

## **Electronic Supporting Information**

for

**Proton sponge-functionalized silica as high performance adsorbents for solid-phase extraction of trace perfluoalkyl sulfonates in the environmental water samples and their direct analysis by MALDI-TOF-MS**

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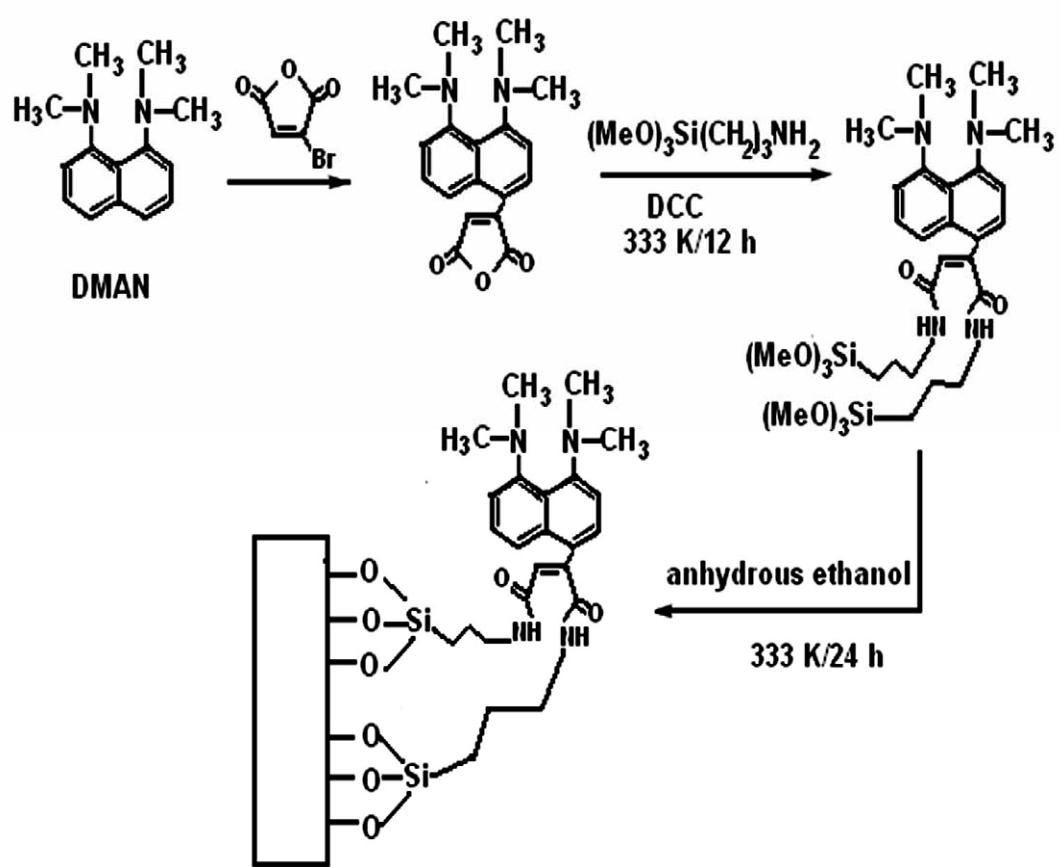
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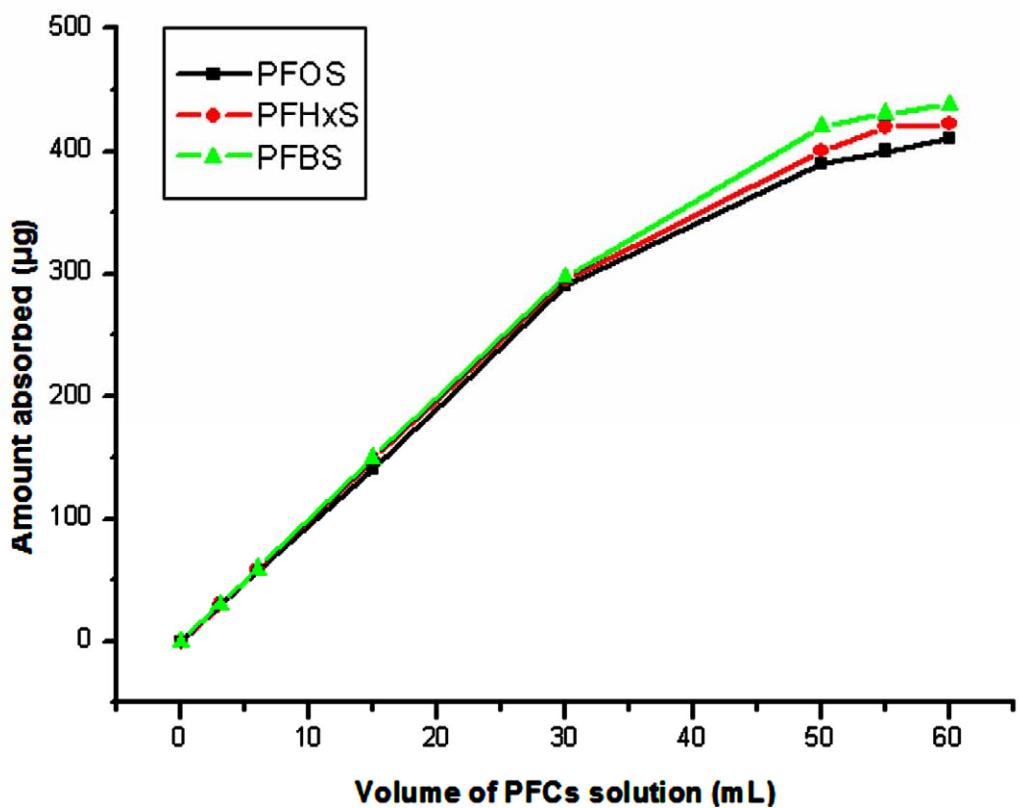
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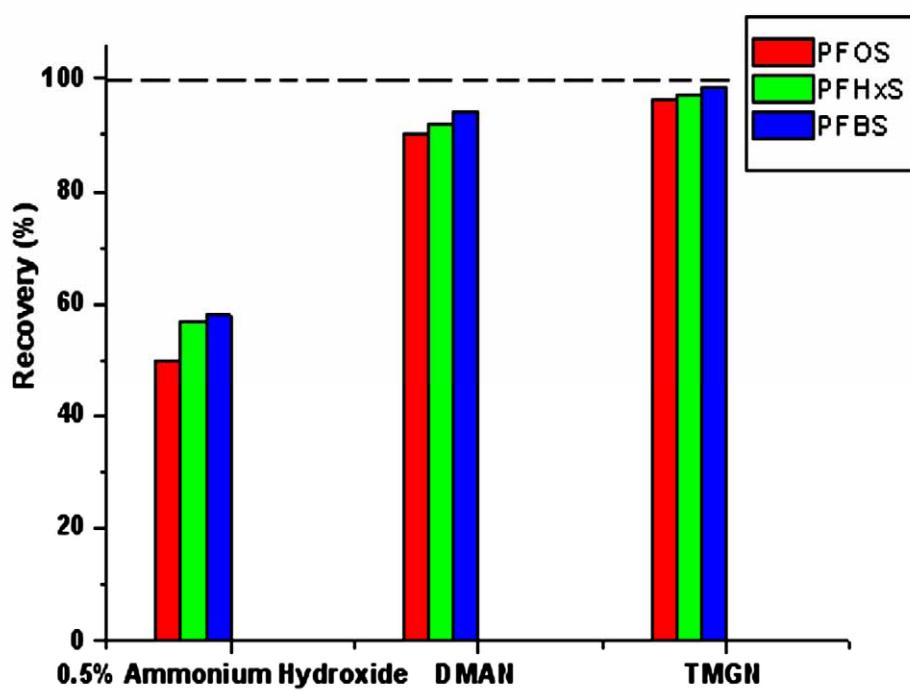
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**Scheme S1.** The scheme of DMAN functionalization



