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Supporting Information

Constructing Synergistic Groups in Porous Aromatic Frameworks for Selective Removal and Recovery of Lead(II) Ions

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Experiment section:

Preparation of the imprinted complex: Pb^{2+} imprinted complex was obtained by mixing 2.5 mmol lead (II) nitrate with 5 mmol methacrylic acid and 5 mmol 4-vinylpyridine into 30 mL double deionized water. This mixture was stirred for 24 hours, and the imprinted complex was isolated by removing the water under vacuum.

Synthesis of MIPAFs: the imprinted complex and divinylbenzene were added into the mixing solution of 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (0.375 mmol) and K_2CO_3 (1.5 mmol) in 15 mL N,N-dimethylformamide (DMF). The molar ratio of vinyl group was 0:10, 1:9, 2:8, 3:7 and 4:6 to produce PAF-10a, PAF-10b, PAF-10c, PAF-10d, and PAF-10e, respectively; the total amount of vinyl group is 1.5 mmol. After three freeze–pump–thaw degassing cycles, tetrakis(triphenylphosphine)palladium was added into the suspension, which was followed by three more freeze–pump–thaw degassing cycles. The system was then heated to 80 ^{o}C for 48 h and then heated to 120 ^{o}C for 72 h. After cooling the residue to room temperature, it was then filtered and washed with $CHCl_3$ (30 mL * 5), THF (30 mL * 5) and H_2O (30 mL * 5), respectively. The product was then treated with HNO_3 (0.5 mol L^{-1}) to remove the Pb^{2+} ions.

Ion sorption experiment: 10 mg PAF sample was added into 40 mL Pb^{2+} water solution (60 ppm) at pH ~ 7. After continuous stirring, Pb^{2+} concentrations at 1, 2, 4, 6, 10, 16, 20, 30, and 40 min in resulting solutions were analyzed by ICP element analysis.

Selectivity examination: 10 mg PAF powder was stirred into 40 mL of Pb^{2+} ion (60 ppm) solution with various inorganic cations (2 ppm, Li^{+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+} and CrO_4^{2+}) at pH ~ 7. After 60 min, each element was valued by ICP element analysis.

Preparation of PAF/polymer film: 200 mg poly(methyl methacrylate) (PMMA) was dissolved in 10 mL CH_2Cl_2 by 12 hours sonication. 132 mg PAF-10d was added in the mixture and stirred for 12 hours. Then the homogeneous solution was poured into the polymer pipe (internal diameter is 3 * 10^{-3} m, exteranl diameter is 3.5 * 10^{-3} m and the length is 3 m). After 24 hours' standing, the pipe with ~ 150 mg PAF-10d composite can be gained.

Reusability test: 20 mL of Pb^{2+} ion (20 ppm) solution with interfering species (2 ppm, Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+} and CrO_4^{2+}) at pH ~ 7 is introduced into the internal of polymer pipe at 1.0 mL min^{-1}. The ion concentrations in the resulting solution were measured by ICP analysis. Then the elution operations were carried out by introducing 100 mL HNO_3 (0.5 mol L^{-1}) for three times to remove the Pb^{2+} ions. The composite pipe could undergo 10 cycles of repeated experiments without any loss of activity.

Physical measurements: TGA was measured on the Netzch Sta 449c thermal analyzer at the 10 °C min^{-1} heating rate in air atmosphere. FT-IR measurements were performed on the Nicolet Impact 410 Fourier transforms infrared spectrometer. N_2 adsorption isotherms and pore size distribution were obtained on the Micromeritics ASAP 2010M analyzer. XRD patterns were carried out on the Riguku D/MAX2550 diffractometer using Cu-Kα radiation, 40 kV, 200 mA. TEM images were measured on the JEOL JEM 3010. SEM was implemented on the JEOS JSM 6700.

