Electronic Supplementary Material (ESI) for RSC Advances.


# Hydrophilic Surface Molecularly Imprinted Naringin Prepared via Reverse Atom Transfer Radical Polymerization with Excellent Recognition Ability in Pure Aqueous phase

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## Supporting Information

### The pre-assembly process

To obtain $^1$H NMR spectroscopy of the pre-assembly solution. The light yellow solution was lyophilized. $^1$H NMR (DMSO-$d_6$, 400 MHz): δ [ppm]=12.03 (s, 1H, Ar-OH); 9.63 (s, 1H, ArOH); 6.74 (dd, 1H, Ar-CH=); 5.88 (d, 1H, $-CH_a=C-$);5.27 (d, 1H, $-CH_b=C-$); 7.34 (dd, 2H, Ar-H); 7.70 (s, 1H, Ar-H); 7.77 (d, 1H, Ar-H);6.81 (d, 2H, Ar-H); 6.12 (s,1H, Ar-H);6.09 (s, 1H, Ar-H); 5.29 (d, 1H, Glu-$C_1$-H); 5.10 (d, 1H, $Rh_aC_1$-H); 1.16 (d, 3H, $Rh_a$-$CH_3$). The chemical shifts of other protons in the sugar part are in the range of 2.75–3.70 ppm. It indicates that the naringin was successfully bond to 4-VPBA and this result is consistent with Fig 3.

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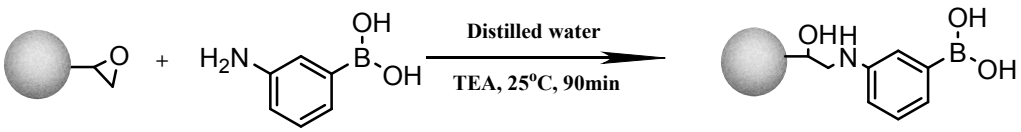
Fig. S1. $^1$H NMR spectroscopy of the pre-assembly solution.

### The synthesis of pGMA-EDMA-APBA polymers

The pGMA-EDMA-APBA polymers were used to optimize the pre-assembly conditions. The reaction mechanism between APBA and naringin is the same as 4-VPBA and naringin. The amino groups of APBA can react with the epoxy groups on the surface of the pGMA-EDMA polymers. The synthesis route of pGMA-EDMA-APBA polymers is illustrated in Fig. S2.

APBA (0.1 g) were dispersed in 20 mL water in a conical flask, followed by the addition of pGMA-EDMA supports (0.5 g) and catalyst TEA (0.25 mL). The reaction mixture was stirred for 24 h at room temperature. The obtained product was separated by centrifugation, washed by ethanol and dried at 60$^o$C under vacuum.




**Macroporous pGMA-EDMAsupports** **pGMA-EDMA-APBA polymers**

Fig. S2 Synthetic strategy for the pGMA-EDMA-APBA polymers.

## The effect of polymerization time on the adsorption of naringin onto SMIPs and SNIPs

Fig. S3 shows the effect of polymerization time on the adsorption of naringin onto SMIPs and SNIPs. It could be seen that the SMIPs with the polymerization time of 6 h have the largest adsorption capacity of naringin. Therefore, 6 h was chosen as the optimal polymerization time.

