOOH was obtained by free radical polymerization of M6AzCOOH in DMSO, using AIBN (2.5 mol%) as initiator, the concentration of monomer was 0.6M. After degassing under vacuum and refilling with argon, the reaction mixture was placed in a pre-heated oil bath at 80 ^{o}C for 48 hours. The reaction mixture was precipitated with methanol. The obtained red solid was filtered off and washed with large amount of methanol. Yield 89%.

2. TEM image of M6AzCOOH in the water/DMF mixed solution

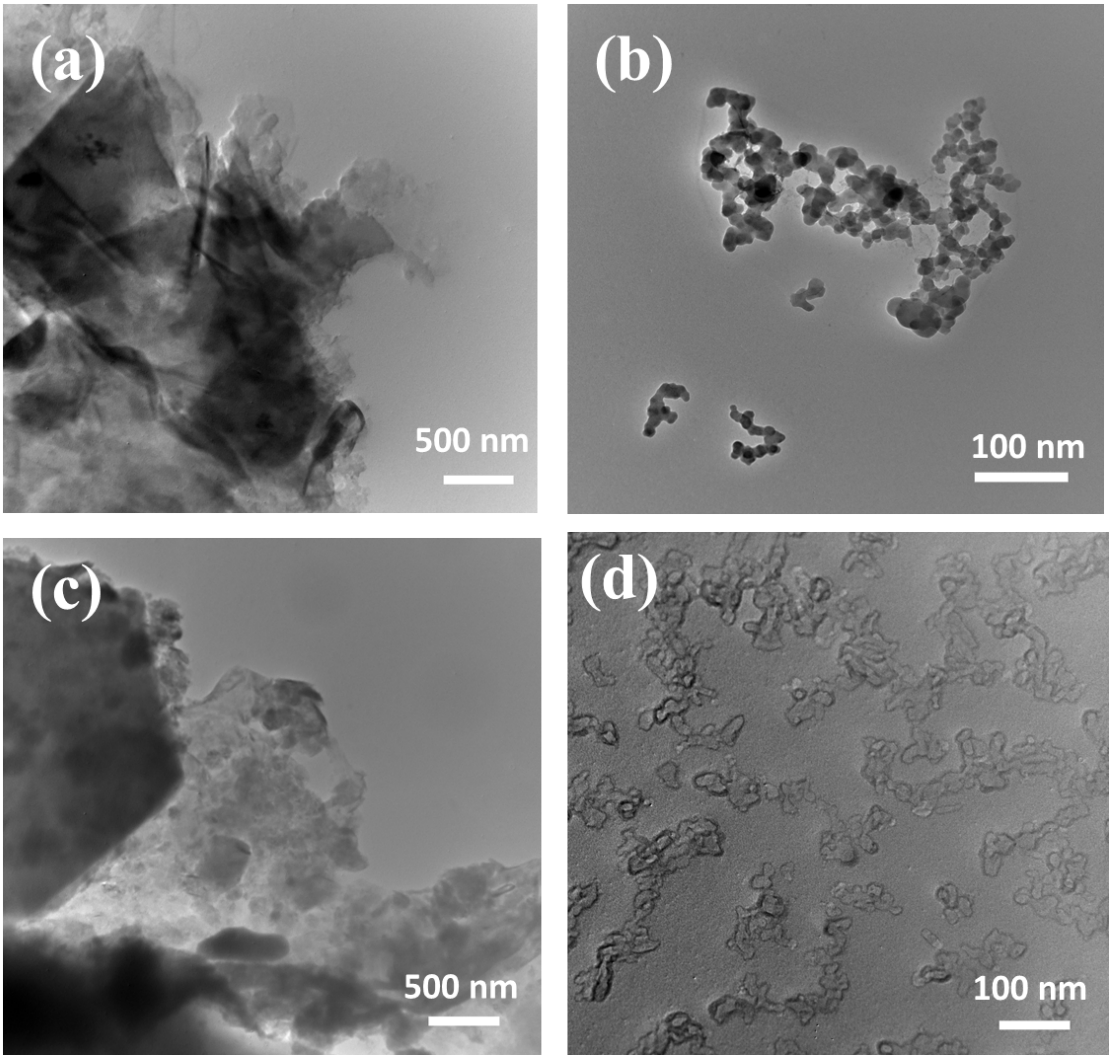


Fig. S2 TEM images of (a).M6AzCOOH/DMF(0.07g/L) ; (b). M6AzCOOH/DMF(0.07g/L)+200% H_2O ; (c). PM6AzCOOH/DMF(0.07g/L);(d). PM6AzCOOH/DMF(0.07g/L)+200% H_2O