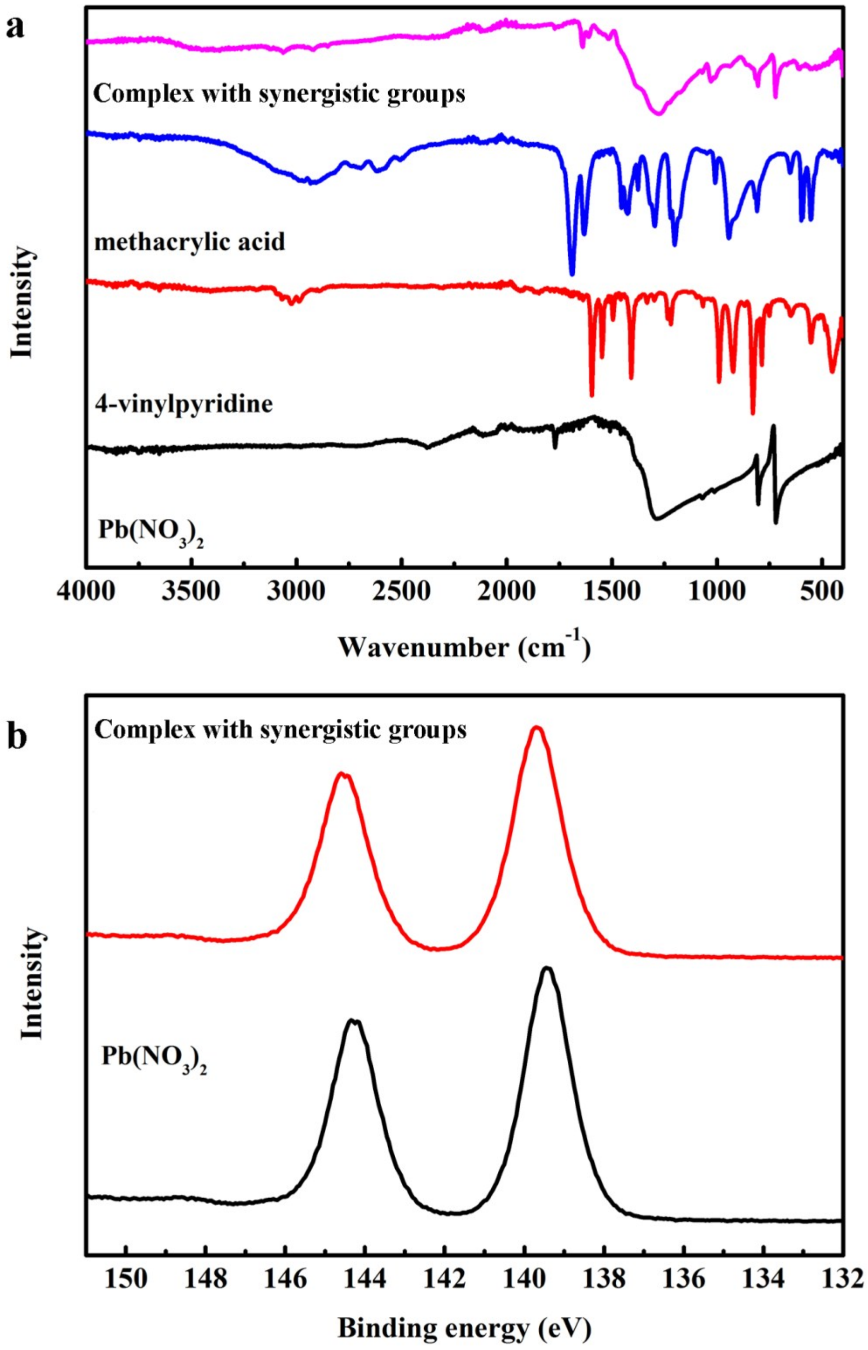

Fig. S1 (a) FT-IR spectra of $Pb(NO_3)_2$, 4-VP, MAA, and imprinted complex. (b) XPS spectra of imprinted complex and $Pb(NO_3)_2$.

