Electronic supplementary information

For

An effective way to imprint protein with the preservation of template structure by using macromolecule as the functional monomer

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Synthesis and characterization of [AVIM] Cl

The micromolecular monomer named [AVIM] Cl was synthesized as follows: ACa (2.69 g, 20 mmol) was dissolved in 5 mL acetone at 25 °C, and then VIM (1.88 g, 20 mmol) was slowly added dropwise into the mixed solution by using constant pressure. The reaction was carried out at 40 °C with a magnetic stirrer for 12 h and solution formed two phases. After collecting the bottom layer of the two phases, the upper layer was further purified by washing with small amounts of acetone and then freeze-dried by lyophilization. The final product was obtained with the yield of 86%. The result of the product ($C_{10}H_{13}N_2O_2Cl$) from elemental analysis for C, H, and N is 52.51, 5.69 and 12.25 % respectively. The calculated results were 52.57, 5.72 and 12.17 % respectively. The ^{1}H-NMR of [AVIM] Cl is shown in Figure. S1.

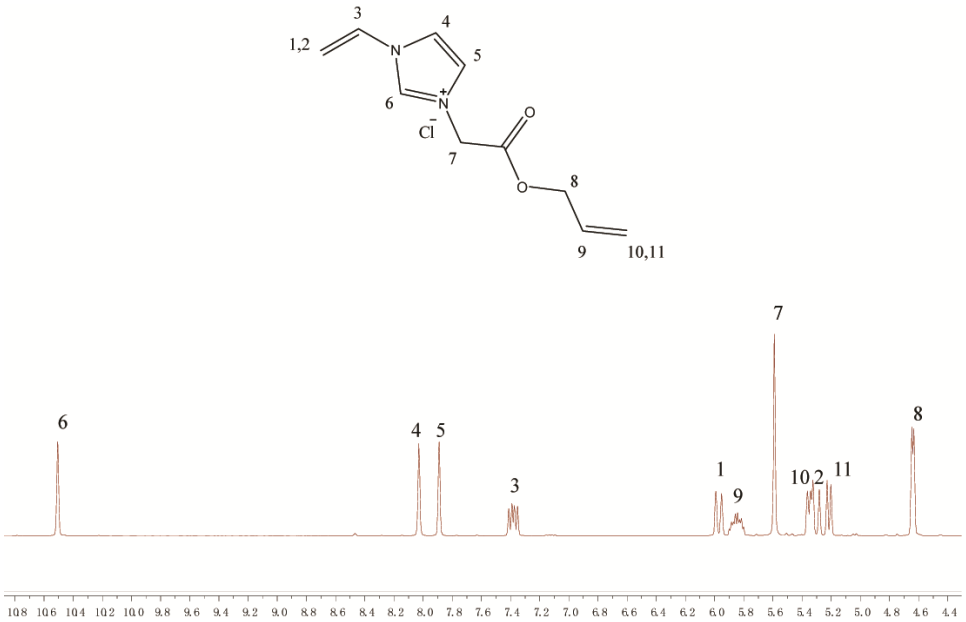

Fig.S1 ^{1}H NMR spectra of [AVIM] Cl in $CDCl_3$

Preparation of protein imprinted hydrogels using micromolecular monomers

A typical synthesis procedure with micromolecular monomers is as follows: The template protein (45 mg for OVA and 14 mg for Lyz respectively) was dissolved in 0.8 mL phosphate buffer (0.01 M, pH 7.0) in a 25 mm×40 mm (diameter×height) weighing bottle. A certain ratio of HEA (86.9 mg), VIM (10 mg) and [AVIM]Cl (35.9 mg) which is the same composition as macromolecular chain calculated by XPS were added into above solution, and followed by mixing with 2 mg APS. The mixed solution was incubated for 20 min at 25°C. Then the solution was deoxygenated by purging with nitrogen for 15 min. Before the weighing bottle was sealed, a volume of 2 μL TEMED was promptly added into the solution and the polymerization was carried out at 25°C for 3 h. After the reaction, the resultant hydrogels were cut into 6 mm diameter disks with a thickness of 1.5 mm. The washing procedure was same as MIH-C-template. The corresponding non-imprinted hydrogel was prepared in the same way, but in the absence of the template protein.

