Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Stimuli-responsive biocompatible nanovalve based on cyclodextrin modified poly(glycidyl methacrylate)

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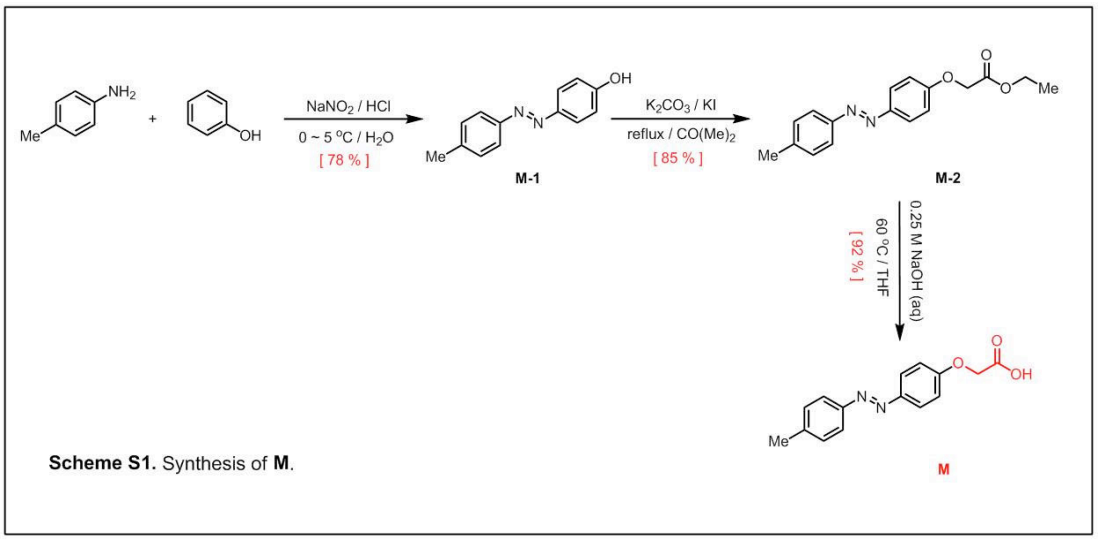
Contents

1. Preparation and Synthesis

1.1. Synthesis of 2-[4-(*p*-tolylazo)phenoxy]acetic acid (M)[S1]



Scheme S1. Synthesis of **M**.

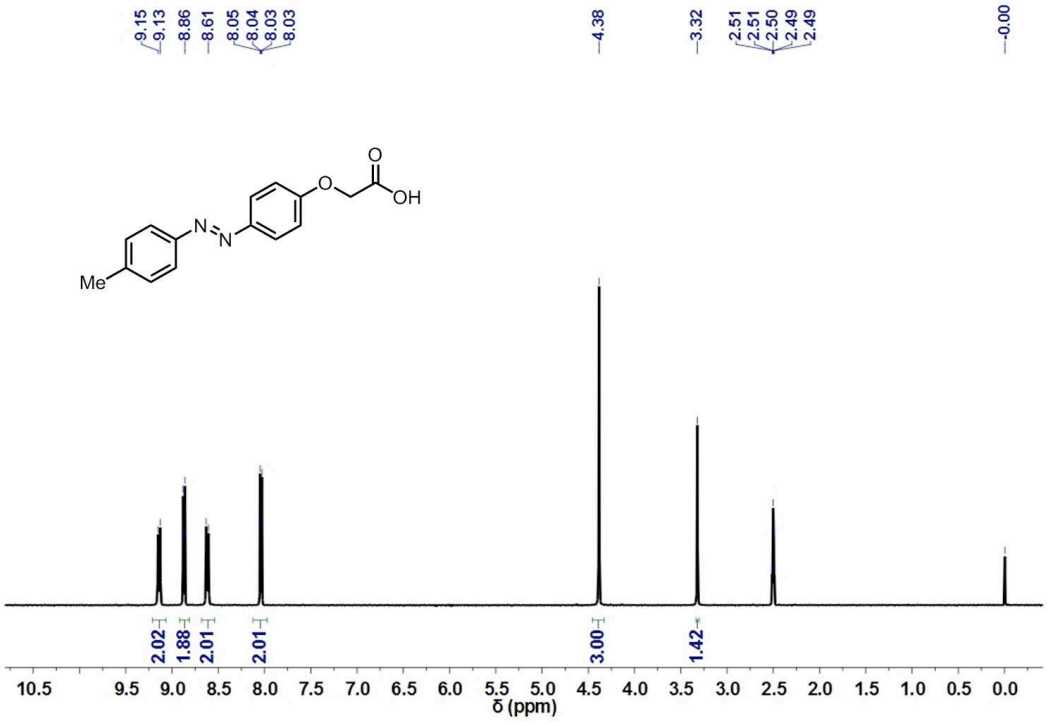


Fig. S1 ^{1}H NMR spectrum of **M**.