**Fig. S1** Determination of the adsorption capacity of PFSSs on DMAN@silica adsorbent.



**Fig. S2** The effect of eluted solution on the recovery of PFSSs.

**Table S1 Matrix effect of environmental water samples on the recovery of PFSSs in 500 mL water samples spiked with standards of PFSSs at two different concentration levels (n=3).**

Water samples	PFOS recovery %	PFHxS recovery %	PFBS recovery %
	(RSD % (n=3))	(RSD % (n=3))	(RSD % (n=3))
<i>Spiked Concn at 2 ng L<sup>-1</sup></i>			
Deionized water	91 (8)	93 (12)	96 (14)
Tap water	89 (10)	92 (6)	94 (9)
Gaobeidian wastewater	82 (8)	79 (12)	88 (10)
Xiaoqinghe river water	85 (6)	90 (9)	89 (13)
<i>Spiked Concn at 8 ng L<sup>-1</sup></i>			
Deionized water	98 (9)	105 (7)	99 (10)
Tap water	102 (12)	98 (15)	99 (12)
Gaobeidian wastewater	78 (16)	119 (11)	87 (13)
Xiaoqinghe river water	90 (8)	86 (11)	106 (16)

**Table S2** Mean concentrations  $\pm$  standard deviation ( $n = 3$ ) of PFSs detected in real water samples, and the spiked recovery of PFSs obtained by spiking the target analytes.

Water samples	PFOS Background conc. (ng L <sup>-1</sup> , n=3)	PFHxS Background conc. (ng L <sup>-1</sup> , n=3)	PFBS Background conc. (ng L <sup>-1</sup> , n=3)
	<sup>a</sup> Spike recovery (% , n=3)	Spike recovery (% , n=3)	Spike recovery (% , n=3)
Detected by MALDI-TOF-MS			
Tap water	0.30 $\pm$ 0.10 98 $\pm$ 6	0.50 $\pm$ 0.09 90 $\pm$ 9	nd <sup>b</sup> 102 $\pm$ 7
Gaobeidian wastewater	3.31 $\pm$ 0.09 89 $\pm$ 6	1.19 $\pm$ 0.10 80 $\pm$ 9	1.16 $\pm$ 0.08 83 $\pm$ 12
Xiaoqinghe river water	1.05 $\pm$ 0.10 90 $\pm$ 8	0.86 $\pm$ 0.06 83 $\pm$ 9	nd 109 $\pm$ 6
Detected by LC-MS/MS [40]			
Tap water	nd 112 $\pm$ 4	na <sup>c</sup>	na
Gaobeidian Wastewater	3.22 $\pm$ 0.02 63 $\pm$ 2	na	na
Xiaoqinghe river water	0.96 $\pm$ 0.06 65 $\pm$ 6	na	na

<sup>a</sup> Recoveries obtained by spiking with the target analytes (1.0 ng L<sup>-1</sup>).

<sup>b</sup> Not detected.

<sup>c</sup> Not analyzed.