
Electronic Supporting information for:

Exploring the Surfactant–Thermal Synthesis of Crystalline Functional Thioarsenates

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Materials and methods

A German Elementary Vario EL III instrument was used to ascertain the concentrations of carbon, hydrogen, and nitrogen in the crystals of **1** and **2**. A JEOL JSM-6700F scanning electron microscope was applied for the energy-dispersive X-ray analysis. A UV-vis-NIR Varian 86 Cary 500 Scan spectrophotometer was used for collecting optical diffuse reflectance spectra at room temperature. The reflectance spectra were converted to the absorption (α/S) data based on the Kubelka-Munk function: $\alpha/S = (1 - R^2)/2R$, α : absorption coefficient, S : scattering coefficient, R : reflectance. A Miniflex II diffractometer equipped with Cu-K α radiation ($\lambda = 1.5406$) was performed for collecting the Powder X-ray diffraction (PXRD) patterns (angular range $2\theta = 5-65^\circ$). The thermogravimetry (TG) curves were recorded on a NETZSCH STA 449F3 thermogravimetric analyzer under a nitrogen atmosphere, a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ was used (temperature range: $25-800\text{ }^\circ\text{C}$). A Quantum Design MPMS-XL SQUID magnetometer was used for magnetic investigation.

Powder SHG measurements

According to the experiment procedures reported by Kurtz and Perry, powder SHG measurements were performed on the powdered samples of **2**. A Q-switched Nd:YAG solid-state laser was employed to produce the fundamental frequency light with wavelength of 1064 nm. The crystals of compound **2** were milled and sieved into seven particle sizes: 50–75, 75–100, 100–130, 130–150, 150–200, 200–270, and

270-325 μm . These samples were filled between two glass slides in a disk, which were further fixed with a tape in an aluminum holder.

Preparation of Photoelectrodes

The ITO substrates were immersed sequentially in the solvents of distilled water, absolute ethanol, and isopropanol by sonication, and then dried in vacuum. 5 mg of the compound and 10 μL of Nafion solution (5 wt%) were dispersed in solvent by at least one hour sonication to prepare a homogeneous catalyst colloid. Then, 150 μL of the catalyst colloid was deposited onto areas of about 1 cm^2 of the ITO conductive glass substrate, which was used as the working electrode after dried in air. The light generated by a 300 W Xe arc lamp was controlled though on and off to record the photo responses of the samples at 0.6 V.

Synthesis

Synthesis of $[\text{pipH}_2][\text{Mn}_2\text{As}_2\text{S}_6]$ (1**)**

Heating the mixture of Mn (0.51 mmol, 0.278 g), As_2S_3 (0.25 mmol, 0.062 g), S (3.02 mmol, 0.097 g), pip (piperazine hexahydrate) (3.49 mmol, 0.678 g), octylamine (2 mL, 99% aq. Soln.), and methanol (0.5 mL, 99% aq. Soln.) in an autoclave equipped with a Teflon liner (28 mL) at 180 $^\circ\text{C}$ for 6 days followed by washing the products by ethanol for several times produced the yellow sheet-like crystals of **1** (yield: 22.2%, 0.030 g, based on As). C, H, N, calcd (%) for $\text{C}_4\text{H}_{12}\text{N}_2\text{As}_2\text{Mn}_2\text{S}_6$: C 8.89, H 2.24, N 5.19; found: C 9.11, H 2.21, N 4.95.

Synthesis of [TMDPH₂][As₄S₆] (**2**)

Heating the mixture of As₂S₂ (0.26 mmol, 0.055 g), S (3.00 mmol, 0.096 g), TMDP (1,3-bis(4-piperidyl)propane) (2.01 mmol, 0.422 g), PEG-400 (poly(ethylene glycol)-400) (2 mL, 99% aq. Soln.), and hydrazine hydrate (0.3 mL, 95% aq. Soln.) in an autoclave equipped with a Teflon liner (20 mL) at 180 °C for 6 days followed by washing the resultants by ethanol for several times yielded the yellow sheet-like crystals of **2** (yield: 56.8%, 0.100 g, based on As). C, H, N, calcd (%) for C₁₃H₂₈N₂As₄S₆: C 22.16, H 4.00, N 3.97; found: C 21.89, H 4.05, N 4.09.