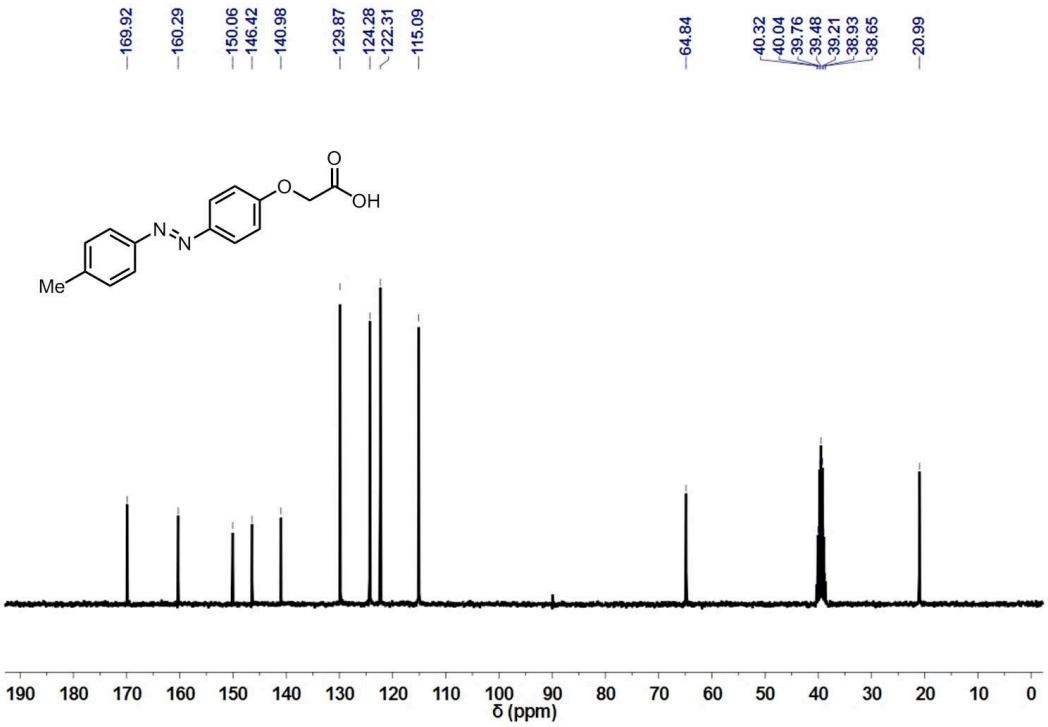


Fig. S2 ^{1}C NMR spectrum of **M**.

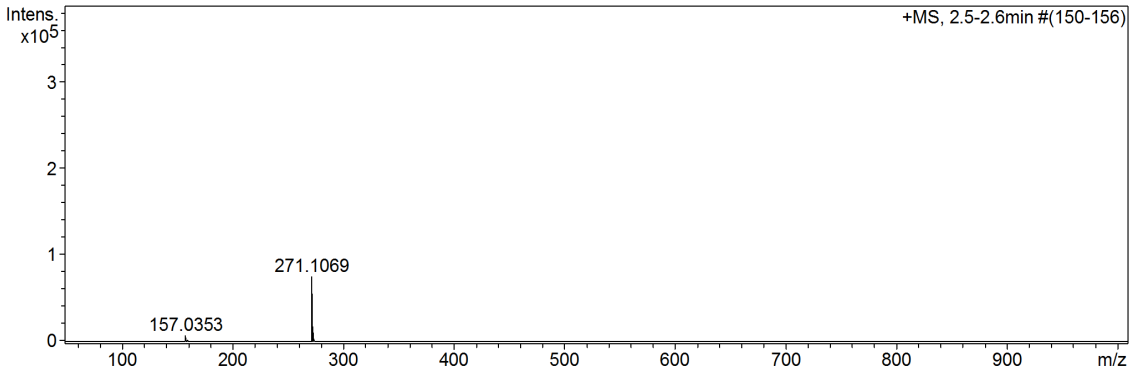
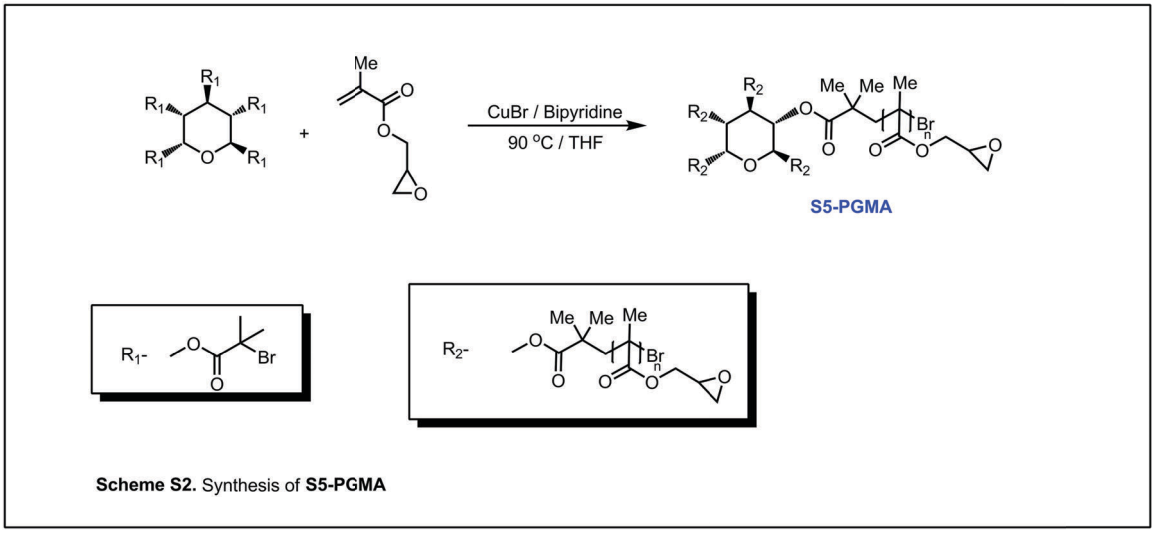


Fig. S3 MS (ESI) of **M**.