3. Effect of pH value on fluorescence property of M6AzCOOH.

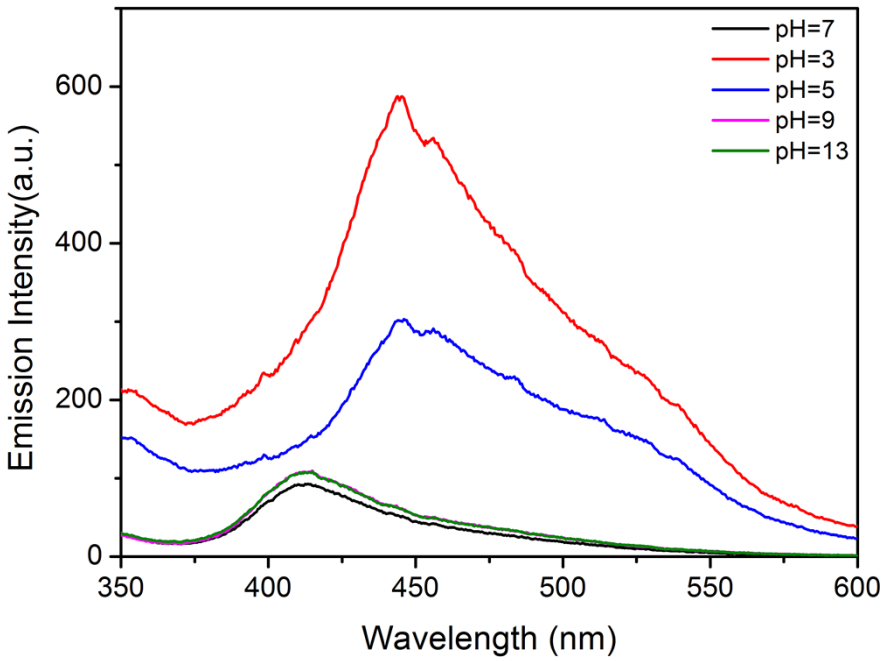


Fig. S3. Fluorescence emission of M6AzCOOH/DMF(0.07g/L)+200% H_2O at different pH values.

4. IR spectrum of M6AzCOOH and M6AzCOONa

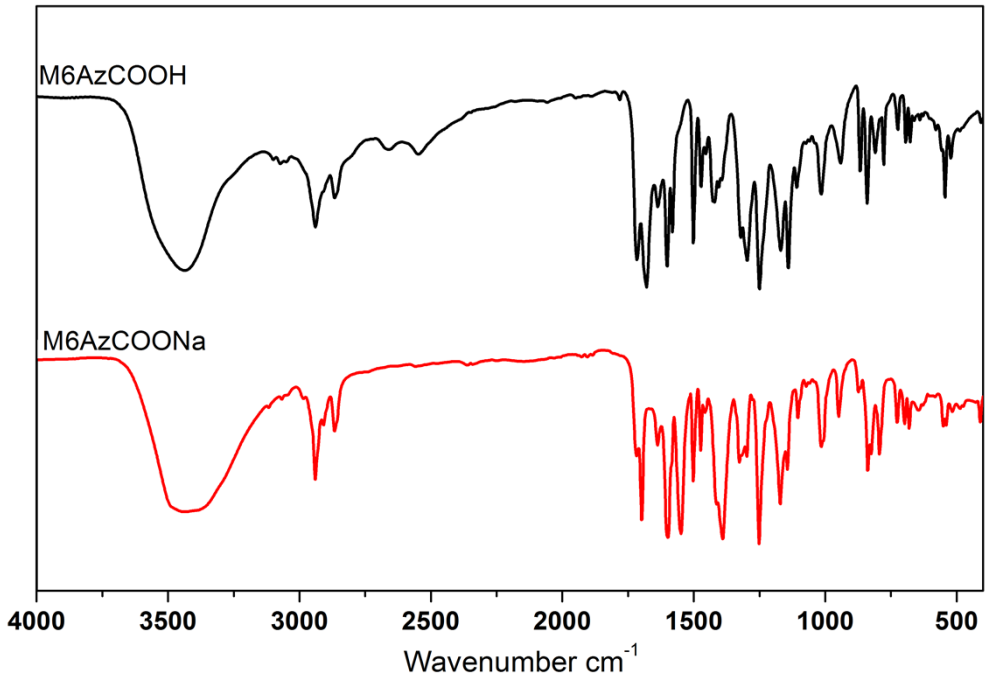


Fig. S4. FT-IR spectra of M6AzCOOH and M6AzCOONa.