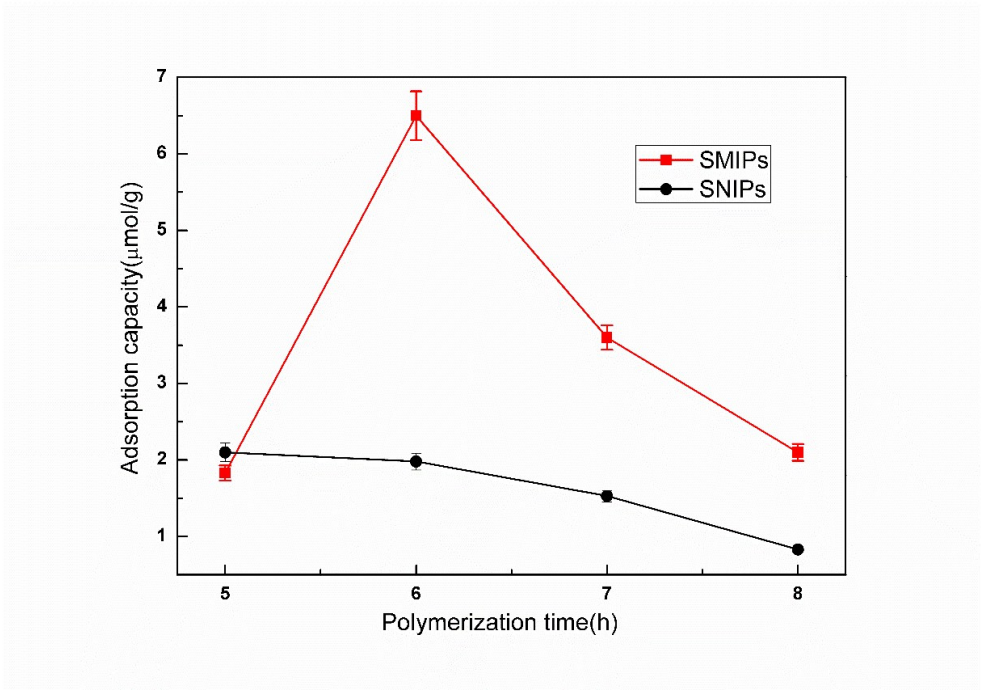



Fig. S3 Effect of polymerization time on the adsorption of naringin onto SMIPs and SNIPs. Initial concentration of naringin=20 mg/L, T=298 K, contact time=5 min.

Fig. S4 The madefaction of water drops on SMIPs.