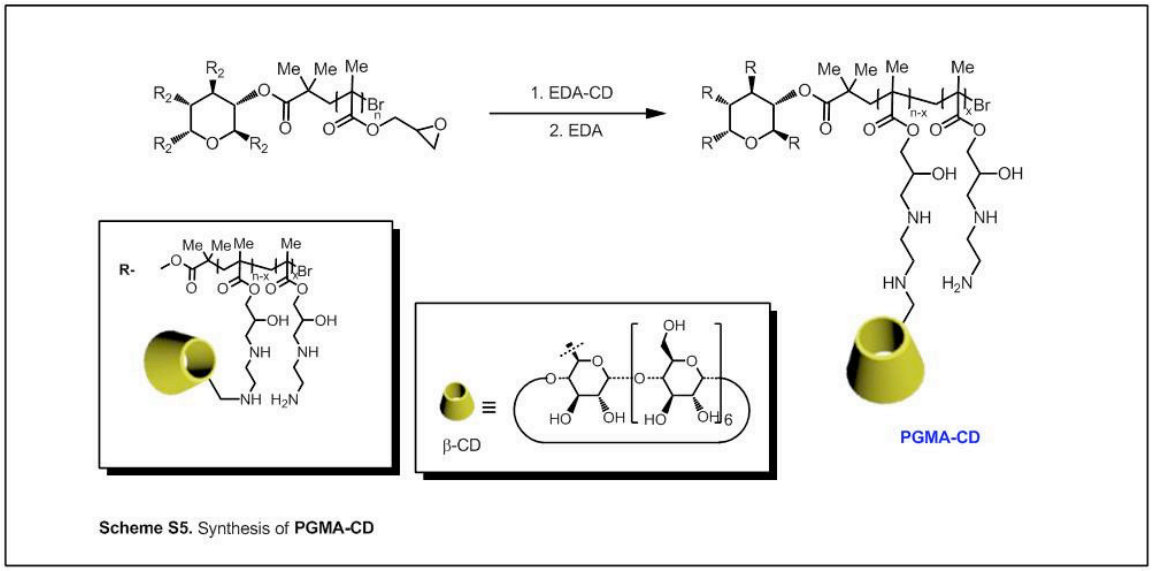
1.2. Preparation of PGMA modified with β-cyclodextrin (PGMA-CD)

1.2.1. Synthesis of star-shaped PGMA (S5-PGMA)



Scheme S2. Synthesis of **S5-PGMA**

1.2.2. Synthesis of star-shaped PGMA-CD



Scheme S5. Synthesis of **PGMA-CD**

1.2.3. Characterization of polymers

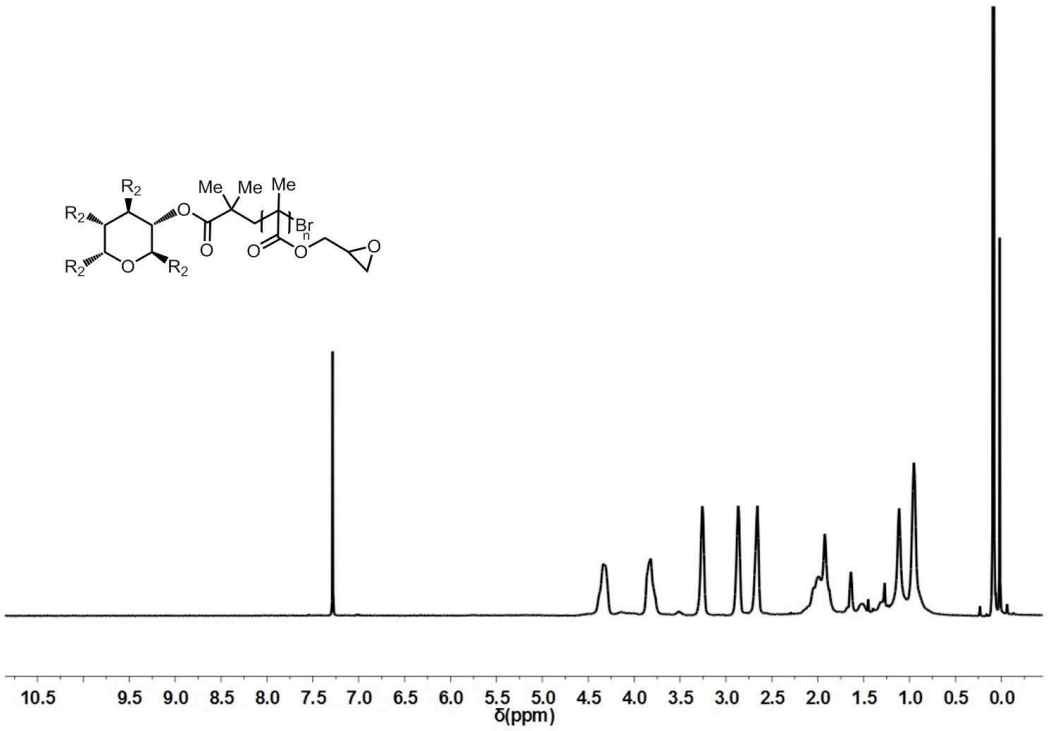


Fig. S4 ^{1}H NMR spectrum of S5-PGMA.

