Supporting Information

Synthesis of a hydrophilic covalent-organic framework@silica composites via oxidation reaction for mixed-mode liquid chromatographic separation

Xingyun Zhao[a,b,], Jiangyan Jin[b], Peng Wang[b], Yonghao Chai[b], Kairui Zhu[b], Liyun Zhang[a], Ruifang Wang[a], Ke Li[b,] *, Rongfang Wu[a,]**

a Shanxi Bethune Hospital, Shanxi Academy of Medical Sciences, Third Hospital of Shanxi Medical University, Tongji Shanxi Hospital, Taiyuan, 030032, China;

b Modern Research Center for Traditional Chinese Medicine, The Key Laboratory of Chemical Biology and Molecular Engineering of Ministry of Education, Shanxi University, No. 92, Wucheng Road, Taiyuan, 030006, Shanxi, P. R. China

* Correspondence

E-mail: wurongfang@sxbqeh.com.cn; xyzhao@sxu.edu.cn, like@sxu.edu.cn, Tel: +86-411-7018379

Preparation of the silica microspheres

10.15 g urea, 5 g K_2SO_4, 68 mL 5-20 nm 20% silica sol, 15 mL 1% Tween were together added to water. The pH of the solution was adjusted to 1~2 by HCl, and thereafter about 12.6 mL formaldehyde was added again which was stirred continuously for 10~15 min. Soon afterwards, the reaction system was stood overnight in which the supernatant was poured off or drained by filtered and washed. And it was finally was vacuum dried and calcinated to obtain the PICA silica microspheres in this work.

Sample Preparation

Dried AR was crushed into powder. About 15 g of AR powder was placed into a beaker and added with deionized water to obtain a material-to-liquid ratio of 1:20. The mixture was stirred on a magnetic stirrer and subjected to hot extraction at 90℃ for 4 h. After water extraction, the sample was centrifuged, filtered, and then concentrated to 150 mL. Enzymatic hydrolysis (adding 200 U papain and reacting in a constant temperature water bath at 45℃ for 6 h) combined with the trichloroacetic acid method (adding 10% trichloroacetic acid to a total volume of 200 mL, placing the reaction system in an ice bath, stirring for 15 min, and then standing still for 30 min, centrifugation at 4,000 rpm for 15 min, discard the precipitate) was performed to remove protein. Anhydrous ethanol was added to a final alcohol concentration of 90%. The precipitate was collected and lyophilized to obtain crude polysaccharide powder for use.

The single factor and orthogonal test of enzymolysis of APS-II by endo α-1,4-glucanase results showed that the best enzyme degradation conditions were 0.5 U/mL (enzyme concentration), 60℃ (enzymolysis temperature), and 90 min (enzymolysis time). Approximately 2 ml of polysaccharide solution (1mg/mL) was mixed with 2 mL of endo α-1,4-glucanase solution (0.5 U/mL) and degraded at 60℃ for 90 min. After enzymolysis, the solution was inactivated by boiling water for 10 min. The supernatant was collected and freeze dried for the preparation of APOS.

Based on the previous work of our group, 10 g of Morinda officinalis medicinal materials were added to 100 mL water and reflow for 2 hours at 100 ℃. After solid-liquid separation, 100 mL water was added to 100 ℃ for reflow for 90 minutes, and the filtrate was combined.

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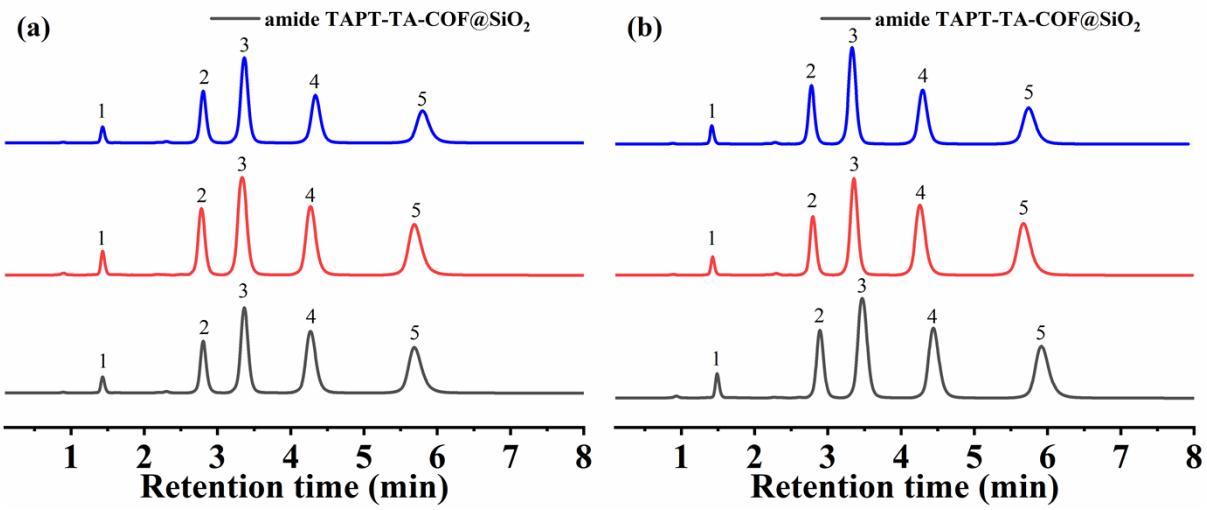

