Supporting Information

Surfactant 1-Hexadecyl-3-methylimidazolium Chloride Can Covert One-Dimensional Viologen Bromoplumbate into Zero-Dimensional

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Materials and Methods:

4,4'-bipyridine, PbBr₂, HBr aqueous solution (> 45%), CH₃CH₂OH, CH₃CH₂CH₂CH₂OH, CH₃CH₂CH₂OH, CH₃CH₂CH₂OH, CH₃CH₂CH₂CH₂CH₂OH, PVP (average molecular weight 10000), SDS, PEG-400 and [HMIM]Cl were purchased from Sigma-Aldrich Company. All starting materials are analytical-grade and were used as received without further purification.

The compounds C2, C3, C4-1 and C5 adopt a similar synthesis method: a mixture of PbBr₂ (0.54 mmol, 200 mg) and 4,4'-bipyridine (1.28 mmol, 200mg) was heated with HBr (> 45%, 1.0 ml) and 5 ml alcohols (CH₃CH₂OH, CH₃CH₂CH₂CH₂OH, CH₃CH₂CH₂OH or CH₃CH₂CH₂CH₂CH₂OH) in 25 ml Teflon-lined stainless-steel autoclaves at 120 °C for 5 days. Upon cooling to room temperature at 10 K h⁻¹, yellow prismatic crystals of C2, C3, C4-1 and C5 were obtained in 71%, 75%, 67% and 70% yield, respectively (based on PbBr₂). When we chose 100, 120, 140, 160 and 180 °C as reaction temperatures, the products are always C2, C3, C4-1 and C5.

To synthesize the compound C4-2, all of the raw materials are kept consistent with the reaction route for preparation C4-1, surfactant [HMIM]Cl (1g) was chosen as additives to induce crystal growth. When the reaction temperature is 180 °C, the yields for C4-2 are about 51% (based on PbBr₂).

We added surfactant [HMIM]Cl (1g) as additive to EV, PV and PeV- bromoplumbate systems at 120 °C and 180 °C. However, the products are still original C2, C3 and C5 crystals.

We have also tried to use PVP, SDS and PEG-400 as additives to induce crystals growth. However, the products are always C2, C3, C4-1 and C5.

Powder X-ray Diffraction:

The phase identity and purity of C2, C3, C4-1, C5 and C4-2 crystals were verified by power X-ray diffraction (PXRD) on a Bruker-AXS D8 ADVANCE X-ray diffractometer equipped with Cu K α radiation ($\lambda = 1.54056$ Å) in the 2 θ range of 9 – 50°, with a step size of 0.02° and scan-speed of 0.2 s/step at room temperature.

IR Spectroscopy:

The attenuated total reflectance Fourier transform infrared spectra (ATR-FTIR) of powder sample C2, C3, C4-1, C5 and C4-2 were recorded on a Thermo-Nicolet Nexus 670 spectrometer in the range of 700-4,000 cm⁻¹ at room temperature.

Single-Crystal X-ray Diffraction:

Suitable C2, C3, C4-1, C5 and C4-2 single-crystals were selected for single-crystal X-ray data collection with a Bruker SMART APEX-II CCD area detector on a D8 goniometer. All data were collected using graphite-monochromated and 0.5 mm-Mono Cap-collimated Mo-K α radiation ($\lambda = 0.71073$ Å) with the ω scan method.¹ Data were processed with the SAINT program of the APEX2 software for

reduction and cell refinement. Multi-scan absorption corrections were applied by using the SADABS program for area detector. All structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 (SHELX-97).² All non-H atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and included as riding with U_{iso} (H) = 1.2 U_{eq} (C). For the C4-1, C4-2 and C5 compounds, the low bond precision on C-C bonds is resulted from a large amount of dynamically disordered side-chains in these structures. And the Ueq of C49 and C52 in the structure of C4-2 is still higher than the neighbors although the DELU and SIMU restraints are applied. Crystallographic data and structural refinements are summarized in Table S1. Additional information in the form of CIF has also been supplied as Supporting Information.