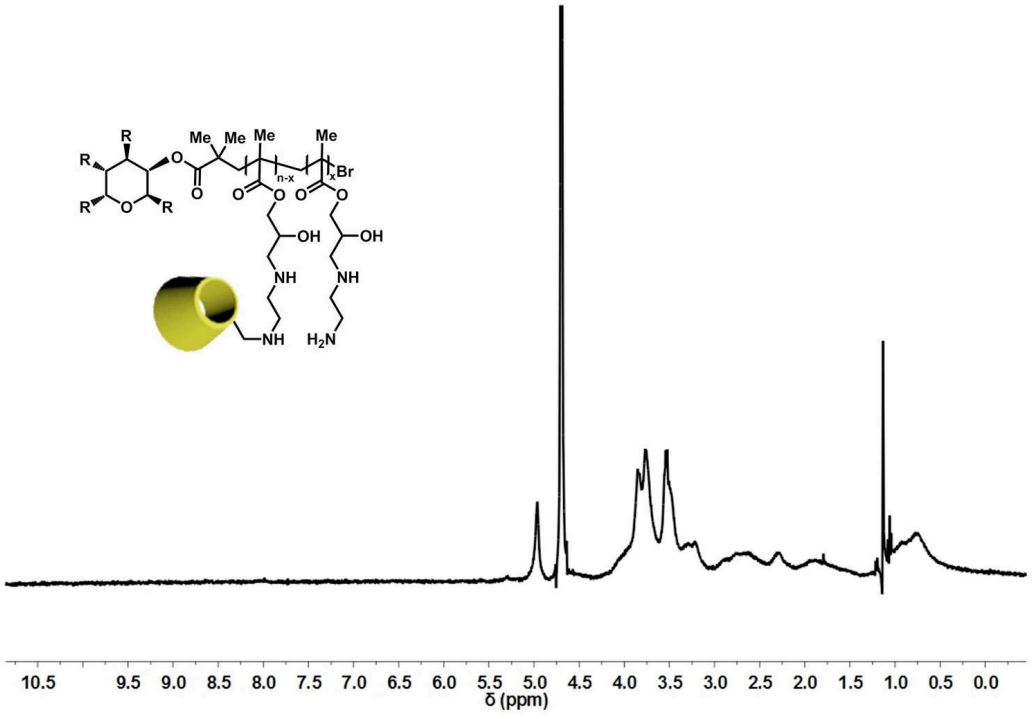


Fig. S5 ^{1}H NMR spectrum of PGMA-CD.

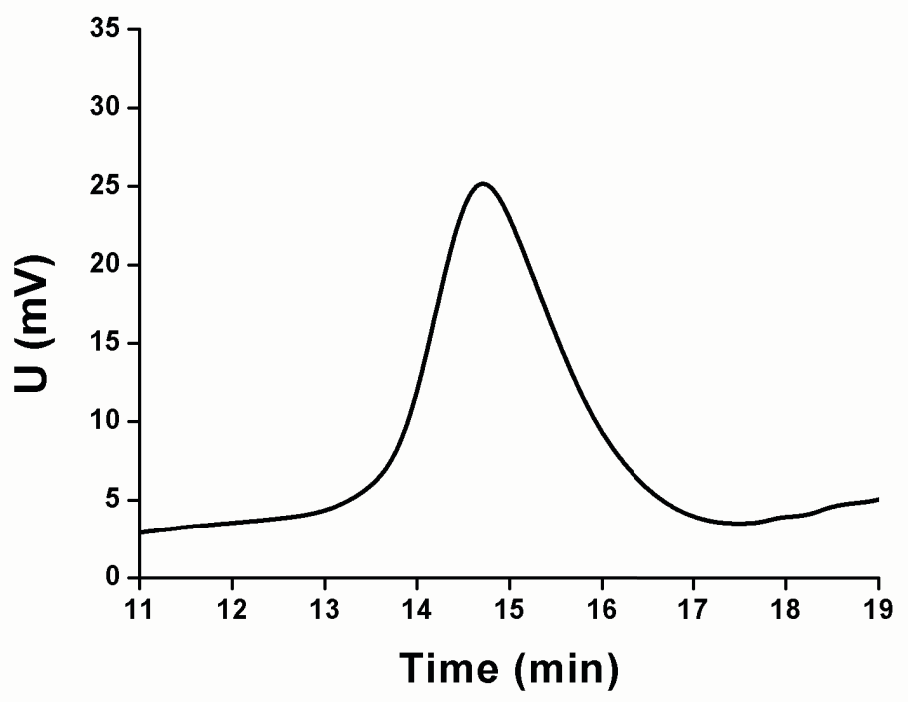


Fig. S6 GPC trace of S5-PGMA (Mn 9 KDa, PDI 1.15).