Fig. S1 Intra-day repeatability (a) and inter-day repeatability (b) of benzenes on the column packed with amide TAPT-TA COF@SiO_2 materials. Experimental conditions: analytes: (1) thiourea; (2) toluene; (3) ethylbenzene; (4) propyl benzene; (5) butylbenzene; mobile phase: ACN/Water (30/70, v/v); detection wavelength: 214 nm. Column size: 150 × 4.6 mm i.d.

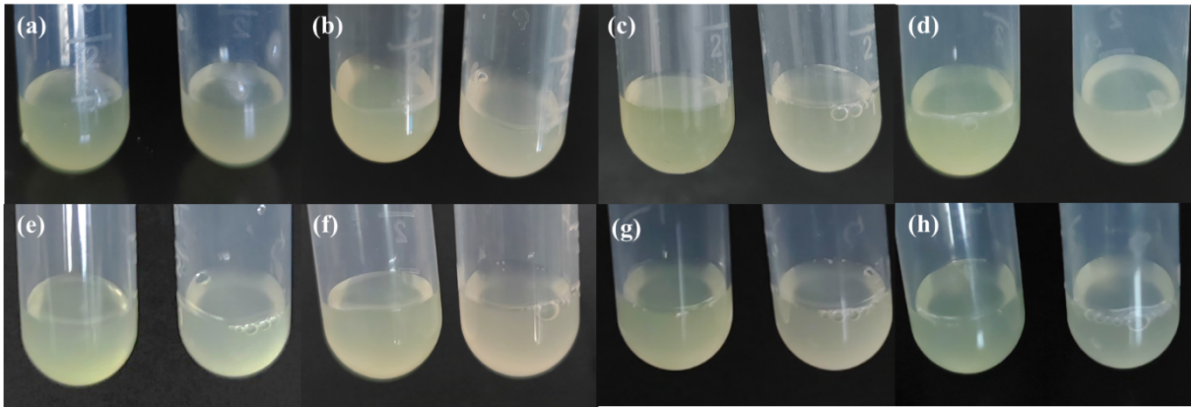

Fig. S2 Photographs of the soaking solution (pH=10) taken at intervals. (a) 0 h, (b) 6 h, (c) 12 h, (d) 18 h, (e) 24 h, (f) 30 h, (g) 42 h, (h) 54 h. The imine linked COF is photoed on the left, and the amide-linked COF is on the right.

