Supporting Information

Exfoliated layered copper phosphonate showing enhanced adsorption capability towards Pb ion

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Experimental section

Materials and methods. All reagents and solvents were commercially available and were used without further purification. Elemental analyses were performed on an Elementar Vario MICRO elemental analyzer. IR spectra were recorded on a Bruker Tensor 27 spectrometer in the spectral range 4000-400 cm⁻¹ using the KBr disk. Thermogravimetric analyses were carried out on a Mettler–Toledo TGA/DSC1 instrument under a nitrogen flow. Powder X-ray diffraction (PXRD) data were recorded on a D8 advance X-ray diffractometer with Cu–K α radiation ($\lambda = 1.54056$ Å) at room temperature. Atom force microscope (AFM) measurements were carried out on VEECO Inc Multimode V. Scan electron microscopy (SEM) measurements were performed on SHIMADZU SSX-550. Inductively Coupled Plasma (ICP) experiments were performed on PE Optima 5300 DV.

Synthesis of 5-(2-bromothienyl)phosphonic acid (2-BTPH₂). 2-BTPH₂ was synthesized according to the method in the previous report¹ which was shown in Scheme S1. A 250 mL three-necked round bottomed flask was charged with 1.5 g (11.6 mmol) of anhydrous NiCl₂ and 102 mL (840 mmol) of 2,5-dibromothiophene. A reflux condenser was attached and the system was purged with nitrogen. The flask was heated to 160 °C on an oil bath, and then 49 mL (280 mmol) of triethyl phosphite was added dropwise over about 4 h. During the course of the addition, the reactant color changed from brown red to faint green, and then turned dark red gradually. After the addition, the reaction was allowed to stir for an additional 4 h. Then diethyl 5-(2-bromothienyl)phosphonate was obtained as a colorless oil by distillation under reduced pressure.

To a solution of diethyl 5-(2-bromothienyl)phosphonate (44.6 g, 149 mmol) in 70 mL of CH₃CN at 25 °C was added Me₃SiBr (68.6 g, 448 mmol). After the addition, the reaction mixture was left stirring for 18 h and the reaction solution turned a faint green, then about 50 mL of CH₃OH was added to decompose the excess reagent. After stirring for 2 h, a large amount of water was added to the reaction system and stirred vigorously for another 40 h. The product was obtained as a white powder by removing water and volatile organic solvent by rotary evaporation. Good quality colorless crystals of 2-BTPH₂ were obtained by evaporating its ethanolic solution at room temperature. Total yield: about 47.4%. ¹H-NMR (500 MHz, DMSO, δ ppm): 7.26(s, 1H); 7.25~7.23(d, 1H). ³¹P-NMR (202 MHz, DMSO, δ ppm): 3.28. IR (KBr, cm⁻¹): 930.84-1013.65 cm⁻¹ (v_{p-0})



Scheme S1. general synthetic route of 2-BTPH₂

Preparation of bulk crystals of $[Cu(H_2O)(2-BTP)]$ (1). A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.05 mmol, 0.0125g) and ligand 2-BTPH₂ (0.10mmol, 0.024g) was stirred in 4.0 mL of methanol and 2.5 mL of water, until a clear solution was formed. Then the solution was transferred into a Teflon-lined autoclave and heated at 12^oC for two days under auto-generated pressure. After the mixture was cooled to room

temperature, blue-green lamellar crystals of $[Cu(H_2O)(2-BTP)]$ (1) were obtained. The crystals which were suitable for both structural and property measurements were manually collected. Yield: 62% based on Cu. Elemental anal. calcd for BrC₄H₄SPO₄Cu: C, 14.89; H, 1.24. Found: C, 15.14; H, 1.56. IR (KBr, cm⁻¹): 3405s, 3060m, 1636m, 1508w, 1409s, 1299w, 1210w, 1093s, 1043s, 993s, 883w, 796m, 740w, 666m, 607m, 587m, 542m, 457w, 433w.

