SUPPORTING INFORMATION

Spatially-directed Magnetic Molecularly Imprinted Polymers with Good Anti-interference for Simultaneous Enrichment and Detection of Dual Disease-related Bio-indicators

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1. Instrumentation

Images of transmission electron microscopy were obtained using a JEM-2100 transmission electron microscope (TEM, JEOL Co., Japan). Hysteresis loops were acquired by a 9600-1 vibrating sample magnetometer (VSM, LDJ Co., USA) for testing the magnetic properties of resultant materials. X-ray diffraction patterns were recorded with a Rigaku D/max/2500v/pc X-ray diffractometer (Rigaku Co., Japan) with Cu *K*α radiation to identify the crystalline phase of nanomaterials. A Nicolet AVATAR-330 Fourier-transform infrared spectrophotometer (FTIR) (Thermo Electron Co. USA) was utilized by the KBr pressing method. An automatic elemental analyzer (EL, EUROVECTOR EA3000, Italy) was used to obtain elemental contents. The HPLC analyses were conducted using a Hitachi L-2130 HPLC system (Japan) equipped with a binary pump, an ultraviolet detector, and a C18 chromatographic column (150 mm×4.6 mm, 5 μm, Shimadzu, VP-ODS). The optimized mobile phase was acetonitrile-ultrapure water (5:95, v/v) with regular flow rate of 0.5 mL/min and injection volume of 10 μL. The column temperature was 40 °C，and the detection wavelength was operated at 283 nm.

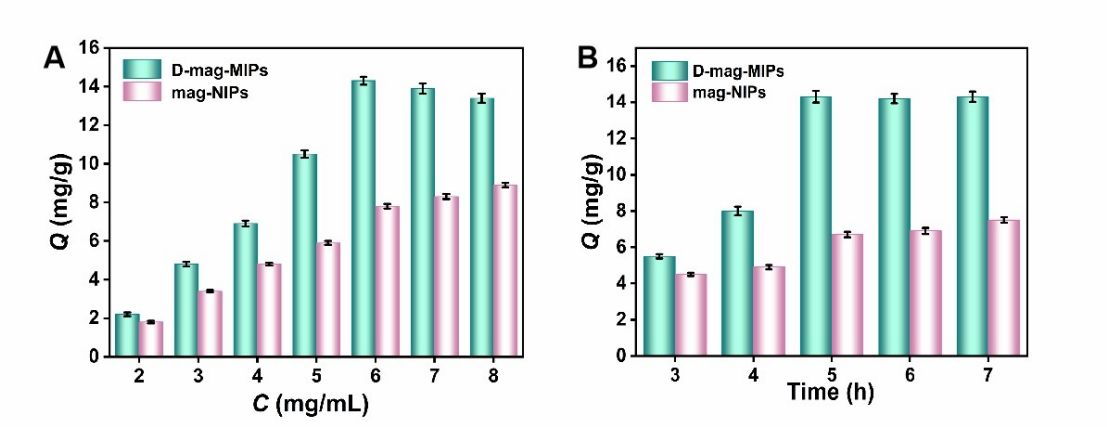

Fig. S1. The effect of the amount of PEI (A) and polymerization time (B) on the imprinting performance of D-mag-MIPs and mag-NIPs towards DOPAC.