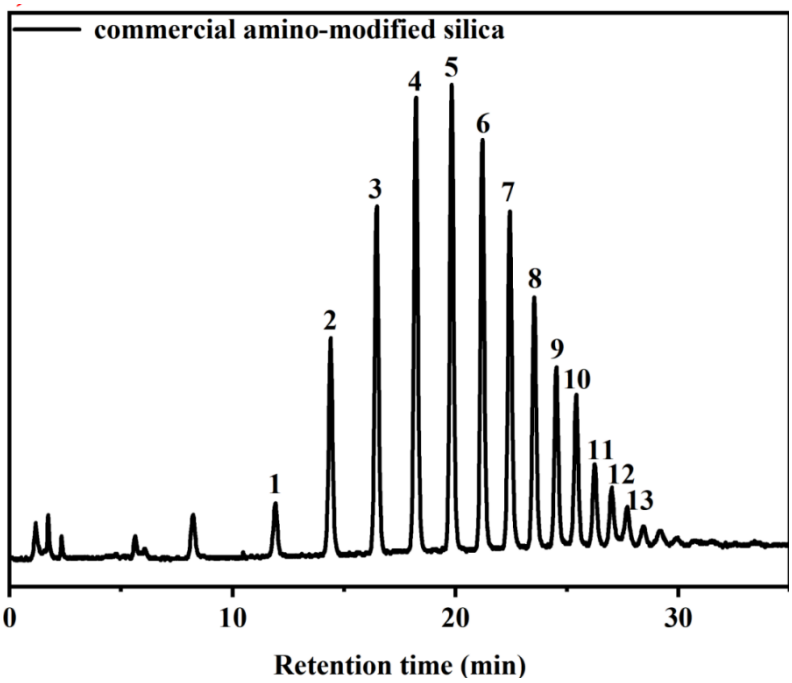

Fig. S3 Separation chromatography of commercial amino-modified silica gel column (4.6×150 mm). Chromatographic conditions: column temperature 25 °C, mobile phase A is water, B is acetonitrile, gradient elution program: 0~40 minutes, B 80%-50%; 40–50 minutes, B 50%-75%; detector: evaporative light scattering detector (nebulizer temperature 80°C), flow rate 1 mL/min. Peaks: 1~13 corresponding to Morinda officinalis oligosaccharides with degrees of polymerization 1~13.

Table S1 Particles S_{BET}, Pore size and Pore volume of the SiO_2, imine TAPT-TA COF@SiO_2 and amide TAPT-TA COF@SiO_2

Materials	Particles S_{BET} (m^2g^{-1})	Pore size (nm)	Pore volume (cm^3g^{-1})
SiO_2	204.12	9.18	0.49
imine TAPT-TA-COF@SiO_2	164.85	7.63	0.35
amide TAPT-TA-COF@SiO_2	156.67	6.94	0.31

Table S2 Chromatographic parameters of monosubstituted benzenes by amide TAPT-TA COF@SiO_2 column

Repeat time	Analyte	t_R	W	K	N_R/m	R
1	thiourea	1.430	0.162	-	15920	-
	toluene	2.805	0.242	0.962	24027	6.807
	ethylbenzene	3.371	0.293	1.357	25773	2.116
	propyl benzene	4.341	0.348	2.036	28927	3.027
	butylbenzene	5.802	0.460	3.057	28220	3.616
2	thiourea	1.441	0.136	-	18573	-
	toluene	2.792	0.267	0.938	30387	6.705
	ethylbenzene	3.340	0.331	1.318	30213	1.833
	propyl benzene	4.279	0.429	1.969	34000	2.471
	butylbenzene	5.690	0.470	2.949	31287	3.139
3	thiourea	1.418	0.174	-	17940	-
	toluene	2.790	0.311	0.968	25253	5.658
	ethylbenzene	3.346	0.367	1.360	23960	1.640
	propyl benzene	4.266	0.466	2.008	36313	2.209
	butylbenzene	5.665	0.480	2.995	28413	2.958

Table S3 Chromatographic parameters of separated phthalates by the imine TAPT-TA COF@SiO_2 column and amide TAPT-TA COF@SiO_2 column

Column (4.6*150 mm)	Analyte	t_R	W	K	N_R/m	R
imine TAPT-TA COF@SiO_2	dimethyl phthalate	2.304	0.250	0.234	26527	-
	diethyl phthalate	2.461	0.215	0.318	28127	0.675
	dicyclohexyl phthalate	2.632	0.260	0.410	24380	0.720
	dioctyl phthalate	4.055	0.298	1.172	36820	5.100
amide TAPT-TA COF@SiO_2	dimethyl phthalate	2.389	0.255	0.280	22567	-
	diethyl phthalate	2.620	0.310	0.403	24080	0.818
	dicyclohexyl phthalate	3.120	0.468	0.671	24093	1.285
	dioctyl phthalate	6.840	0.875	2.664	19060	5.540

Table S4 Chromatographic parameters for oligosaccharides of different polymerization degree at varying ACN content by the amide TAPT-TA COF@SiO_2 column

ACN%	Analyte	t_R	W	K	N_R/m	R
80%	glucose	2.668	0.153	0.429	31780	-
	maltose	3.280	0.190	0.757	30327	3.569
	raffinose	4.160	0.226	1.228	33647	4.231
	stachyose	5.871	0.310	2.145	34833	6.384
87%	glucose	3.493	0.192	0.871	33247	-
	maltose	5.361	0.373	1.871	20647	6.612
	raffinose	8.929	0.443	3.783	38300	8.745
	stachyose	18.948	0.869	9.149	35613	15.273