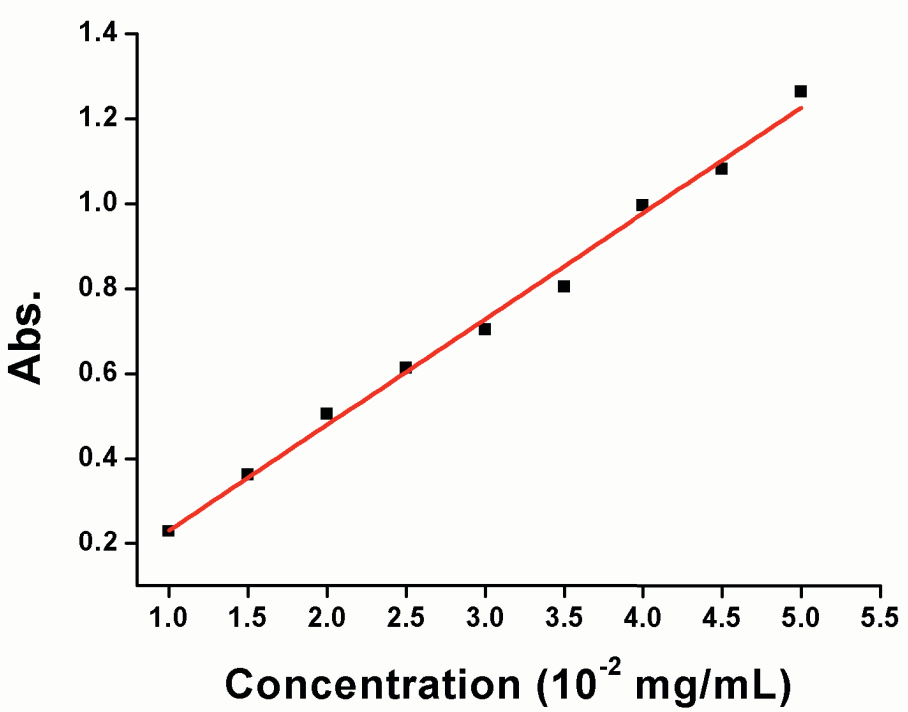
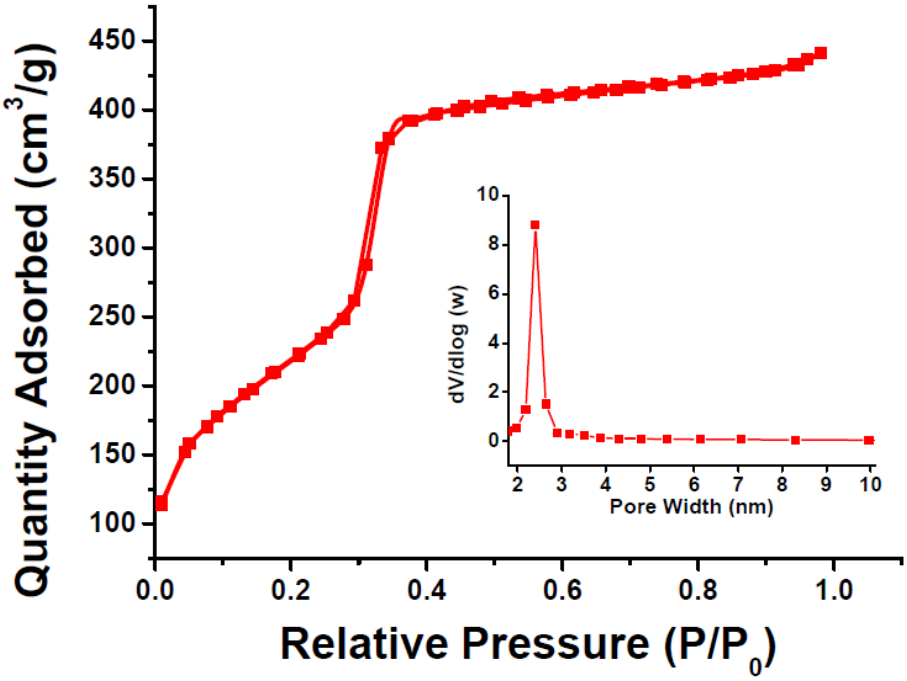


Fig. S7 The standard curve of *β*-CD solution done by using phenol-sulphuric acid assay.

The average ultraviolet absorbancy of PGMA-CD (4×10^{-2} mg/mL) done by using phenol-sulphuric acid assay[S2] is 0.430. According to the standard curve of CD solution above, we can calculate that the conjugate ratio of β-CDs to the side chain of S5-PGMA was 11.8%.