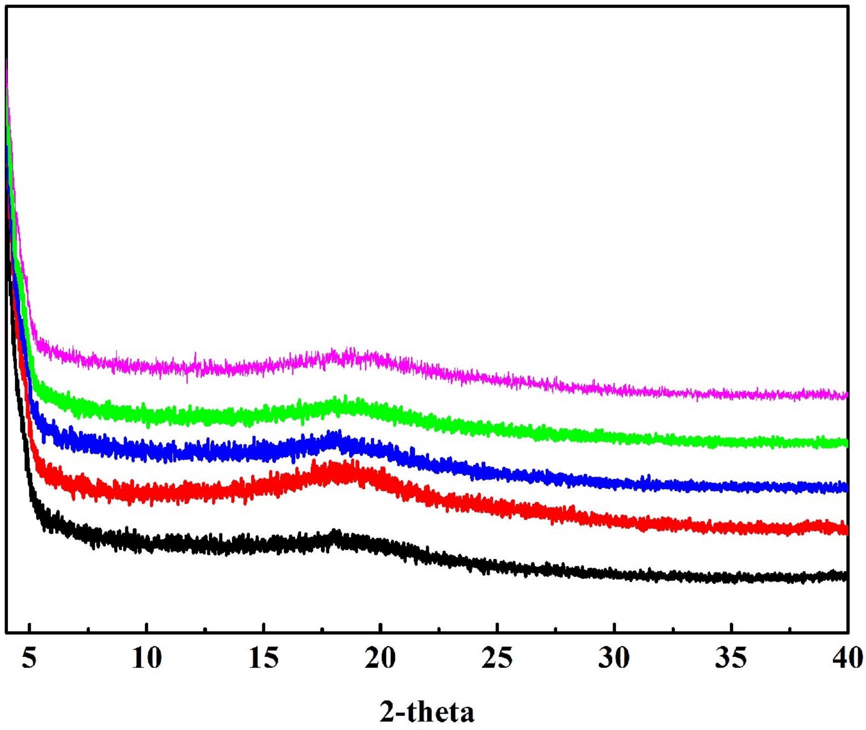

Fig. S2 Powder X-ray diffraction patterns of PAF-10a (black), PAF-10b (green), PAF-10c (red), PAF-10d (blue) and PAF-10e (pink), respectively.

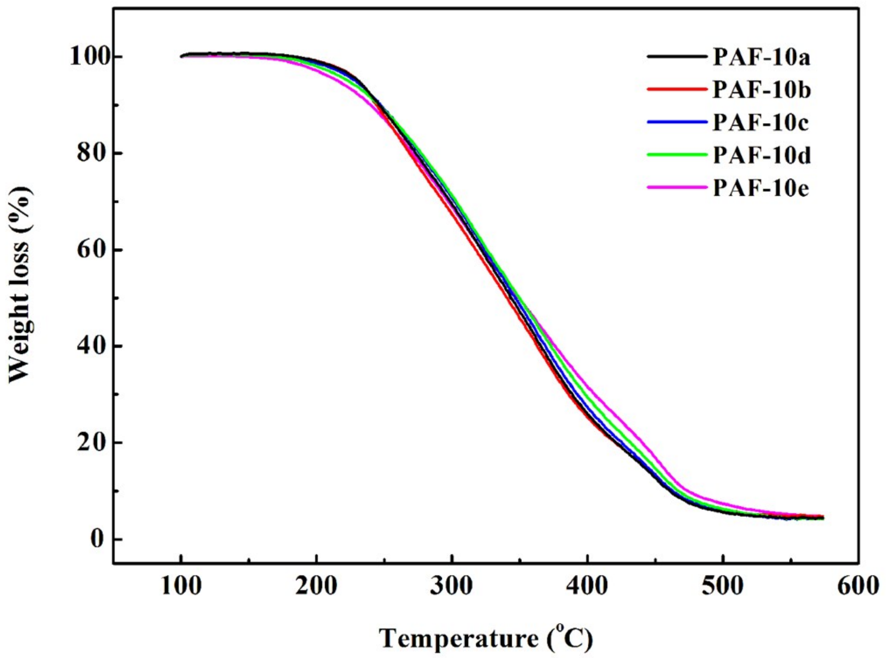

Fig. S3 TGA plots for PAFs at air condition with the rate of 5 °C min^{-1}.