Crystallographic studies. A single crystal of dimensions $0.25 \times 0.20 \times 0.12 \text{ mm}^3$ for **1** was selected for indexing and intensity data collection on a Brucker X–ray CCD APEX II diffractometer with graphite-monochromatized Mo–K α radiation ($\lambda = 0.71073 \text{ Å}$) at room temperature. The data were integrated using the Siemens SAINT program, ² with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. The structures was solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL.³ All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined isotropically with the isotropic vibration parameters related to the non-hydrogen atom to which they are bonded. Crystallographic and refinement details are listed in Table S1. Selected bond lengths and angles for **1** are given in Table S2.

References

1 L.-R. Guo, F. Zhu, Y. Chen, Y.-Z. Li and L.-M. Zheng, *Dalton Trans.*, 2009, **40**, 8548.

2 *SAINT: Program for Data Extraction and Reduction*, Siemens Analytical X-ray Instruments, Madison, WI, 1994–1996.

3 *SHELXTL (version 5.0), Reference Manual, Siemens Industrial Automation, Analytical Instruments, Madison, WI, 1995.*

compound	1				
Empirical formula	C ₄ H ₄ BrCuO ₄ PS				
Formula weight	322.55				
Crystal system	Monoclinic				
space group	<i>P</i> 2 ₁ /c				
a (Å)	15.899(4)				
b (Å)	7.627(2)				
c (Å)	7.3440(19)				
α (°)	90				
β (°)	100.075(4)				
γ (°)	90				
Volume (Å ³)	876.7(4)				
Z	4				
$ \rho_{\text{calcd}} \left(\text{g} \cdot \text{cm-3} \right) $	2.444				
F(000)	620				
Total, unique data, R _{int}	5973, 1696, 0.0706				
Goodness-of-fit on F^2	1.001				
$R_{1,} wR_2 [I > 2 \text{sigma}(I)]^a$	0.0591, 0.1549				
R_1 , wR_2 (All data)	0.0632, 0.1572				
$(\triangle \rho)_{\max}, (\triangle \rho)_{\min} \text{ (e Å}^{-3})$	1.077, -1.750				
$\overline{{}^{a}R_{1}} = \sum F_{o} - F_{c} / \sum F_{o} ; wR_{2} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o})^{2}]^{1/2}$					

Table S1. Crystallographic data for [Cu(H2O)(2-BTP)] (1).

Cu1-O1	1.919(4)	P1-O2	1.531(4)	
Cu1-O3B	1.960(4)	P1-O3	1.534(4)	
Cu1-O2A	1.965(4)	P1-O1	1.534(4)	
Cu1-O1W	1.991(5)	P1-C1	1.786(6)	
Cu1-O3C	2.314(4)			
O1-Cu1-O3B	162.63(17)	O1-Cu1-O3C	109.17(16)	
O1-Cu1-O2A	94.04(17)	O3B-Cu1-O3C	87.75(16)	
O3B-Cu1-O1W	88.62(18)	O2A-Cu1-O3C	89.93(16)	
O1-Cu1-O1W	89.86(18)	P1-O2-Cu1A	129.2(3)	
O3B-Cu1-O1W	88.62(18)	O2-P1-O3	111.7(2)	
O2A-Cu1-O1W	171.94(17)	O2-P1-C1	109.2(3)	
O1W-Cu1-O3C	82.12(16)			

Table S2. Selected bond lengths [Å] and angles [deg] for compound 1.