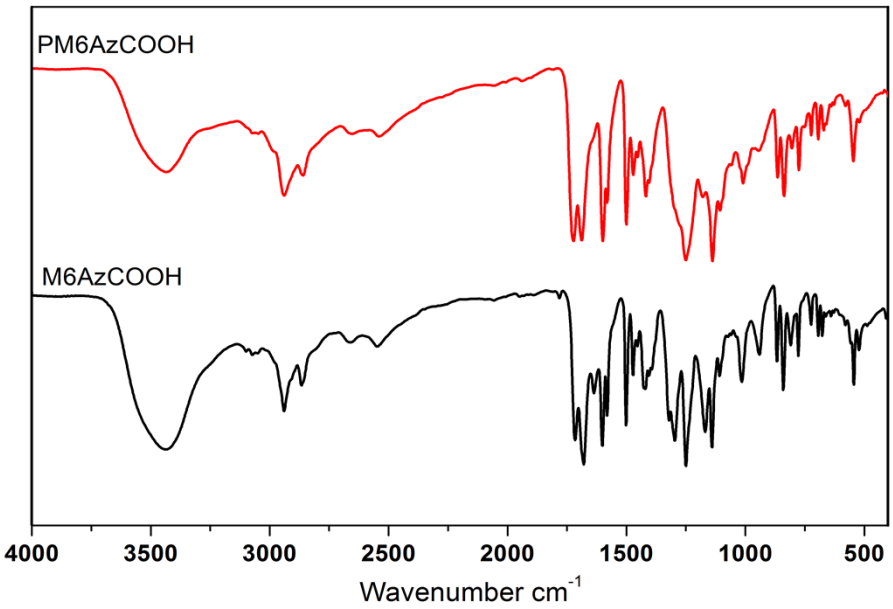


Fig. S5. FT-IR spectra of PM6AzCOOH and M6AzCOOH.

5. Photoresponsive behavior of PM6AzCOOH in DMF solution

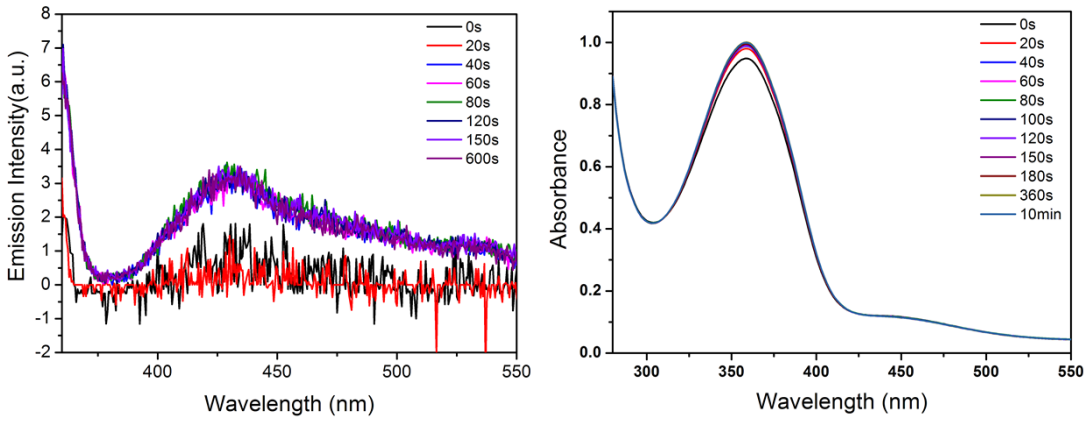


Fig. S6. (a). Fluorescence intensity and (b)UV-vis absorption spectra of PM6AzCOOH/DMF(0.07g/L) after UV irradiation.

The PM6AzCOOH/DMF (0.07g/L) solution was nonfluorescent, and the fluorescence emission intensity of PM6AzCOOH/DMF(0.07g/L) solution changes little after UV irradiation.

