Electronic Supplementary Material (ESI) for Analytical Methods.

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Supplementary Information

Dual functional monomers surface molecular imprinted microspheres for polysaccharide recognition in aqueous solution

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Preparations of mono-functional monomers MIPs

*Synthesis of spherical **MIPs-APBA***: 1 mL of starch solution (0.77 mg mL^{-1}) and 2 mL of APBA (6.1 mg mL^{-1}) were added into the 50 mL centrifugal tube containing 14 mL phosphate buffer (pH 9.0). Then mixed 5 min under ultrasound and carried on pre-polymerization at room temperature with the static setting. An hour later, 30 mg of SiO_2@COC nanoparticles and 3 mL of APS (13.69 mg mL^{-1}) were added into the solution to initiate polymerization. After nitrogen filling, sealed centrifugal tube on vapor-bathing constant temperature vibrator under 60 ℃ with the speed of 200 r min^{-1}. After 24 hours of reaction, the solution was centrifuged for 10 min at 4500 rpm. The precipitate was activated by successively with phosphate buffer (pH 5.0) and a mixture of methanol and acetic acid (9:1, v/v) for remove the template. The precipitate was dried at 45 ℃ in vacuum for overnight. The synthesis method of the starch silica surface non-molecular imprinted polymers (NIPs-APBA) was the same as that of MIPs-APBA but the template molecule was not added.

*Synthesis of spherical **MIPs-AMPS***: 1 mL of starch solution (0.77 mg mL^{-1}) and 2 mL of AMPS (4.15 mg mL^{-1}) were added into the 50 mL centrifugal tube containing 14 mL phosphate buffer (pH 9.0). Then mixed 5 min under ultrasound and carried on pre-polymerization at room temperature with the static setting. An hour later, 30 mg of SiO_2@COC nanoparticles and 3 mL of APS (13.69 mg mL^{-1}) were added into the solution to initiate polymerization. After nitrogen filling, sealed centrifugal tube on vapor-bathing constant temperature vibrator under 60 ℃ with the speed of 200 r min^{-1}. After 24 hours of reaction, the solution was centrifuged for 10 min at 4500 rpm. The

precipitate was activated by successively with phosphate buffer (pH 5.0) and a mixture of methanol and acetic acid (9:1, v/v) for remove the template. The precipitate was dried at 45 ℃ in vacuum for overnight. The synthesis method of the starch silica surface non-molecular imprinted polymers (NIPs-AMPS) was the same as that of MIPs-AMPS but the template molecule was not added.

Table S1. Numerical value of two diffusion coefficients

$T_{1/2}$ (s)	D_p (cm^2/s)	D_f (cm^2/s)
150	9.25×10^{-14}	1.09×10^{-12}
300	4.62×10^{-14}	5.47×10^{-13}
450	3.08×10^{-14}	3.65×10^{-13}
600	2.31×10^{-14}	2.73×10^{-13}
900	1.54×10^{-14}	1.82×10^{-13}
1200	1.16×10^{-14}	1.37×10^{-13}
1800	7.70×10^{-15}	9.12×10^{-14}
2400	5.78×10^{-15}	6.84×10^{-14}
3600	3.85×10^{-15}	4.56×10^{-14}
4500	3.08×10^{-15}	3.65×10^{-14}
5400	2.57×10^{-15}	3.04×10^{-14}

Table S2. Distribution coefficient and selectivity coefficient data for MIPs and NIPs

Tested compounds	MIPs			NIPs			k'
	C_e (mg L^{-1})	K_d (L g^{-1})	k	C_e (mg L^{-1})	K_d (L g^{-1})	k	
starch	16.15	0.810	-	20.47	0.288	-	-
G70000	21.86	0.163	4.959	22.70	0.095	3.027	1.638
G10000	20.54	0.281	2.883	21.64	0.182	1.586	1.818
G5000	22.21	0.134	6.037	22.79	0.0886	3.249	1.858

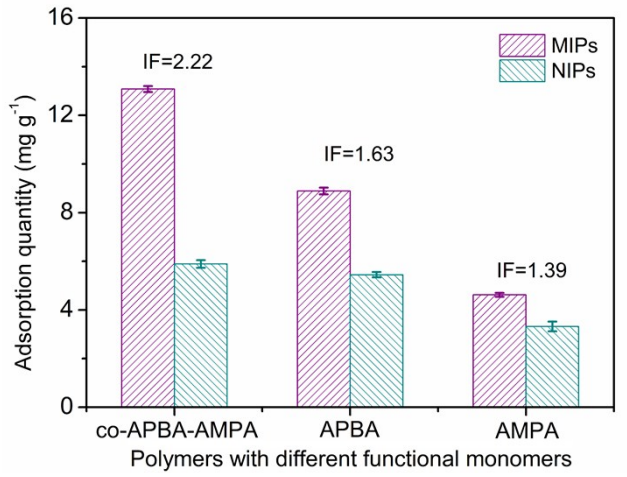

Fig. S1 The adsorption capacity and imprinting factor of dual functional monomer MIPs and mono-functional monomer MIPs.

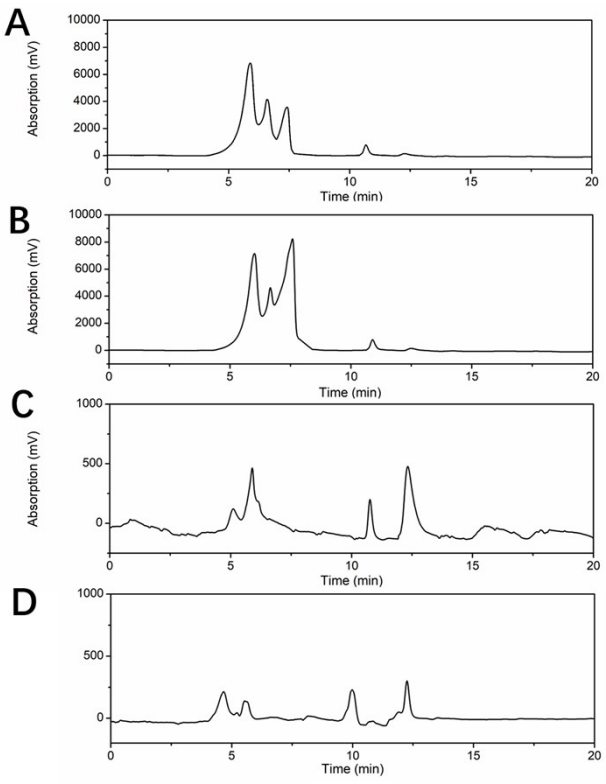

Fig. S2 The HPLC chromatograms of the eluent by solid phase extraction columns. DEAE-52 (A), Sephadex-100 (B), silica gel (C), ODS (D).

1. B. Zijun, C. Yang, Y. Jin, W. Shuangshou and L. Zhen, *Angewandte Chemie*, 2015, **54**, 10211-10215.