UV-Vis spectra:

Absorption data were collected on a Hitachi U-4100 UV–vis–NIR spectrophotometer equipped with an integrating sphere operating in diffuse-reflectance mode at 298 K For crystalline samples C2, C3, C4-1, C5 and C4-2.

Thermal Measurement:

Thermogravimetric and differential scanning calorimetry synergetic tests (TGA-DSC) for C2, C3, C4-1, C5 and C4-2 were carried out on a TGA/DSC/1600HT analyzer (METTLER TOLEDO Instruments). The samples were placed in Al₂O₃ crucible, and heated at a rate of 10 K min⁻¹ from room temperature to 400 °C under flowing nitrogen gas.



Fig S1. (a)-(e), the asymmetric units of C2, C3, C4, C4-1, C4-2 and C5 crystals with 50% thermal ellipsoids.



Fig S2. (a) The obtained C4-1 and C4-2 crystals in one batch at 160 °C with the surfactant [HMIM]Cl as a additive. (b) The pure C4-2 crystals were obtained by sieving (the mesh size is about $30 \ \mu m$)_o



Fig S3. Simulated (red lines) and experimental XRD (black lines) powder patterns for C2-C5 compounds.



Fig S4. The FT-IR spectra for C2, C3, C4-1, C5 and C4-2 compounds.



Fig S5. The TGA-DSC curves for the compounds C2-C5.

	C2	C3	C4-1	C5	C4-2			
$T(\mathbf{K})$	296	296	296	296	296			
Formula	$C_{21}N_3H_{27}Pb$	$C_{24}N_3H_{32}Pb$	$C_{27}N_{3}H_{37}Pb$	$C_{30}N_3H_{42}Pb$	$C_{108}N_{12}H_{15}$			
	3 Br 9	3 Br 9	3 Br 9	3 Br 9	6Pb9Br30			
Formula	1662.16	1703.23	1744.00	1785.37	5883.00			
weight								
Crystal	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic			
system								
Space	<i>P</i> 2 ₁ /c	<i>C2/c</i>						
group								
<i>a</i> (Å)	11.8158 (11)	12.3896	15.779 (3)	15.4972	30.6471 (4)			
		(17)		(17)				
<i>b</i> (Å)	13.3127(13)	13.6687	24.507 (5)	25.327 (3)	24.3702 (3)			
		(19)						
<i>c</i> (Å)	23.777(2)	23.797 (3)	11.845 (2)	12.1255	21.9002 (3)			
				(13)				
α (deg)	90	90	90	90	90			
β (deg)	90.569 (1)	90.0047	105.010 (2)	100.8400	102.1900			
		(19)		(10)	(10)			
γ(deg)	90	90	90	90	90			
$V(Å^3)$	3739.9 (6)	4029.9 (10)	4424.1 (14)	4674.3 (9)	15987.9 (4)			
λ (Μο	0.71073	0.71073	0.71073	0.71073	0.71073			
$K\alpha$) (Å)								
Collected	21639	43076	31917	41119	143652			
reflns								
Unique	7894	8301	7821	10693	14114			
reflns								
Parameter	329	355	355	408	610			
S								
R (int)	0.0551	0.0929	0.0851	0.0871	0.1098			
$R_1 [I >$	0.0361	0.0416	0.0673	0.0653	0.0541			

Table S1. Crystallographic data and structure refinement parameters of C2-C5

$2\sigma(I)$]					
$w \mathbf{R}_2 [I >$	0.0658	0.0980	0.1892	0.1752	0.1526
$2\sigma(I)$]					
GOF	0.888	1.016	1.132	1.042	1.038

References;

- 1. APEX2 (version 2009.9); Bruker AXS Inc., (Madison, WI, 2009).
- 2. G. M. Sheldrick, A short history of SHELX. Acta.crystallogr. A64, 112 (2008).