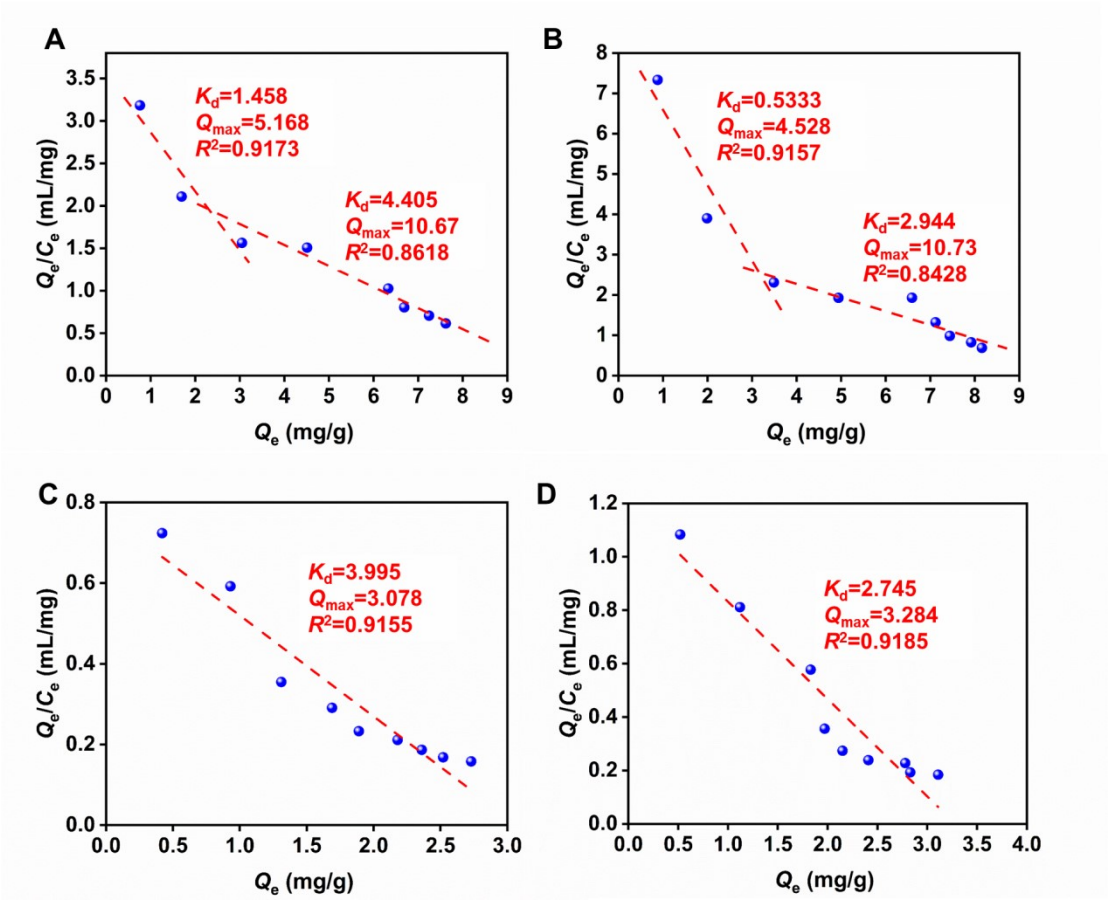

Fig. S2. Scatchard plots for D-mag-MIPs towards DA (A) and DOPAC (B). Scatchard plots for mag-NIPs towards DA (C) and DOPAC (D).

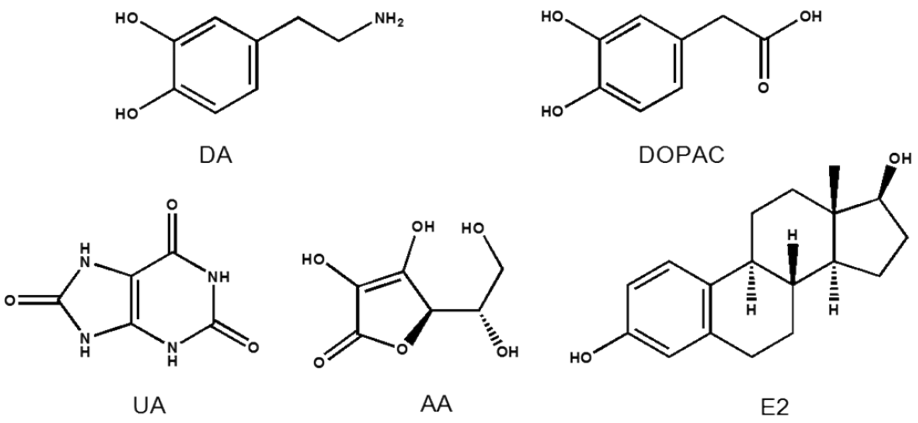

Fig. S3. Chemical structures of DA, DOPAC, and their coexisting competitors.