Symmetry transformations used to generate equivalent atoms:

A: -x, -y, -z+1; B: -x, y+1/2, -z+1/2; C: x, -y+1/2, z+1/2

	Compound 1 in water Solution sample c [Cu] (mg/L) (%)		In 0.1 M Pb(NO ₃) ₂ Solution sample c [Cu] Dissolution (mg/L) (%)		Dissolution in solution resulting from metal-replac	c(Pb)/c(Cu) expected in solid sample resulting from metal-replac	Experimental c(Pb)/c(Cu) in solid sample in adsorption experiments-2	Experimental c(Pb)/c(Cu) in solid sample in adsorption experiments-1
					ement (%)	ement		
Method-1	1.38	0.65	1.85	0.88	0.22	2.23×10 ⁻³	1.89×10 ⁻³	1.91×10 ⁻³
Method-2	3.82	1.84	3.43	1.66	-0.18		5.14×10 ⁻³	4.63×10 ⁻³
Method-3	4.80	2.25	7.32	3.43	1.18	11.3×10 ⁻³	17.7×10 ⁻³	20.1×10 ⁻³

 Table S3. ICP results and analyses in adsorption experiments of compound 1.

Table S4. ICP results and analyses in adsorption experiments of compound $[Cu(H_2O)(O_3PC_6H_5)]$ (A).

	Compoun Solutio c [Cu] (mg/L)	d A in water on sample Dissolution (%)	In 0.1 I Soluti c [Cu] (mg/L)	M Pb(NO ₃) ₂ ion sample Dissolution (%)	Dissolution in solution resulting from metal-replac ement (%)	c(Pb)/c(Cu) expected in solid sample resulting from metal-replac ement	Experimental c(Pb)/c(Cu) in solid sample in adsorption experiments-1	Experimental c(Pb)/c(Cu) in solid sample in adsorption experiments-2
Method-1	1.164	0.403	6.201	2.17	1.767	17.9×10 ⁻³	2.51×10 ⁻³	1.80×10 ⁻³
Method-2	1.752	0.613	9.069	3.20	2.587	26.5×10 ⁻³	2.53×10 ⁻³	4.67×10 ⁻³
Method-3	2.496	0.864	26.96	9.26	8.396	91.6×10 ⁻³	23.1×10 ⁻³	15.3×10 ⁻³



Figure S1. TGA curves of compound 1. The weight loss of compound 1 in the temperature range from 100 $^{\circ}$ C to 150 $^{\circ}$ C is 5.6%, corresponding to the release of one coordinated water molecule (calcd. 5.6%). When temperature is higher than 350 $^{\circ}$ C, compound 1 would be decomposed.



Figure S2. IR spectrum of compound 1.



Figure S3. TGA curves of compound **2**. No weigh loss is observed below 350 $^{\circ}$ C. When temperature is higher than 350 $^{\circ}$ C, compound **2** would be decomposed.



Figure S4. IR spectrum of compound 2.



Figure S5. PXRD patterns of compound 1 simulated from single crystal data (black line), crystalline sample of 1 (red line), compound 1 dehydrated at 100° C (pink line), rehydrated sample after immersing 1-dehydrated in water for 70 hours (blue line), and compound 2 (brown line).



Figure S6. The χ_M and $\chi_M T vs. T$ plots for **1.** The solid lines represent the best fits with the parameters g = 2.22, J = -2.3 cm⁻¹, $\rho = 5.02$ % and zJ' = 0.15 cm⁻¹



Figure S7. PXRD patterns of nanosheets of **1** in colloidal solution after centrifuging (pink line) and the precipitate after ultrasonication (brown line). The experimental and simulated PXRD patterns of compound **1** are also shown for comparison.



Figure S8. AFM images and the corresponding thickness of nano-sheets of **1** (b for a; d for c).



Figure S9. SEM images of the precipitates after ultrasonic treatment.



Figure S10. Comparison of IR spectrums of **1** bulk crystals (black line) and nanosheets samples after adsorption of Pb ions in aqueous solution with different methods (method-1: pink line; method-2: brown; method-3: blue).



Figure S11. The PXRD patterns of samples of $[Cu(H_2O)(O_3PC_6H_5)]$ (**A**) after adsorption treatments using method-1 (purple), method-2 (blue) and method-3 (brown). The patterns for the bulk crystalline sample (red) and that simulated from the single crystal data (black) of the same compound are also presented for comparison.