**The Scatchard curve of SMIPs and SNIPs**

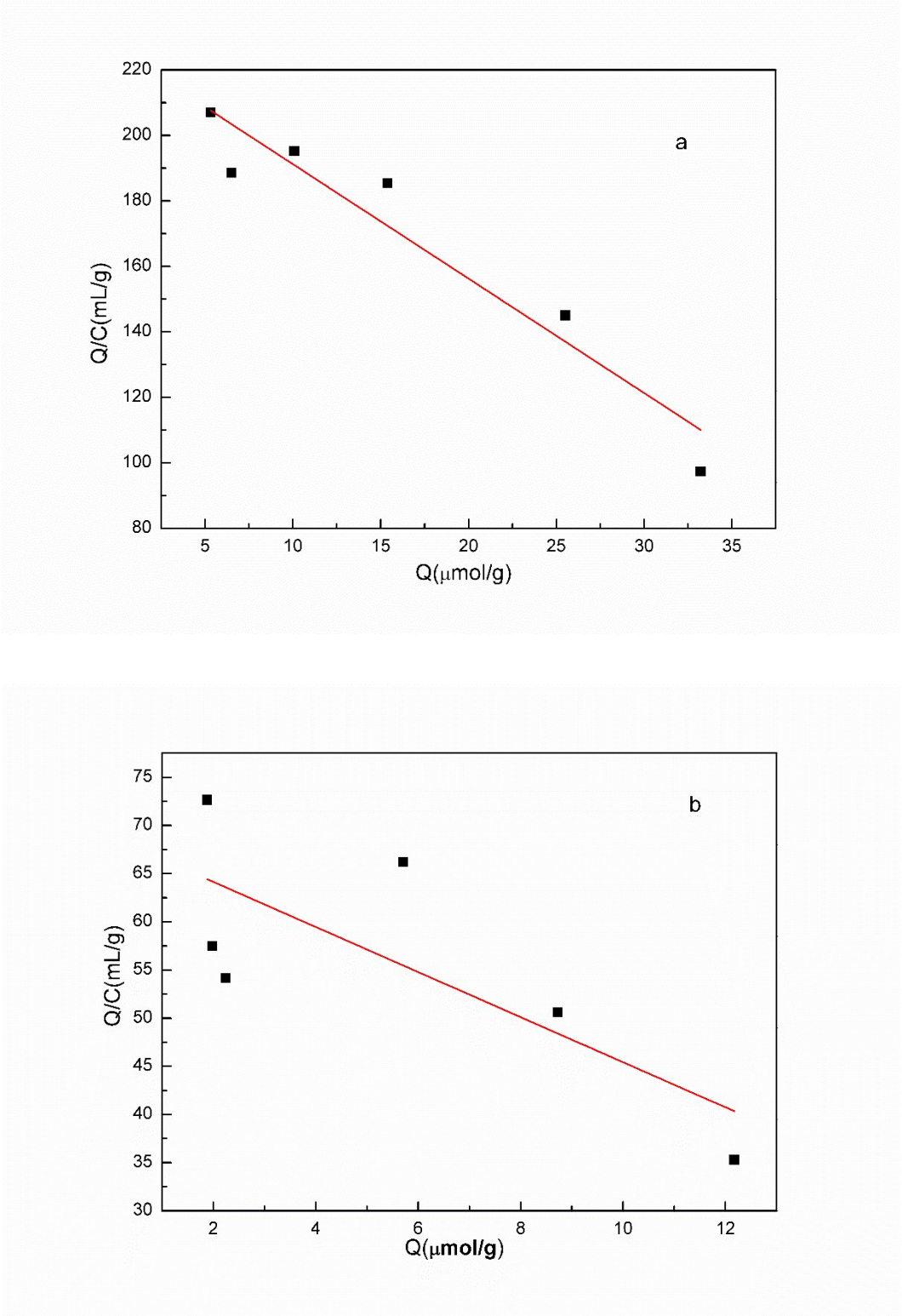



Fig. S5 Scatchard plot analysis of the binding of naringin to SMIPs (a) and SNIPs (b).

**The standard curve of naringin.**

An UV spectrophotometer was used to detect the concentration of naringin at 282 nm. The standard naringin (17 mg) was accurately weighed, dissolved with hot water and then kept at 25 ml with water. 200, 400, 600, 800, 1000 μL of the solution was accurately taken out and kept at 10 ml with water, respectively. The absorbance was measured at 282 nm and the standard curve of naringin was obtained. The adsorption ability was calculated as follow eq. (1)

$$q_e = \frac{(C_0 - C_e)V \times 10^3}{mM} \qquad (1)$$

Where $q_e$ (μmol/g) is the adsorption ability of SMIPs (SNIPs); $C_0$ and $C_e$ is the concentration of naringin at initial and equilibrium time (mg/L), respectively; $V$ is the volume of naringin solution (mL), $m$ is the mass of SMIPs or SNIPs (mg) and $M$ is the molecular weight of naringin.

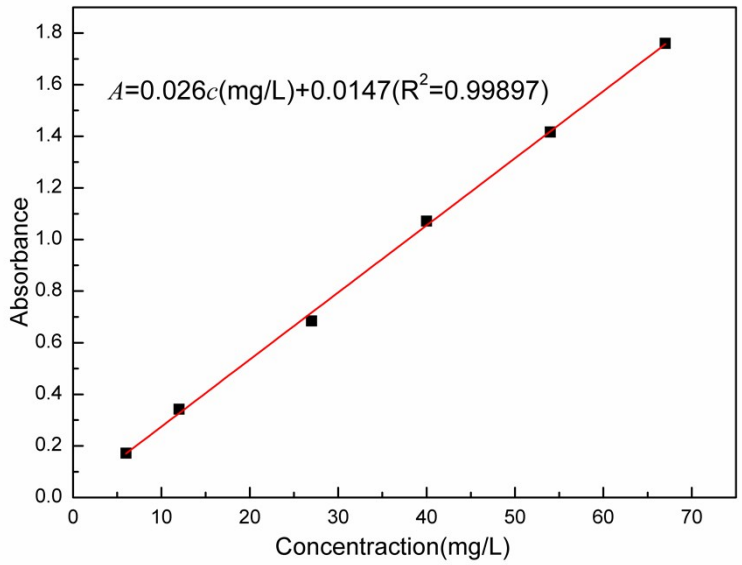



Fig. S6 The standard curve of naringin.