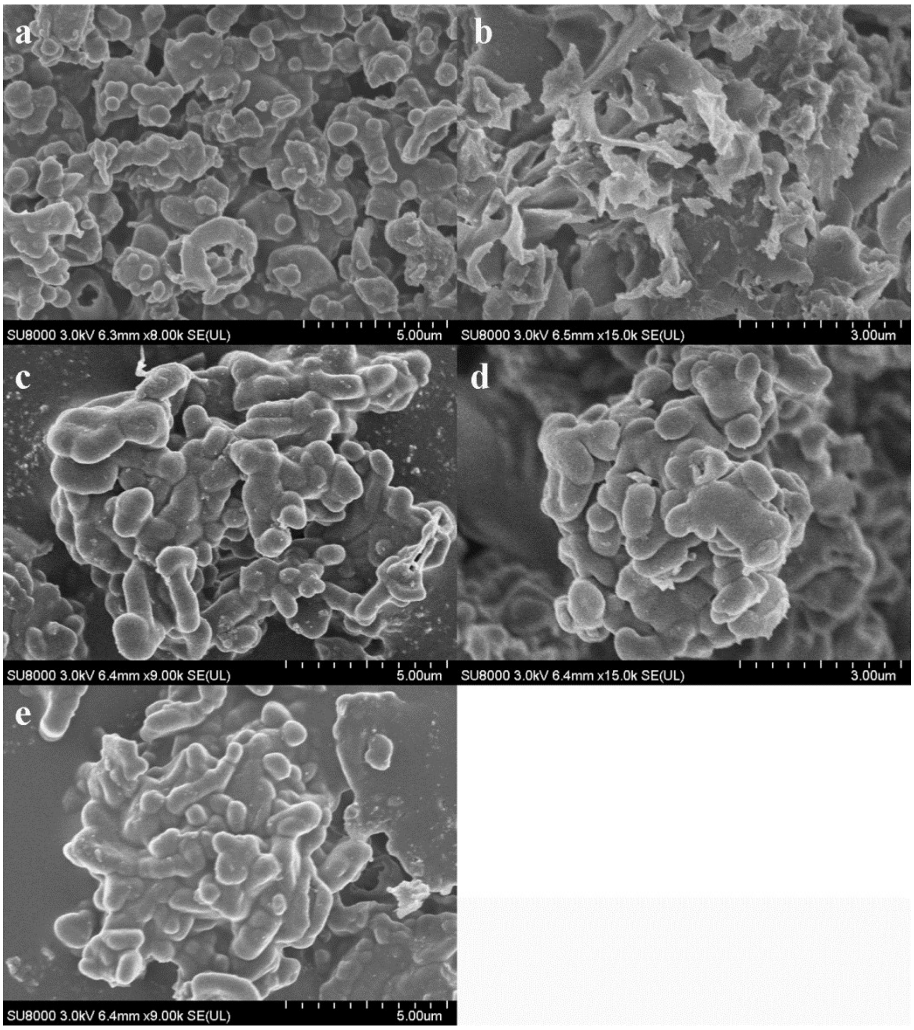

Fig. S4 SEM images of PAF-10a (a), PAF-10b (b), PAF-10c (c), PAF-10d (d) and PAF-10e (e), respectively.

