Supporting Information

Viologen-Templated Bromoplumbate: A New in situ Synthetic Method and Energy Gap Engineering

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1. Experimental section

Materials. All chemicals were used as purchased without further purification. Water was deionized and distilled before use.

Measurements. The elemental analyses of C, H, and N were measured on an Elementar Vario EL III microanalyzer. The FT-IR spectrum was measured on a PerkinElmer Spectrum One FT-IR spectrometer using a KBr pellet. The electronic absorption spectra were measured in the diffuse reflectance mode on a PerkinElmer Lambda 900 UV/vis/near-IR spectrophotometer equipped with an integrating sphere, and a $BaSO_4$ plate was used as the reference. Powder X-ray diffraction (PXRD) patterns were measured on a Rigaku Desktop MiniFlexII diffractometer using Cu K_α radiation (λ = 1.54056 Å) powered at 30 kV and 15 mA. The simulated PXRD pattern was derived from the Mercury Version 3.5.1 software. A Mettler TOLECO simultaneous TGA/DSC apparatus was used to obtain the TGA curve under N_2 atmosphere in the range of 30–800 °C with a heating rate of 10 °C/min.

Synthesis of $\{(H_2CV)_3[Pb_6Br_{18}]\cdot 2H_2O\}_n$ (1, H_2CV = 1,1'-bis(2-carboxyethyl)-4,4'-bipyridimium-1,1'-diium). Compound **1** was prepared by the hydrothermal reaction of $PbBr_2$ (110 mg, 0.3 mmol), 4,4'-bipyridine (47 mg, 0.3 mmol), 3-hydroxypropionic acid (1 mL), concentrated HBr (1.0 mL, 40% v/v), and H_2O (8 mL) at 120 °C for 3 d. Upon cooling to room temperature, orange prism crystals of **1** were obtained. Compound **1** also could be prepared by the new *in situ* strategy both at 120 °C and room temperature with acrylic acid instead of 3-hydroxypropionic acid. Two different strategies had a similar yield (>80% based on $PbBr_2$). Elem anal. Calcd for $C_{48}H_{58}N_6O_{14}Pb_6Br_{18}$: H, 1.61; C, 15.91; N, 2.32. Found: H, 1.55; C, 16.12; N, 2.32. IR(KBr, 4000–400 cm^{-1}): 3409(m), 3050(m), 1718(s), 1636(s), 1601(w), 1557(s), 1500(m), 1439(s), 1408(m), 1373(m), 1284(w), 1255(w), 1188(m), 1051(w), 985(w), 946(w), 867(w), 828(m), 768(w), 711(w), 670(w), 590(w), 536(w), 492(w). PXRD patterns (**Figure S2**) and elemental analysis data indicate that the crystalline sample of **1** is pure phase.

X-ray crystallographic study. The single-crystal X-ray diffraction measurements of **1** was performed on a Rigaku Pilatus 200K diffractometer, using graphite monochromated Mo *Kα* radiation (λ = 0.71073 Å). Intensity data sets were collected using ω scan techniques, and corrected for *Lp* effects. The structure was solved and refined by full-matrix least squares on F^2 using the Siemens SHELXTL^{TM} Version 5 package of crystallographic software,[1] with anisotropic thermal parameters for all nonhydrogen atoms. H atoms of water molecules were added from the difference Fourier maps and set the temperature factor 1.5 times as large as the parent atoms, and other H atoms were added geometrically and refined using the riding model. Crystal data and structure refinement results for the compounds are summarized in **Table S1**.

The entry of CCDC-1548932 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK. Fax: (internat.) +44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk.

Computational approach. The crystallographic data of **1** and $PbBr_2$[2] were used to build calculation models. Plane wave-based density functional theory (DFT) calculations of the total and partial densities of states were performed using the Cambridge Sequential Total Energy Package (CASTEP) code.[3] The exchange-correlation energy was described by the Perdew−Burke−Eruzerhof (PBE) functional within the generalized gradient approximation (GGA).[4] The norm-conserving pseudopotentials were chosen to modulate the electron−ion interaction.[5] Pseudo atomic calculations were performed for C $2s^2 2p^2$, H $1s^1$, N $2s^2 2p^3$, O $2s^2 2p^4$, Br $4s^2 4p^5$ and Pb $5d^{10} 6s^2 6p^2$. The number of plane waves included in the basis was determined by a cutoff energy of 750 eV. Other parameters used in the calculations were set by the default values of the CASTEP code. The calculations of linear optical properties described in terms of the complex dielectric function $\varepsilon = \varepsilon_1 + \varepsilon_2$ were also made in this work. The imaginary part of the dielectric function $\varepsilon_2(\omega)$ was given in the following equation:[6]