2. Material Characterization

2.1. N_2 adsorption and desorption of MSN-OH nanoparticles.



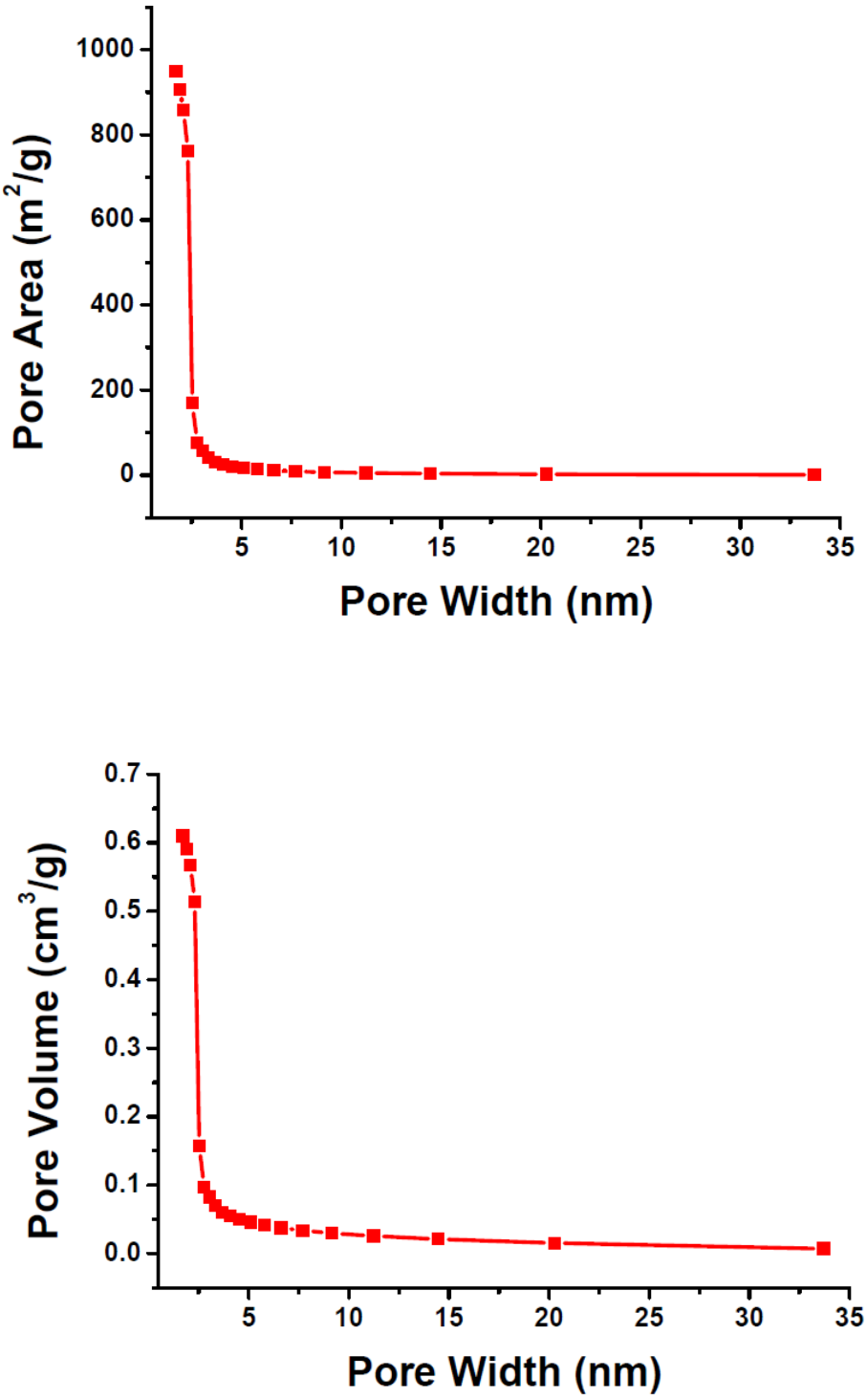


Fig. S8 BET and BJH isotherm of MSN-OH nanoparticles.

2.2. TEM and SEM images of MSN-OH nanoparticles.

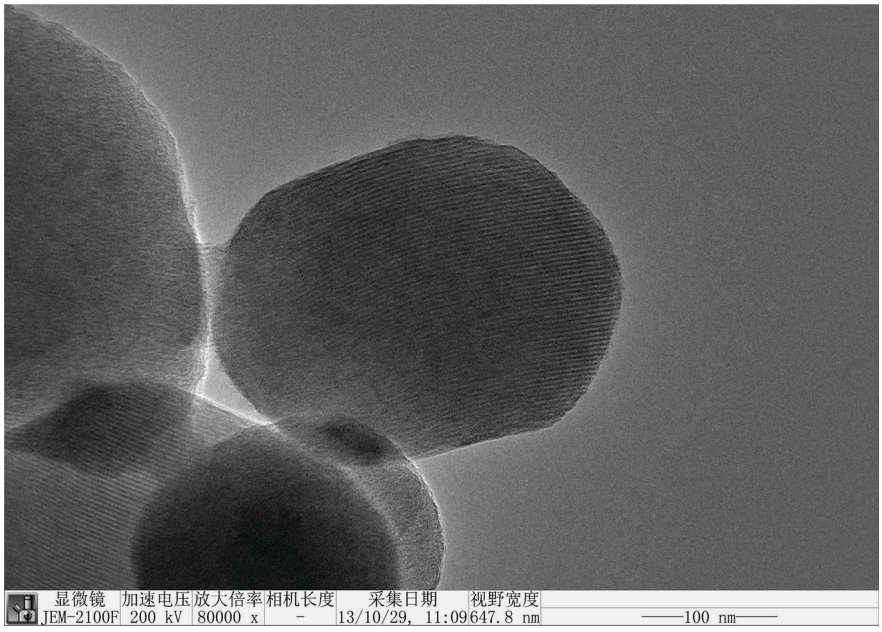


Fig. S9 TEM image of MSN-OH nanoparticles.