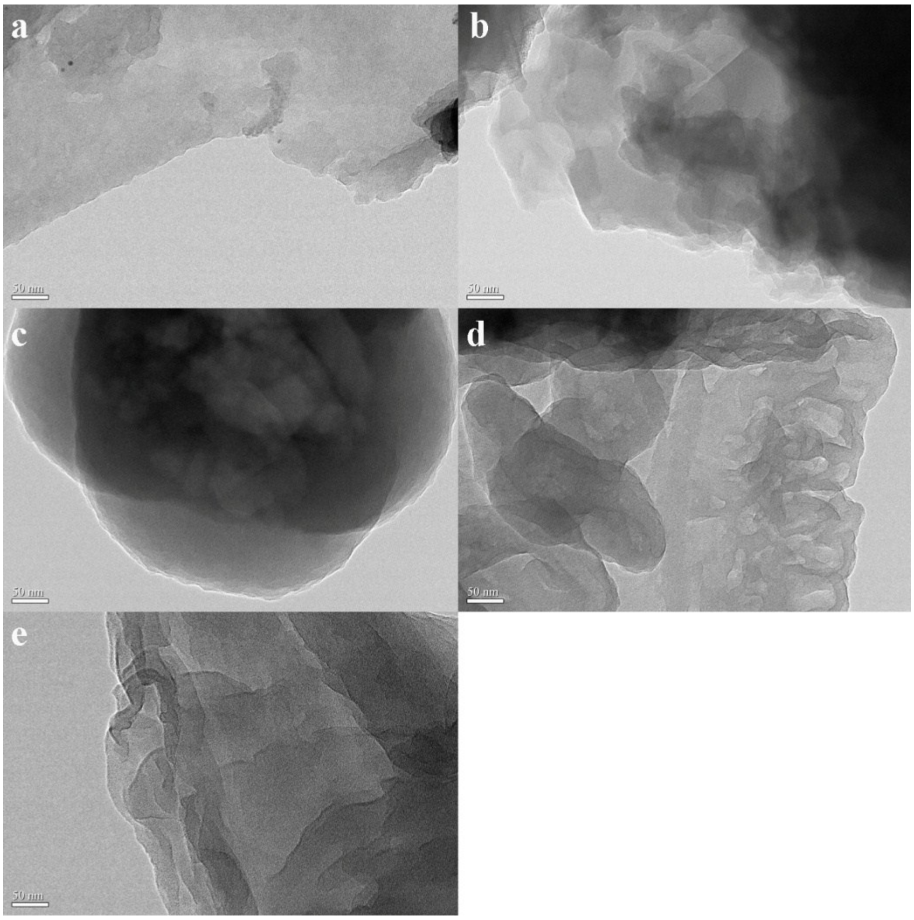

Fig. S5 HRTEM images of PAF-10a (a), PAF-10b (b), PAF-10c (c), PAF-10d (d) and PAF-10e (e), respectively.

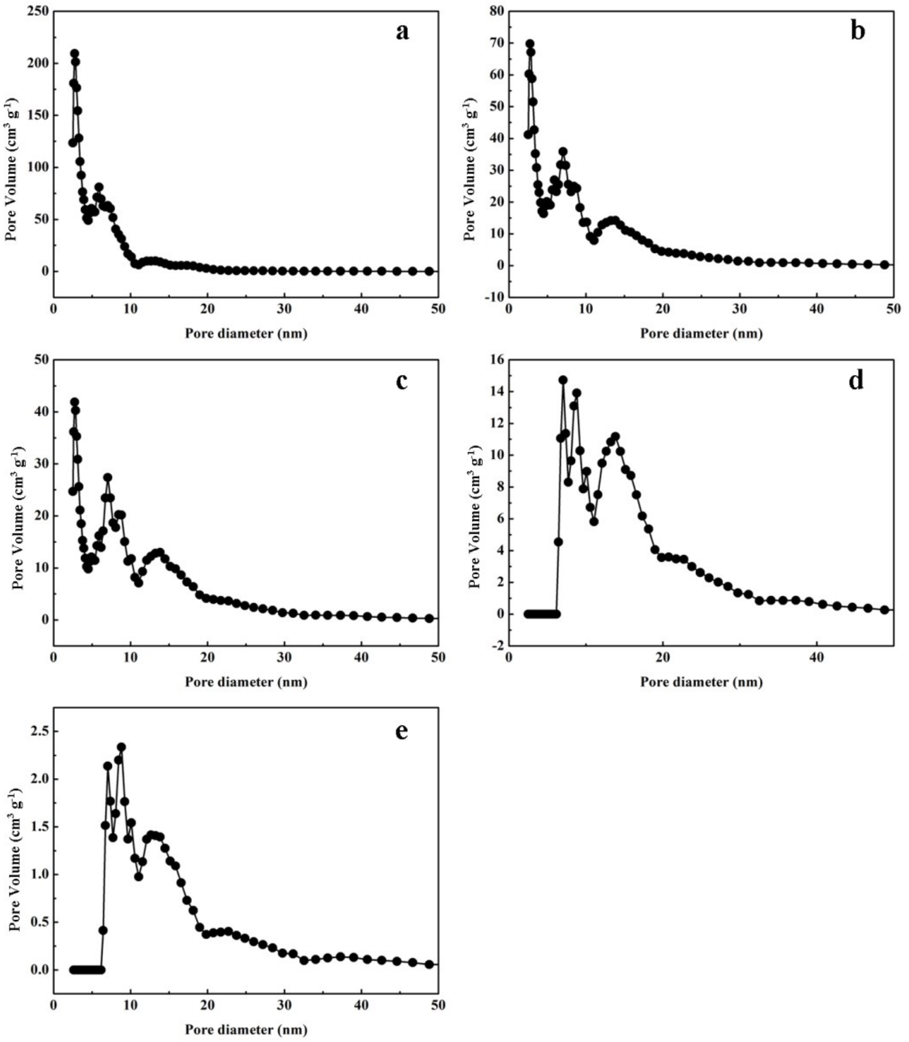

Fig. S6 DFT pore size distributions of PAF-10a (a), PAF-10b (b), PAF-10c (c), PAF-10d (d) and PAF-10e (e), respectively.