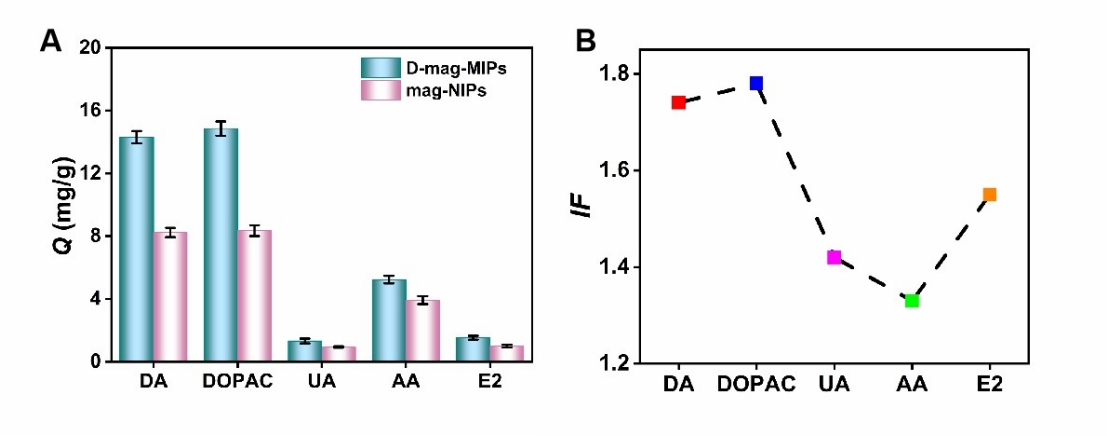

Fig. S4. Selective adsorption capacity (A) and *IF* (B) of D-mag-MIPs and mag-NIPs towards different compounds in the single solutions.

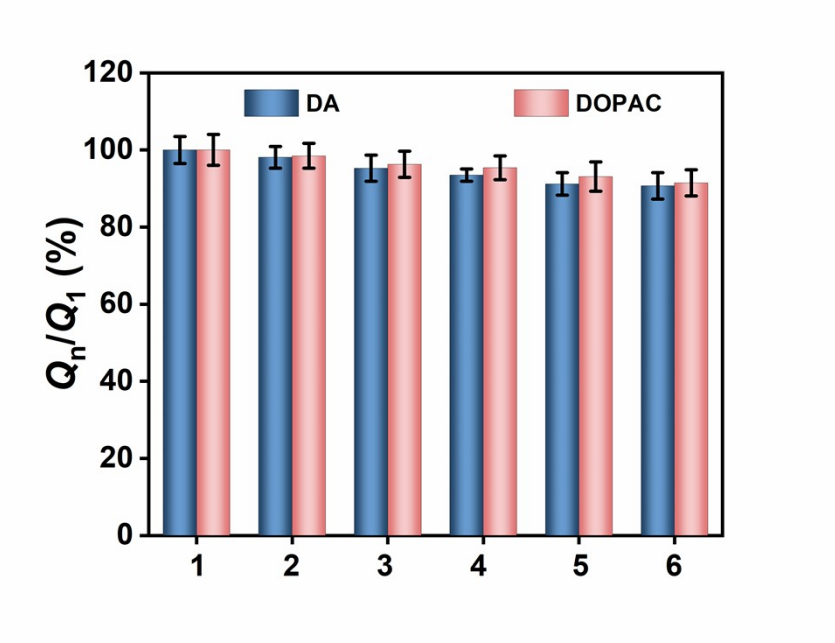

Fig. S5. The reusability test of D-mag-MIPs after six adsorption-desorption cycles.

To assess the reusability, which is of great importance when it comes to transitioning from lab scales to any realistic practical applications, we performed six adsorption-desorption cycles on the same D-mag-MIPs (Fig. S5). The adsorption capacities of D-mag-MIPs for DA and DOPAC show a slight decrease after 6 cycles, likely due to the minor destruction of imprinted cavities caused by the ethanol-HAC (98:2, v/v) eluent used to remove the adsorbed templates by disruption the interaction between templates and functional monomer. However, it still maintains above 91% of the initial adsorption amount, revealing that D-mag-MIPs are stable and possess good reusability in applications.

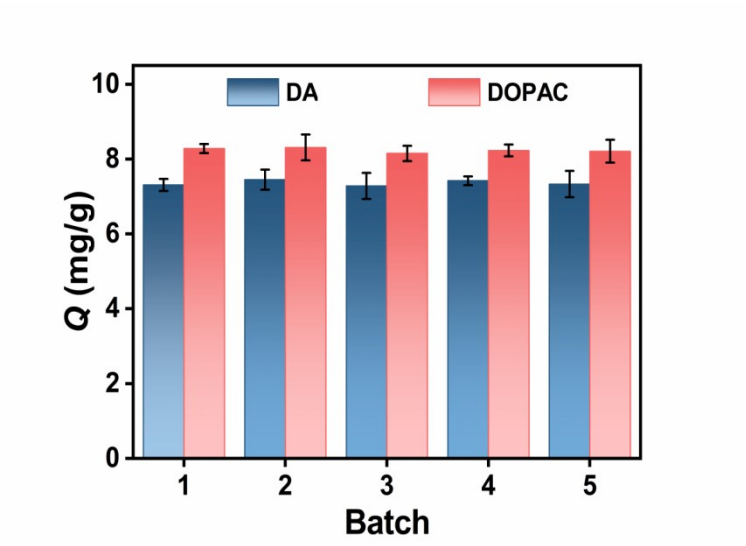

Fig. S6. The reproducibility of D-mag-MIPs prepared in five batches.