Computational Descriptions

Energy band structures of **2** were accomplished by using the density functional theory (DFT) calculations with CASTEP code provided by the Material Studio package. Interaction of the electrons with ion cores was represented by the norm-conserving pseudo potentials, and the valence electrons were treated as As, 3d¹⁰4s²4p³; S, 3s²3p⁴; C, 2s²2p³; C, 2s²2p²; H, 1s¹. Generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Eruserh of (PBE) was used to describe the exchange and correlative potential of electron–electron interactions. For DOS calculations, we used a 2×2×2 Monkhorst–Pack scheme. The X-ray crystal structure data were used without further optimization.

Photoelectrochemical Measurements

The photoelectrochemical properties were investigated on a CHI 760E electrochemical working station. A three electrode configuration was made up of a platinum foil (counter electrode), a Ag/AgCl (saturated KCl) (reference electrode), and a sample coated indium doped tin oxide (ITO) glass (working electrode). The electrolyte was a 0.5 M Na₂SO₄ aqueous solution. The light source was provided by a 300 W Xe arc lamp.

Single-crystal structure determination

Single-crystal X-ray diffraction data of **1** and **2** were collected at room temperature on a Super Nova Oxford and a Xcalibur E Oxford diffractometer, respectively, both of which were equipped with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). The SHELX-2016 program package was used to solve the structures through direct methods and refine the structures by full-matrix least-squares on F^2 . All non-hydrogen atoms were anisotropically refined, and the hydrogen atoms were geometrically located. More structural details are listed in Tables S1–S4.

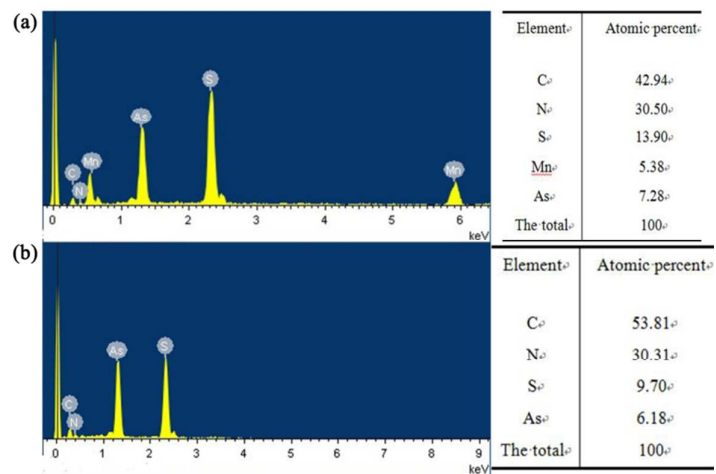


Figure S1. Energy-dispersive X-ray analysis (EDXA) patterns of compounds 1 (a) and 2 (b).

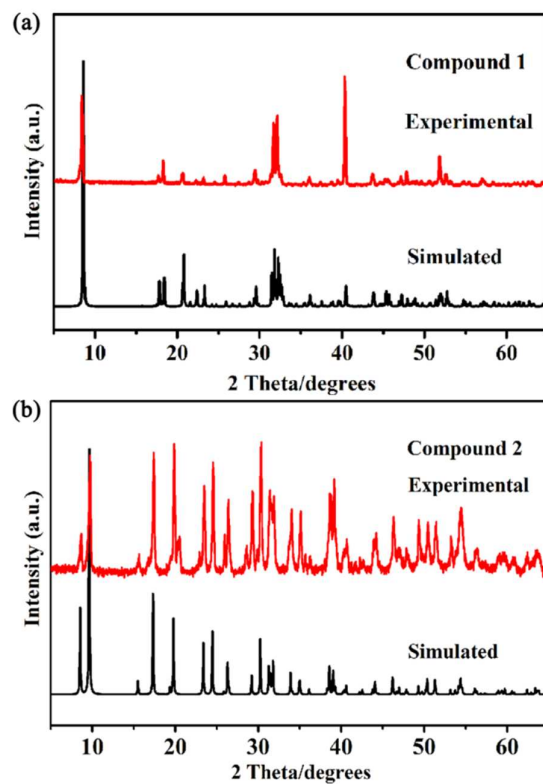


Figure S2. The experimental (red) and simulated (black) PXRD patterns of compounds 1 (a) and 2 (b).