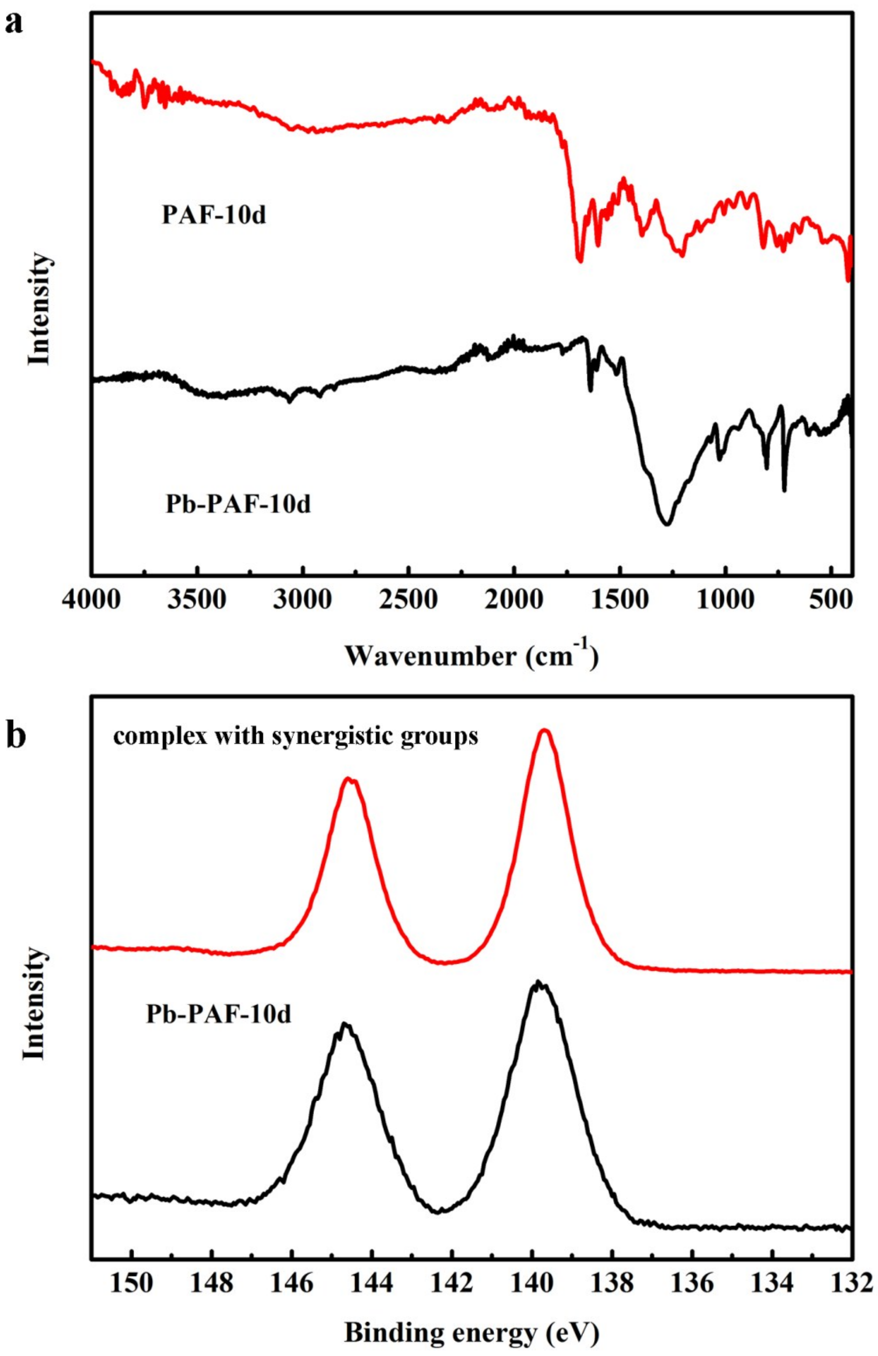

Fig. S7 (a) FT-IR and (b) XPS spectra of PAF-10d and Pb-PAF-10d.