To investigate the long-term utilization of D-mag-MIPs, the reproducibility of obtained nanomaterials were tested. Five different batches of D-mag-MIPs were synthesized on different days. The adsorption of DA and DOPAC on each batch of nanomaterials was performed by five times independently (Fig. S6). The average Q values of the different batches of D-mag-MIPs towards DA and DOPAC are found to be 7.35 and 8.24 mg/g with RSD <5.5% and 6.2%, respectively. These results demonstrate that D-mag-MIPs possess satisfactory reproducibility, indicating the satisfactory stability of the prepared nanomaterials.

77 **Table S1** The adsorption kinetic constants for pseudo-first-order and pseudo-second-

78 order rate kinetic models of D-mag-MIPs.

Sorbents	Targets	Pseudo-first-order		Pseudo-second-order		
		R^2	k_1 （/min）	R^2	k_2 （g/mg·min）	v_0 (mg/g·min)
D-mag-MIPs	DA	0.8631	0.5977	0.9563	0.0296	3.292
	DOPAC	0.9068	0.5370	0.9775	0.0473	5.030

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Table S2. Adsorption equilibrium constants for *Langmuir* and *Freundlich* isothermal fitting constants of D-mag-MIPs.

Sorbents	Targets	$Q_{e,E}$ (mg/g)	*Langmuir* isothermal equation			*Freundlich* isothermal equation		
			R^2	$Q_{m,L}$ (mg/g)	K_L(mL/mg)	R^2	K_F(mL/mg）	n
D-mag-MIPs	DA	7.52	0.9936	8.7873	0.3671	0.9352	2.0422	0.5268
	DOPAC	8.16	0.9967	9.0334	0.6123	0.9396	2.8035	0.4473

$Q_{e,E}$ is the experimental value of Q_e;

$Q_{m,L}$ is the calculated value of Q_e by *Langmuir* isotherm equation.

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87 **Table S3.** The performance parameters of D-mag-MIPs-HLPC method for DA and

88 DOPAC detection. (*n*=5)

Analyte	Linearity range (μg/mL)	R^2	RSD (%)		LOD (μg/mL)	LOQ (μg/mL)
			intra-day	inter-day		
DA	0.10-100	0.9981	1.5-3.3	2.8-3.9	0.020	0.065
DOPAC	0.10-100	0.9987	1.6-3.1	2.3-3.6	0.031	0.096

Table S4. Comparison with other methods for detection of DA or DOPAC.

Analytical system	Linear range (μg/mL)	RSD (%)		$LOD_{DA/DOPAC}$ (μg/mL)	Spiking concentration (μg/mL)	Sample	Recovery (%)	RSD (%)	Reusability	Magnetic Separation	Ref.
		intra-day	inter-day								
GEM[a]	0.61-15.3	--	--	0.404 / --	--/--	--	--/--	--/--	--	No	[35]
CS/N,GODs@SPCE[b]	0.16-15.3	0.9	--	0.023/ --	4.5	Human urine	~ 100	2.0	94.5 (after 1 month)	No	[36]
DE-MIPs[c]	0-0.183	--	--	0.023/--	3.0,1.2, 45.9, 91.8	Human serum	100.1-103.8	3.6-4.9	--	No	[37]
MISPE-HPLC-FL[d]	0.15-2.23	2.2-4.6	1.6-4.7	0.025/ --	0.15, 0.3, 0.76, 1.5, 2.3	Human urine	98.3-101.1	--	--	No	[38]
D-mag-MIPs-HPLC-UV	0.1-100	1.5-3.1	2.3-3.9	0.020/ 0.031	0.1, 1.0, 5.0	Human urine	95.5-98.6	2.7-5.1	91.0 (after 6 cycles)	Yes	This work

a: Graphene modified electrode.

b: Nitrogen-doped graphene quantum dots-chitosan nanocomposite-modified nanostructured screen printed carbon electrode.

c: Dual-emission fluorescent molecularly imprinted polymers.

d: Molecularly imprinted solidphase extraction.