$$\varepsilon_2(\omega) = 4\left(\frac{\pi e}{m\omega}\right)^2 \sum_{v,c} \int_{BZ} 2dk/(2\pi)^3 \left|e\cdot M_{cv}(k)\right|^2 \delta\left(E_c(k') - E_v(k) - \hbar\omega\right)$$

The symbol Σ is summation over the valence bands (υ) and conduction bands (c), the symbol $\int$ is integration over $\boldsymbol{k}$ vectors in Brillouin zone (BZ), the $\boldsymbol{e}\cdot\boldsymbol{M}_{c\upsilon}(\boldsymbol{k})$ is an electron transition moment between the conduction and valence bands at the k point, and δ function is the energy difference between the conduction and valence bands at $\boldsymbol{k}$ point with absorption of a quantum $\hbar\omega$. The smearing width for the spectra of $\varepsilon_2(\omega)$ is 0.2 eV and a scissors operator revises the theoretical and experimental band gap values.

The electronic properties of ligands were optimized and evaluated with density functional theory (DFT) computations using the Gaussian 09 suite of programs at the B3LYP/6-31+G(d,p) level.[7]

2. Supporting data.

1) Crystal and Structure Refinement Data.

Table S1. Crystal and Structure Refinement Data for **1.**

	1
Formula	$C_{48}H_{58}N_6O_{14}Pb_6Br_{18}$
Mr	3624.52
cryst size (*mm³*)	0.188 ×0.071 ×0.054
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	11.7804(5)
b (Å)	12.0677(6)
c (Å)	14.8096(8)
α (°)	99.043(2)
β (°)	94.199(2)
γ (°)	93.992(2)
V (Å³)	2066.57(18)
D_{calcd} (g/cm³)	2.912
Z	1
F(000)	1622
abs coeff (mm⁻¹)	20.931
reflns collcd/unique (R_{int})	16502/8936 (0.0461)
data/params/restraints	5200/421/0
R_1[a]	0.0393
ωR_2[b]	0.0794
GOF on F^2	0.985
$\Delta\rho_{\max}$ and $\Delta\rho_{\min}$ (e/Å³)	1.327 and –1.784

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, [b] $\omega R_2 = \{\sum\omega[(F_o)^2-(F_c)^2]^2/\sum\omega[(F_o)_2]^2\}^{1/2}$.

2) Supplier item price report.

Table S2. Supplier item price report of 3-hydroxypropionic acid and acrylic acid.

	3-hydroxypropionic acid	**acrylic acid**
TCI	25g /1990.00 CNY	500g / 228.00 CNY
Aldrich	1g / 621.04 CNY	500g / 515.97 CNY
J&K	25g / 2869 CNY	500g / 542 CNY

3) Thermogravimetric analysis.