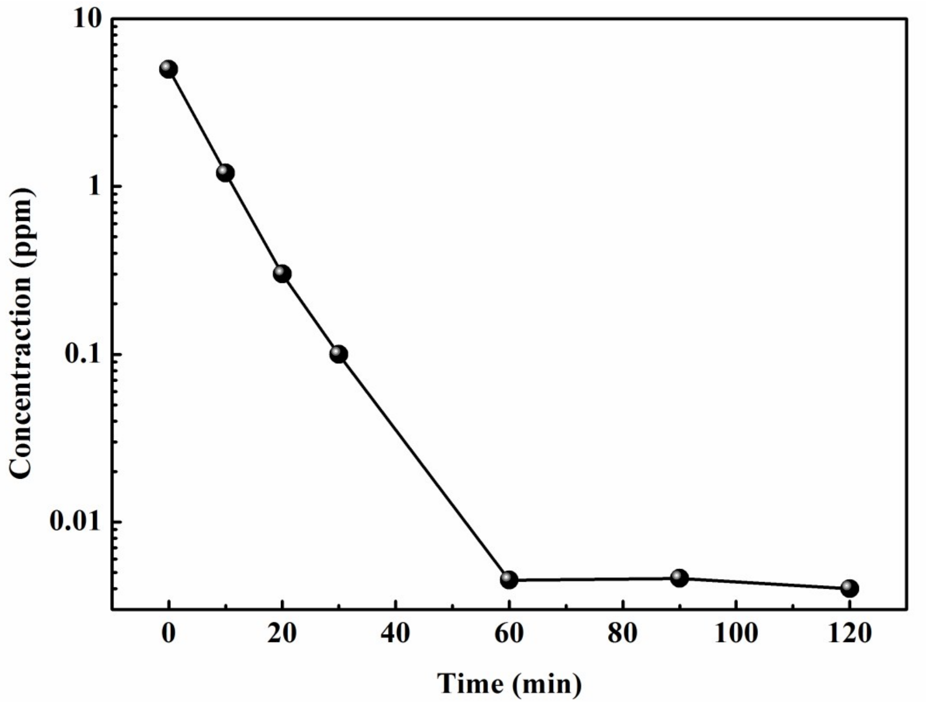

Fig. S8 Pb^{2+} sorption kinetics over PAF-10d.

Synthesis of traditional MIP

$Pb(NO_3)_2$ (2.5 mmol) was dissolved in 30 mL of DDI water, followed by adding MAA and 4-VP as functional monomers individually at 5 mmol. Then, EGDMA (20 mmol) and 2,2'-Azobis-(isobutyronitrile) AIBN (40 mg) were added in the mixing solution. The solution was degassed for 10 min in an ultrasonic bath and then was purged for 15 min with nitrogen, followed by cooling for 15 min in an ice bath. The polymerization reaction was carried out at 50 °C for 6 h in a water bath, and then at 60 °C for 8 h. The resultant polymer particles were filtered first and then washed with acetone/water (1:1, v/v) several times to remove the residual monomers and cross-linker. Then the particles were dried for 24 h to constant weight in vacuum. The product was treated with 0.5 mol/L HNO_3 under vigorous stirring to remove the Pb^{2+} ions. At last, the polymers were washed with DDI water to neutral and were dried in vacuum.

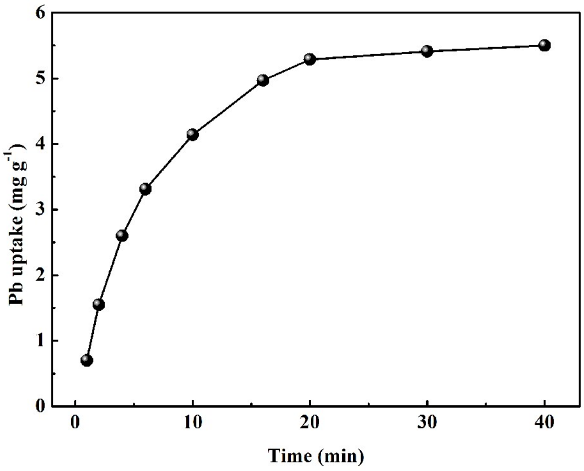

Fig. S9 Pb^{2+} ion adsorption isotherm for MIP.