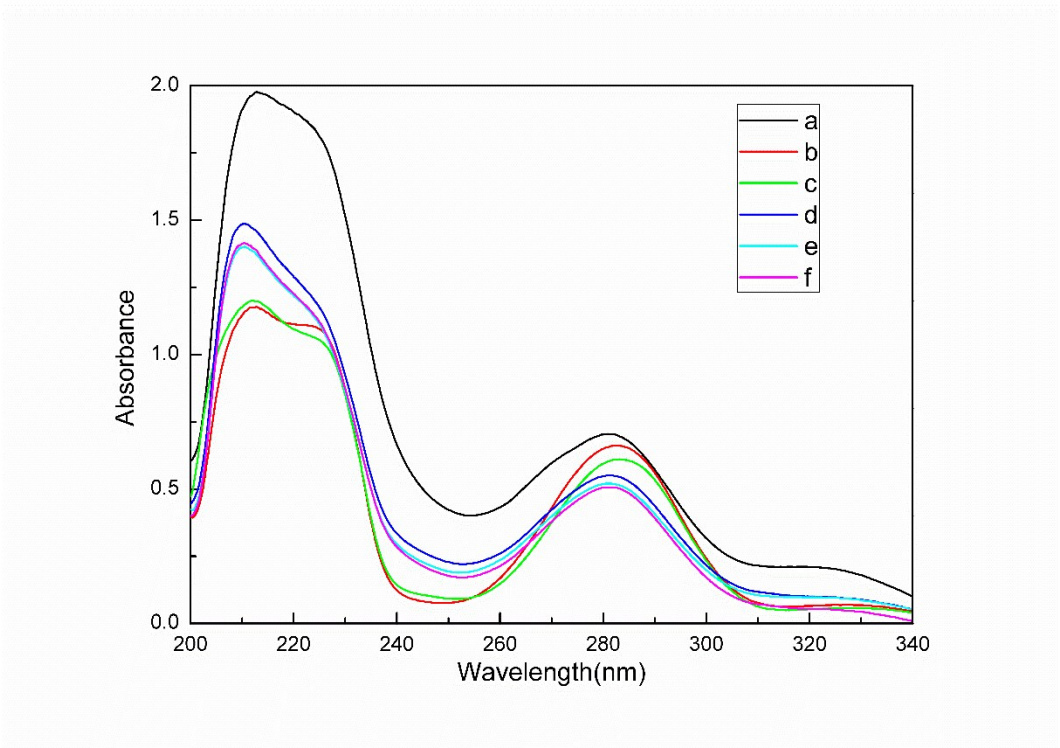



Fig. S7 UV absorption spectra of the grapefruit extract (a), the pure naringin (c), the solution after the first adsorption of SNIPs(b), the solution after adsorption of SMIPs(d, e, f): (f) after the first adsorption; (e) after the second adsorption, (d) after the third adsorption.