The FTIR analysis of macromolecular chain, MIH-C and MIH-M

As shown in Fig.S2 The wide bond at 3380 cm^{-1} in precursor of macromolecular chain corresponds to characteristic stretching vibration band of hydrogen bonded O-H group,[1] the C=O stretching vibration of ester group also appears at 1730 cm^{-1}, and the typical bands of the imidazolium ring shows at 1630 (C=C, C=N), 1558

(C-C, C-N), 1450 (CH alkyl deform) 1164 (CH ring deform) cm^{-1}.[2] In the spectrum of macromolecular chain, the existence of a new band at 1654 cm^{-1} (C=C in allyl) proves the alkylation reaction of ACa with imidazolium ring. After the polymerization of macromolecular chain, the typical C=C band at 1654 cm^{-1} in MIH-C was totally disappeared indicating that the double bonds were almost polymerized. In addition, the FT-IR spectrum of MIH-M is same as MIH-C, suggesting that MIH-M has been successfully synthesized and it had the same chemical composition as MIH-C.

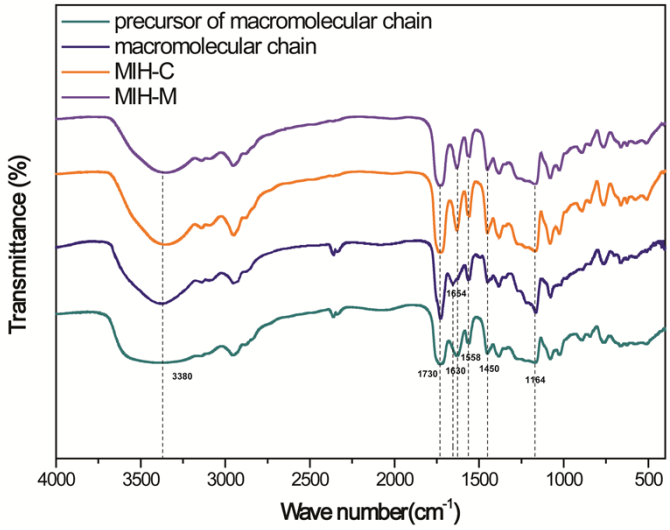

Fig.S2 FT-IR spectrum of MIH-M, MIH-C, the macromolecular chain and its precursor

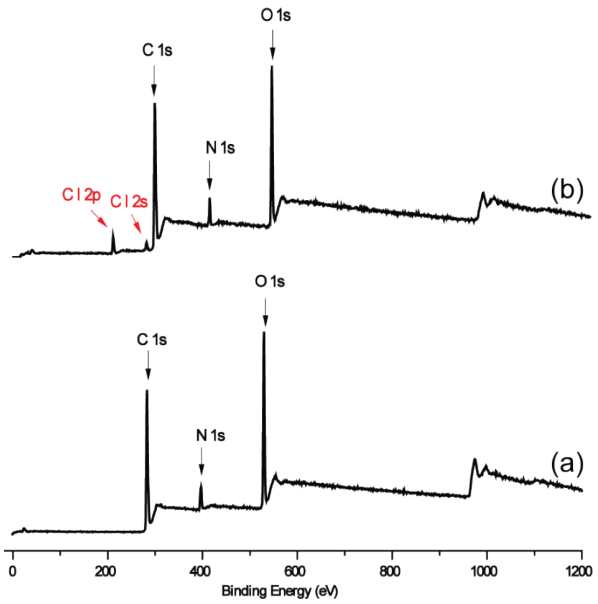

Fig.S3 XPS spectra of the macromolecular chains (b) and their precursor (a)