Synthesis of traditional NPAF material

0.22 mmol methacrylic acid, 0.22 mmol 4-vinylpyridine and 1.05 mmol divinylbenzene were added into the mixing solution of 2,2',7,7'-tetrabromo-9,9'-spirobifluorene (0.375 mmol) and K_2CO_3 (1.5 mmol) in 15 mL N,N-dimethylformamide (DMF). After three freeze–pump–thaw degassing cycles, tetrakis(triphenylphosphine) palladium was added into the suspension, which was followed by three freeze–pump–thaw degassing cycles. The system was then heated to 80 °C for 48 h and then heated to 120 °C for 72 h. After cooling the residue to room temperature, it was filtered and washed with $CHCl_3$ (30 mL * 5), THF (30 mL * 5) and H_2O (30 mL * 5), respectively. The product was then treated with HNO_3 (0.5 mol L^{-1}) to remove the Pb^{2+} ions to give NPAF material.

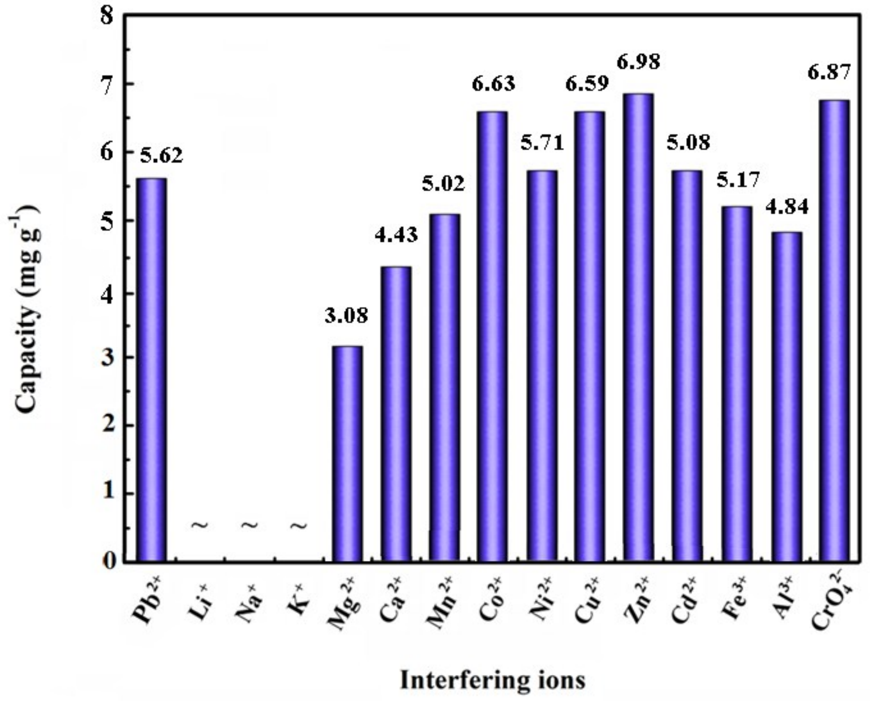

Fig. S10 Pb^{2+} adsorption isotherm for NPAF material.

Table S1. Element analysis of PAF materials.

Sample		C	H	N	O	Pb
PAF-10a	Theoretical value	95.4%	4.6%	0	0	0
	Actual value	92.5%	5.9%	0.5%	1.1%	0
PAF-10b	Theoretical value	94.4%	4.5%	0.3%	0.8%	0
	Actual value	91.5%	5.3%	0.9%	2.3%	0
PAF-10c	Theoretical value	93.4%	4.5%	0.6%	1.5%	0
	Actual value	91.4%	5.5%	1.2%	1.8%	0.1%
PAF-10d	Theoretical value	92.4%	4.6%	0.9%	2.1%	0
	Actual value	90.3%	5.8%	1.4%	2.4%	0.1%
PAF-10e	Theoretical value	91.5%	4.6%	1.2%	2.7%	0
	Actual value	89.4%	5.1%	1.6%	2.4%	1.5%

Table S2. Ion capture experiments of PAF materials.

Sample	Molecularly imprinted site	Calculated ion capacity	Experimental ion capacity	Utilization level
PAF-10b	$1.70*10^{-4}$ mol g^{-1}	35.22 mg g^{-1}	33.81 mg g^{-1}	96 %
PAF-10c	$3.33*10^{-4}$ mol g^{-1}	69.00 mg g^{-1}	62.79 mg g^{-1}	91 %
PAF-10d	$4.90*10^{-4}$ mol g^{-1}	101.53 mg g^{-1}	90.36 mg g^{-1}	89 %
PAF-10e	$6.40*10^{-4}$ mol g^{-1}	132.61 mg g^{-1}	75.59 mg g^{-1}	57 %