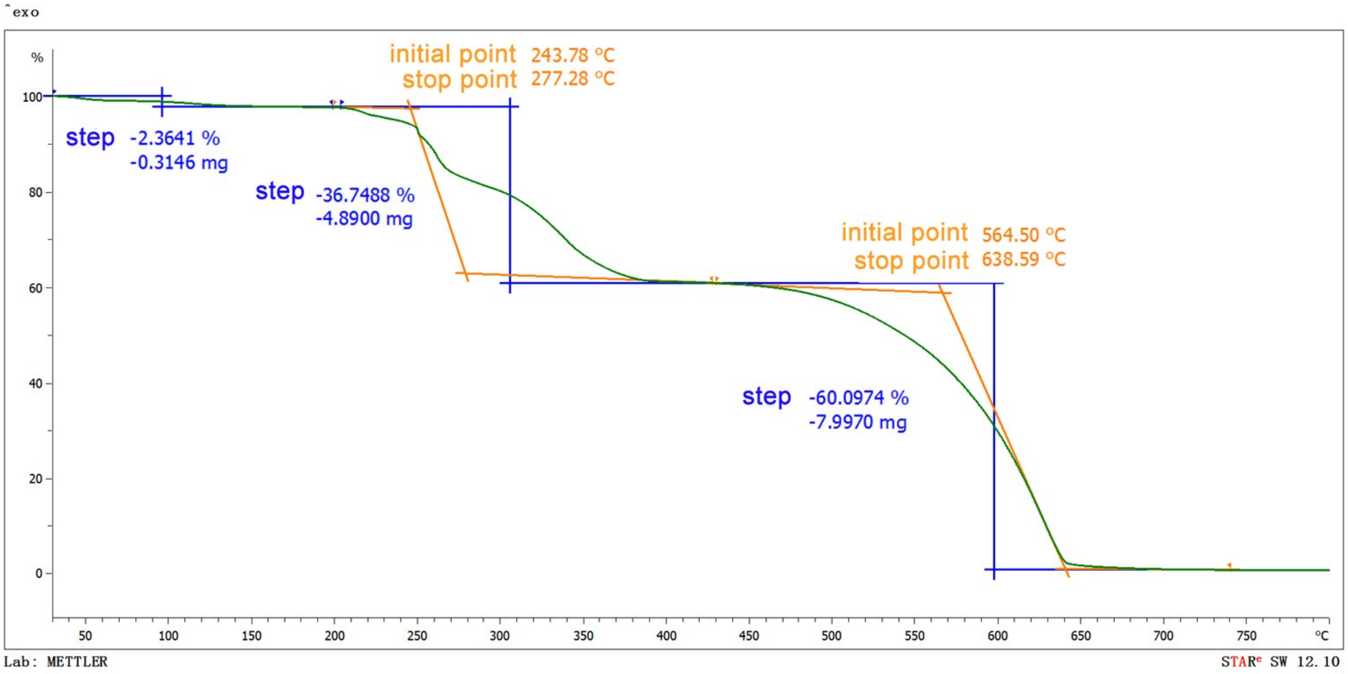

Figure S1. Thermogravimetric analysis of 1. As can be seen, a complete dehydration process occurred around 100 °C.

4) PXRD patterns.

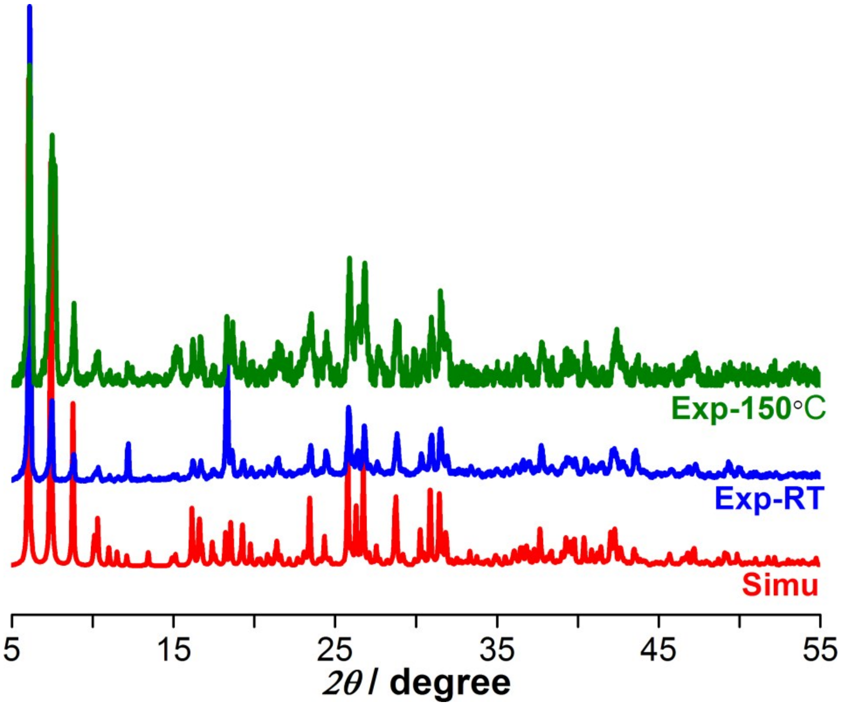

Figure S2. Experimental (Exp) and simulated (Simu) PXRD patterns of **1**. The time for heat-treatment at 150 °C was 24 h.

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