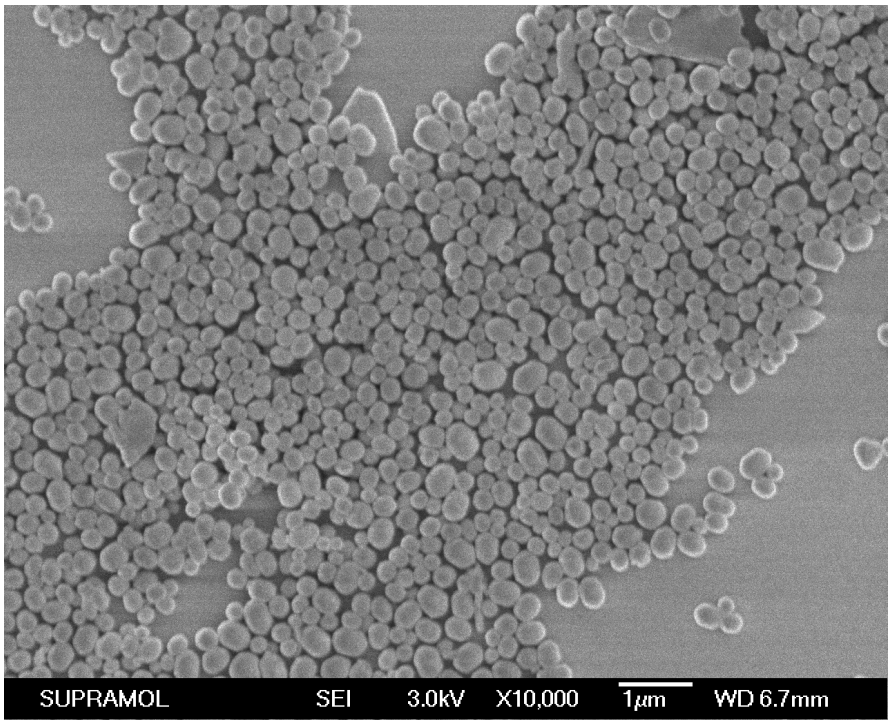


Fig. S10 SEM image of MSN-OH nanoparticles.

2.3. Average particle diameter of MSN-azo

Table S1 Average particle diameters of MSN-azo measured by DLS and TEM

MSN-azo		Particle diameter [nm]	Average [nm]
DLS	Run 1	244.2	254.7
	Run 2	247.3	
	Run 3	272.7	
TEM		210	

2.4. Fiber optical spectroscopy

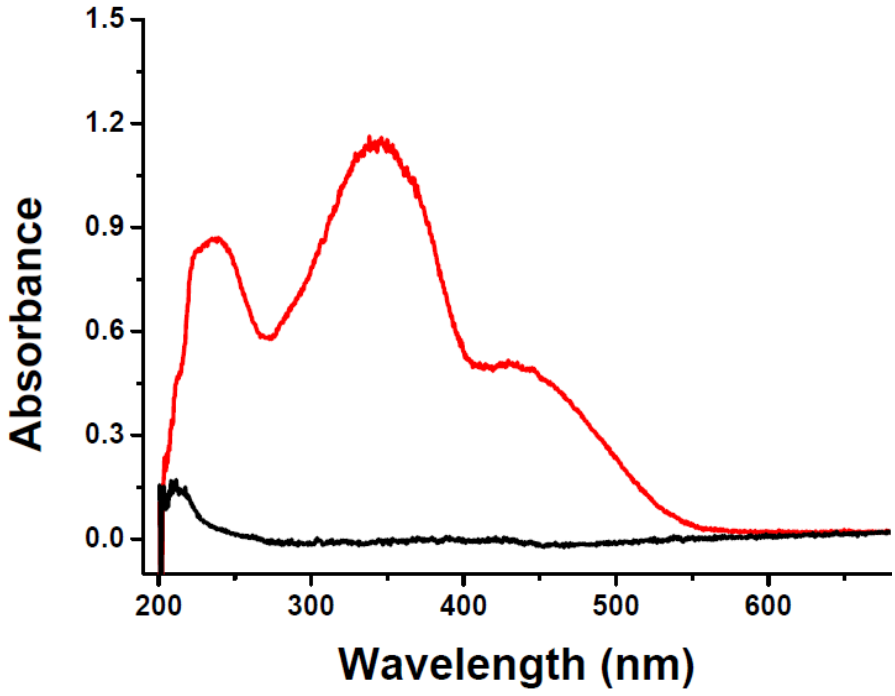


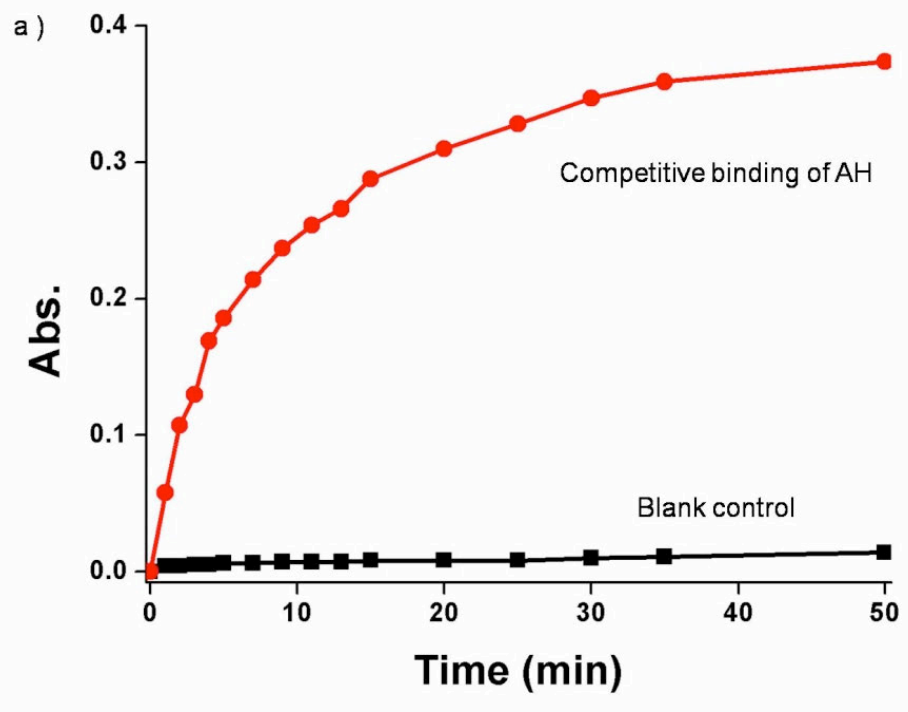
Fig. S11 Fiber optical spectra of a) MSN-NH_2 (black), b) MSN-azo (red).