Table S1 Selected bond lengths (Å) and bond angles (°) for **1**.

As(1)-S(1)	2.2452(8)	Mn(1)-S(1)	2.6473(9)
As(1)-S(3)	2.2606(8)	Mn(1)-S(1)#3	2.6800(10)
As(1)-S(2)	2.2659(9)	S(1)-Mn(1)#1	2.6800(10)
Mn(1)-S(3)	2.5325(10)	S(2)-Mn(1)#3	2.5466(10)
Mn(1)-S(2)#1	2.5466(10)	S(2)-Mn(1)#4	2.6308(9)
Mn(1)-S(2)#2	2.6308(9)		
S(1)-As(1)-S(3)	96.62(3)	S(2)#1-Mn(1)-S(1)#3	100.09(3)
S(1)-As(1)-S(2)	101.45(3)	S(2)#2-Mn(1)-S(1)#3	99.03(3)
S(3)-As(1)-S(2)	101.29(3)	S(1)-Mn(1)-S(1)#3	89.41(3)
S(3)-Mn(1)-S(2)#1	170.28(3)	As(1)-S(1)-Mn(1)	89.70(3)
S(3)-Mn(1)-S(2)#2	92.74(3)	As(1)-S(1)-Mn(1)#1	99.12(3)
S(2)#1-Mn(1)-S(2)#2	89.67(3)	Mn(1)-S(1)-Mn(1)#1	97.87(3)
S(3)-Mn(1)-S(1)	80.99(3)	As(1)-S(2)-Mn(1)#3	95.86(3)
S(2)#1-Mn(1)-S(1)	95.15(3)	As(1)-S(2)-Mn(1)#4	96.35(3)
S(2)#2-Mn(1)-S(1)	169.42(3)	Mn(1)#3-S(2)-Mn(1)#4	90.33(3)
S(3)-Mn(1)-S(1)#3	88.83(3)	As(1)-S(3)-Mn(1)	92.32(3)

Symmetry transformations used to generate equivalent atoms: #1 -x+1, y-1/2, -z+1/2; #2 x, -y+3/2, z-1/2; #3 -x+1, y+1/2, -z+1/2; #4 x, -y+3/2, z+1/2.

Table S2 Selected hydrogen bonds data for **1**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...S(3)	0.92(4)	2.19(4)	3.075(3)	159(3)
N(1)-H(1B)...S(3)#6	0.89(4)	2.23(4)	3.123(3)	174(4)
C(2)-H(2B)...S(3)#7	0.97	2.97	3.698(4)	132.7

Symmetry transformations used to generate equivalent atoms: #6 x, y-1, z; #7 -x, -y+1, -z.

Table S3 Selected bond lengths (Å) and bond angles (°) for **2**.

As(1)-S(1)	2.224(3)	As(2)-S(2)	2.151(4)
As(1)-S(1)#1	2.224(3)	As(2)-S(1)#3	2.294(3)
As(1)-As(1)#2	2.551(3)	As(2)-S(1)	2.294(3)
S(1)-As(1)-S(1)#1	105.84(18)	S(2)-As(2)-S(1)	99.95(10)
S(1)-As(1)-As(1)#2	100.30(7)	S(1)#3-As(2)-S(1)	93.67(16)
S(1)#1-As(1)-As(1)#2	100.30(7)	As(1)-S(1)-As(2)	104.84(11)
S(2)-As(2)-S(1)#3	99.95(10)		

Symmetry transformations used to generate equivalent atoms: #1 x, -y, z; #2 -x, -y, z; #3 -x, y, z.

Table S4 Selected hydrogen bonds data for **2**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...S(2)#6	0.89	2.42	3.160(10)	141.4
N(1)-H(1D)...S(2)#7	0.89	2.29	3.179(10)	178.1

Symmetry transformations used to generate equivalent atoms: #6 -x+1/2, -y+1/2, z-3/2; #7 -x+1/2, -y+1/2, z-1/2.