Table S5 Chromatographic parameters for oligosaccharides of Morinda officinalis separated by the amide TAPT-TA COF@SiO_2 column

Peak	t_R	W	K	N_R/m	R
1	2.019	0.167	-	15127	-
2	3.263	0.268	0.748	13713	5.720
3	4.229	0.237	1.265	32460	3.826
4	6.168	0.326	2.304	36600	6.888
5	8.131	0.365	3.355	49587	5.682
6	10.063	0.362	4.390	73267	5.315
7	11.868	0.404	5.357	91193	4.713
8	13.620	0.412	6.295	107160	4.294
9	15.186	0.430	7.134	128973	3.720
10	16.570	0.442	7.875	144267	3.174
11	17.814	0.443	8.542	146853	2.811
12	18.938	0.449	9.144	171147	2.520
13	19.942	0.422	9.681	201873	2.305

In the table S2-S5, the resolution between two compounds Rs was calculated as $Rs= 2(t_{R2}-t_{R1})/(W_{b1}+W_{b2})$. The t_R is representative for retention time of peaks. The W is the width of separating compounds. K is retention factor of separated compound. $N_{R/m}= (100/15) *16*(t_r/W)^2= (100/15) *5.54*(t_r/W_{1/2})^2$, where t_r is retention time, W is width of the peak, $W_{1/2}$ is half width of the peak.

Table S6 The synthesized SiO_2@COF used as stationary phases in previous works

Materials	Pore diameter (nm)	BET surface area（m^2/g）	Column size	Analytes	Column efficiency (Max, /m)	Ref
SiO_2@rLZU1	8-12	194	100×4.6 mm	Naphthalene	-	[1]
TAPT-TFPB COF@SiO_2	8.1	77.2	150×4.6 mm	4′ - methylpropiophenone	23460	[2]
SiO_2@COF	-	306.0	150×4.6 mm	aniline	-	[3]
SiO_2@TpBD-$(OH)_2$	8	268.52	150×4.6 mm	propyl benzene	32753	[4]
AVI-(TPB-DVA COF) @SiO_2	12.20	157.6	150×4.6 mm	prednisone	31194	[5]
TAPT-TP-COF@SiO_2	11.8	148.2	150×4.6 mm	sulfanilamide	35787	[6]
Amide TAPT-TA-COF@SiO_2	6.9	156	150×4.6 mm	benzene	40000	This work

It can be seen from the table S6 in this work that COF was successfully bonded onto the silica (2.4-5 μm, 90 A). Column efficiency was higher than the previous reported work. Also, this COF synthesized by this simple method demonstrated improved hydrophilic performance and provide a anal method for saccharide separation.

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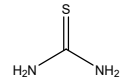
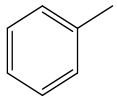
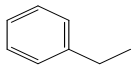
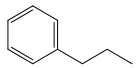
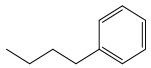
Table S7 The structural formula of the partial separated substances

Monosubstituted benzene					
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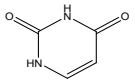
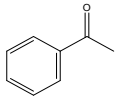
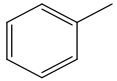
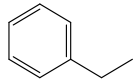
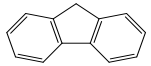
Alkylbenzenes					
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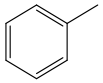
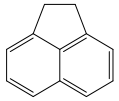
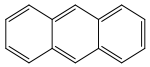
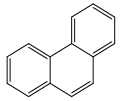
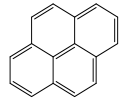
PAHs					
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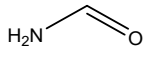
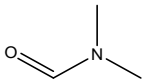
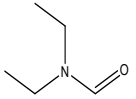
Formamides					
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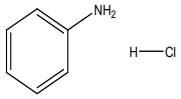
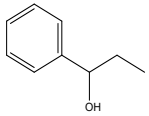
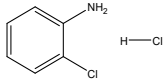
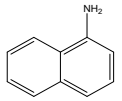
Anilines					
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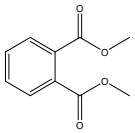
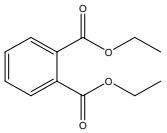
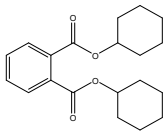
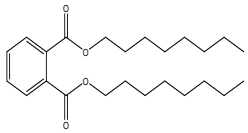
Phthalates					
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