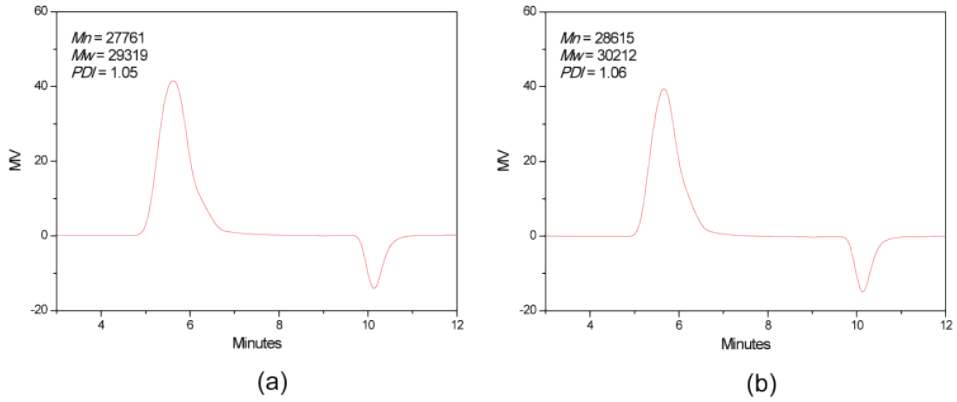

Fig.S4 GPC analysis of the macromolecular chain (b) and its precursor (a)

Table S1 Gel fraction yield and swelling ratio of MIH-C-OVA, MIH-M-OVA, MIH-C-Lyz and MIH-M-Lyz

	MIH-C-OVA	**MIH-M-OVA**	**MIH-C-Lyz**	**MIH-M-Lyz**	**NIH-C**	**NIH-M**
Gel fraction yield (%)	68±5	73±2	75±3	79±2	78±4	82±2
Swelling ratio (%)	754±38	739±23	721±11	719±24	704±31	688±25

Table S2 Selective adsorption experiments for MIH-C-OVA, MIH-M-OVA, MIH-C-Lyz, MIH-M-OVA, NIH-C and NIH-M

Amount of the proteins adsorbed (mg g^{-1} dry gel)									
	OVA	BSA	Lyz	Cyc		OVA	BSA	Lyz	Cyc
MIH-C-	77.8	36.2	25.6	24.3	**MIH-M-**	52.9	41.7	26.3	25.1
OVA	±5.5	±1.1	±2.3	±1.9	**OVA**	±3.9	±2.8	±0.7	±0.9
NIH-C	30.5	31.6	23.9	21.7	**NIH-M**	34.2	30.7	30.0	28.6
	±3.2	±2.8	±2.6	±1.5		±1.7	±1.2	±2.2	±1.4
IF	2.55	1.15	1.07	1.12	**IF**	1.55	1.36	0.87	0.88
β		2.23	2.38	2.28	**β**		1.14	1.77	1.76
	OVA	**BSA**	**Lyz**	**Cyc**		**OVA**	**BSA**	**Lyz**	**Cyc**
MIH-C-Lyz	26.8	25.1	51.0	23.9	**MIH-M-Lyz**	28.9	26.6	44.3	27.4
	±1.2	±0.7	±3.8	±2.1		±1.2	±0.6	±4.1	±3.3
NIH-C	30.5	31.6	23.9	21.7	**NIH-M**	34.2	30.7	30.0	28.6
	±3.2	±2.8	±2.6	±1.5		±1.7	±1.2	±2.2	±1.4
IF	0.88	0.79	2.13	1.10	**IF**	0.85	0.87	1.48	0.96
β	2.43	2.69		1.94	**β**	1.75	1.70		1.54

Notes and references

1 L. Ferreira, M.M. Vidal and M.H. Gil, International Journal of Pharmaceutics., 2000, **194**, 169-180

2 T. Erdmenger, J. Vitz, F. Wiesbrock, and U. S. Schubert, J. Mater. Chem., 2008, **18**, 5267-5273.