6. DLS analysis of PM6AzCOOH in mixed solvent

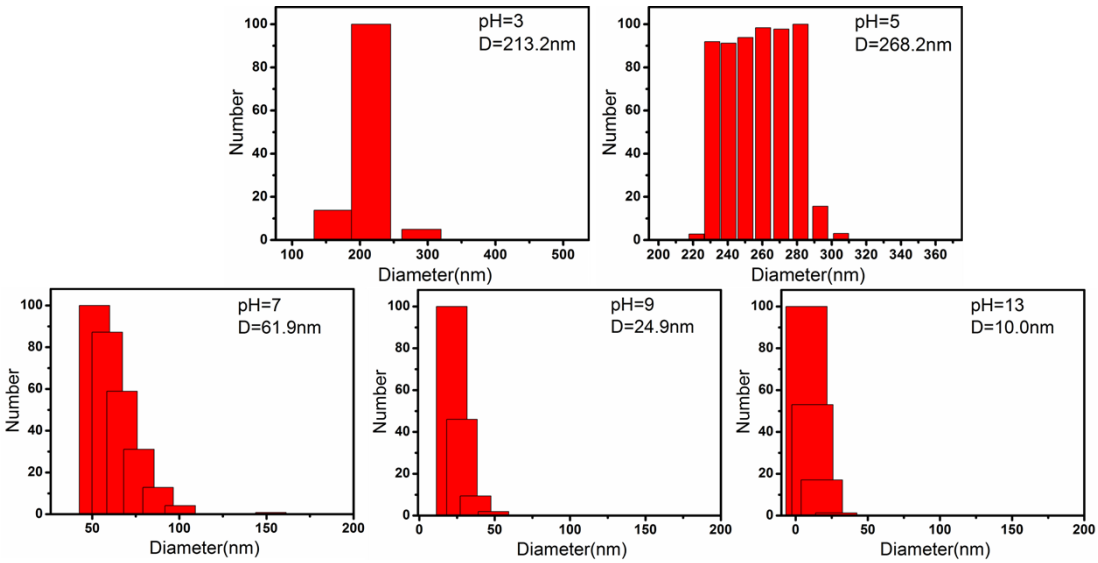


Fig. S7 The DLS analysis of PM6AzCOOH (0.07g/L)+200% H_2O with different pH values.

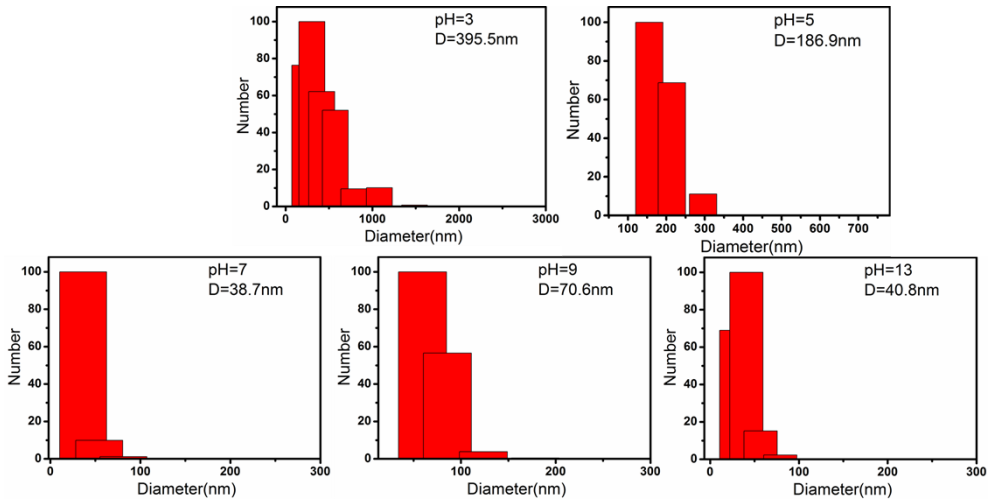


Fig. S8 The DLS analysis of M6AzCOOH (0.07g/L)+200% H_2O with different pH values.

7. GPC of PM6AzCOOH

The GPC analysis of PM6AzCOOH was carried out by Agilent GPC-Addon DMF as eluent, PLgel(divinyl benzene copolymer in ethylbenzene), flowrate was 1.0 mL/min. the result reflected that number-average molecular weight was $1.35*10^7$ g/mol, weight-average molecular weight is $2.51*10^7$ g/mol and polydispersity index (PDI) was 1.84.

8. Thermal properties of M6AzCOOH and PM6AzCOOH

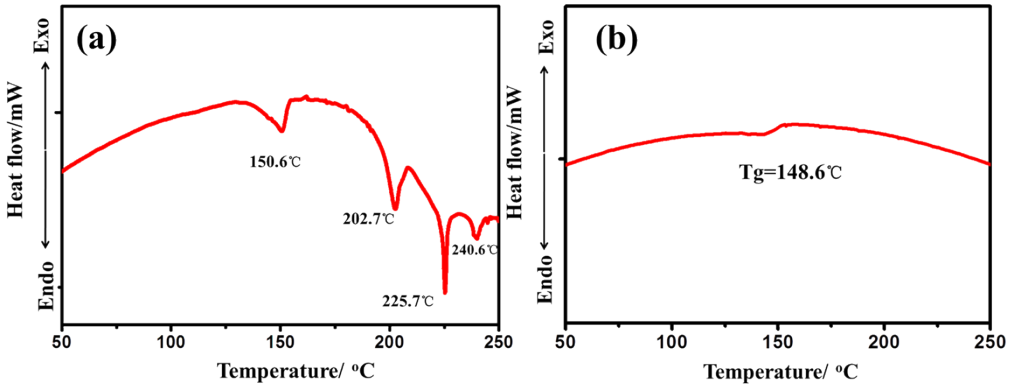


Fig. S9 DSC heating curves (second scan) of the monomer M6AzCOOH (a) and the homopolymer PM6AzCOOH (b).