## Effects of changing the ratio of the GMA and EDMA on adsorption capacity of macroporous pGMA-EDMA supports

The content of epoxy groups on the surface of macroporous pGMA-EDMA supports was determined by acetone methods[1]. In this work, different proportions of GMA and EDMA were adjusted from 2:1 to 2:3 and the data are listed in Table S1. It could be seen that, when the ratio of GMA and EDMA was lower than 3:2, the adsorption ability of SMIPs increased with the increased content of the epoxy. The reason is that more ACPA is attached to the surface of the support with the increasing of the epoxy content, leading to more functional monomers and cross-linkers copolymerized on its surface. It could also be seen that, when the ratio of GMA and EDMA was higher than 3:2, the adsorption ability of SMIPs decreased with the decreased content of the epoxy. It indicates that the amounts of ACPA should not be too high. The reason is that the azo initiator ACPA which attached to the surface of supports will break under ultraviolet, resulting in two free radicals. One of the free radicals initiates surface graft polymerization and the other is dispersed in the solution. When the contents of ACPA were too high, the free radical concentration in the solution increased correspondingly, leading to the bulk polymerization of the functional monomers and the cross-linkers, making the beads attach to each other. The above results indicate that the adsorption ability can be well tuned by changing the ratio of the GMA and EDMA.

**1. Z. Wu, S. Li, J. Lu, J. Wuhan Inst. Chem. Tech., 2006, 01-0005-03, 1004-4736.**

Table S1 Effect of epoxy content on the adsorption ability of SMIPs

| n(GMA):n (EDMA) | Epoxy content (mmol/g) | Adsorption ability of SMIPs ( μ mol/g) |
|---|---|---|
| 2: 1 | 2.47 | 1.90 |
| 3: 2 | 1.85 | 6.55 |
| 1: 1 | 1.36 | 5.00 |
| 2: 3 | 0.93 | 2.76 |

## Binding studies

**The effect of adsorption pH, adsorption time, adsorption temperature on the binding capacity in self-assembly process.**

Effect of pH on the binding capacity was studied in the pH ranging from 4.0 to 9.0. The adsorption kinetics was explored by changing the adsorption time from 3 to 90 min while adopting the same initial concentration of naringin at 20 mg/L. The adsorption thermodynamics was explored by keeping the initial concentration of naringin at 20 mg/L and the shaking temperature was controlled at preset temperature (288, 298, and 308K) for 1 h. According to the data, pH 7.0 was chosen as the optimum adsorption pH, the optimum adsorption time was 75 min and the optimum adsorption temperature was 15$^{o}$C.

pGMA-EDMA-APBA polymers (30 mg), the naringin solution (10 mL) were dispersed in a conical flask. The reaction mixture was stirred for 24 h at room temperature. Then, the mixture was separated by centrifuging at 9,000 rpm for 5 min, and the concentration of naringin in the supernatant was determined using a UV spectrometer at 282 nm.

Table S2. Effect of pH on the binding capacity in self-assembly process.

| pH | A0[a] | △A[b] |
|---|---|---|
| 4.0 | 0.677 | 0.156 |
| 5.0 | 0.682 | 0.286 |
| 6.0 | 0.711 | 0.311 |
| 7.0 | 0.687 | 0.314 |
| 7.5 | 0.661 | 0.309 |
| 8.0 | 0.661 | 0.315 |
| 8.5 | 0.635 | 0.306 |
| 9.0 | 0.597 | 0.277 |

[a] The absorbance of naringin at initial time;

[b] The difference of the absorbance at initial and equilibrium time.

Table S3. Effect of adsorption time on the binding capacity in self-assembly process.

| Adsorption time/min | △A[a] |
|---|---|
| 5 | 0.180 |
| 10 | 0.178 |
| 20 | 0.185 |
| 30 | 0.186 |
| 45 | 0.193 |
| 60 | 0.197 |
| 75 | 0.203 |
| 90 | 0.192 |

[a] The difference of the absorbance at initial and equilibrium time; $A^0$=0.586.

Table S4. Effect of adsorption temperature on the binding capacity in self-assembly process.

| Temperature/$^o$C | △A[a] |
|---|---|
| 15 | 0.200 |
| 25 | 0.184 |
| 40 | 0.041 |

[a] The difference of the absorbance at initial and equilibrium time; $A^0$=0.746.