2.5. Elemental analysis

Table S2 The elemental analysis of MSN-NH_2, MSN-azo and MSN@PGMA-CD

Samples	Element Content (Average)			
	C [%]	H [%]	N [%]	S [%]
MSN-NH_2	10.70	2.64	3.77	0.00
MSN-azo	15.29	2.55	4.08	0.00
MSN@PGMA-CD	20.92	3.42	3.30	0.03

3. Release Experiments



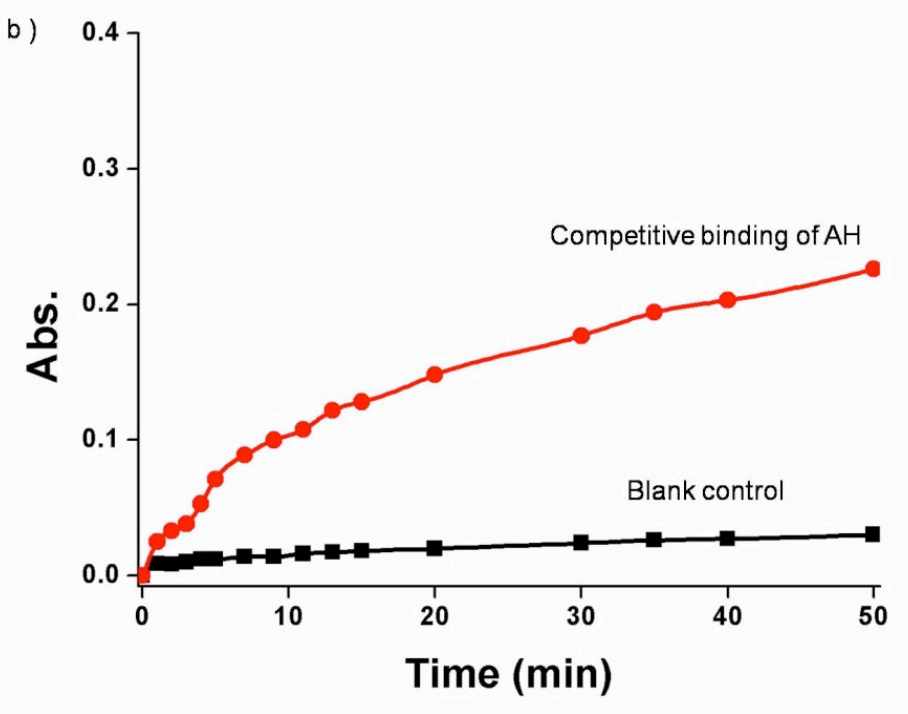


Fig. S12 RhB release profiles of RhB-loaded MSN@PGMA-CD made in a) distilled water, b) in ethanol.

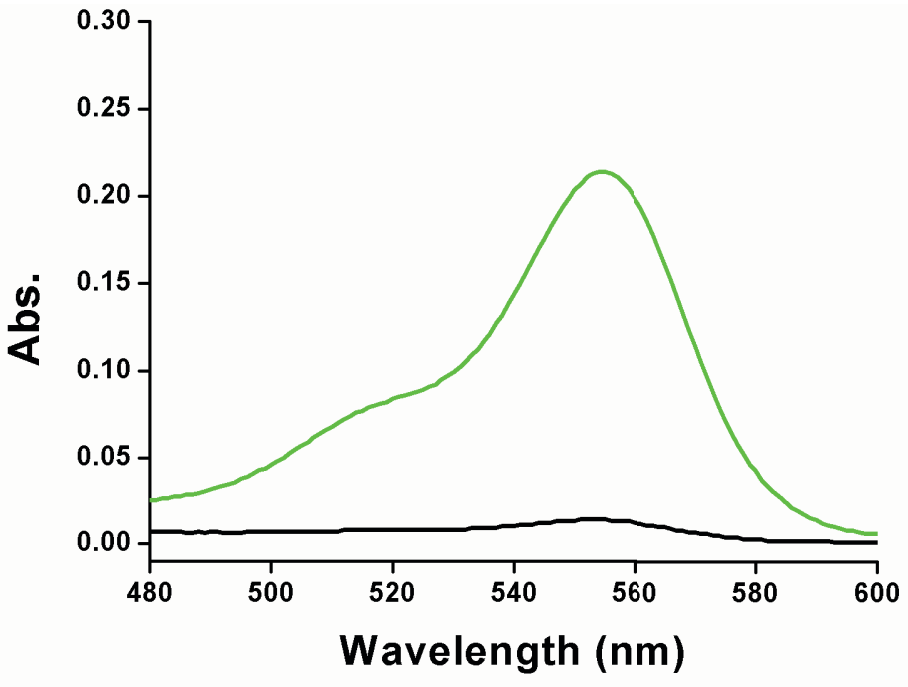


Fig. S13 The ultraviolet absorption spectra of the RhB pre-release (black) and its stimulated release at 50 °C after 50 minutes of RhB-loaded MSN@PGMA-CD.

4. References

[S1] K. Lang, P. Prošková, J. Kroupa, J. Morávek, I. Stibor, M. Pojarová and P. Lhoták, *Dyes Pigments*, 2008, **77**, 646.

[S2] G.-L. Koh and I. G. Tucker, *Int. J. Pharm*., 1986, **34**, 183.