## Supplementary Information

# Assembly of Heterometallic Polynuclear $\mathrm{Sn}^{\text {IV }}-\mathrm{Cu}^{\text {I }}$ Cluster Based on <br> $\operatorname{Sn}(\text { edt })_{2}($ edt $=$ ethane-1,2-dithiolate $)$ as Metalloligand 

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## 1. Materials and General Procedures.

All chemicals were obtained from commercial sources without further purification. $\mathrm{Sn}(\mathrm{edt})_{2}^{[1]}$ and $\left[\mathrm{Cu}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{MeCN})_{2}\right] \mathrm{ClO}_{4}{ }^{[2]}$ were prepared according to the literature.

The crystal data collection was performed on a Mercury-CCD diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares techniques on $F^{2}$ using SHELXTL-97. ${ }^{[3]}$ All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms attached to carbon atoms were generated geometrically.

Infrared spectra were recorded on a Nicolet magna 750 FT-IR spectrophotometer using KBr pellets. Raman spectrum were recorded on a Nicolet raman 950 FT-IR spectrophotometer. Elemental analyses were carried out with a Vario EL III element analyzer. Fluorescent properties of solid $\mathbf{1}$ and $\mathbf{2}$ were performed with FLS920 under room temperature. Powder X-ray diffraction (XRD) patterns were acquired on a DMAX-2500 diffractometer using Mo-K $\alpha$ radiation at ambient environment. ${ }^{1} \mathrm{H}$ NMR spectroscopy was recorded on a Varian UNITY-500 spectrometer at room temperature using TMS as an internal reference. ${ }^{31}$ P NMR spectra were measured on a Varian UNITY-500 spectrometer using $85 \% \mathrm{H}_{3} \mathrm{PO}_{4}$ as external standard.

## References

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2. Barron, P. F.; Dyason, J. C.; Engelhardt, L. M.; Healy, P. C.; White, A. H. Aust. J. Chem. 1985, 38, 261.
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## 2. Synthesis of compound 2

All synthetic operations were performed under an oxygen-free nitrogen atmosphere by using standard Schlenk techniques. To a dichloromethane ( 20 mL ) solution of $\left[\mathrm{Cu}\left(\mathrm{PPh}_{3}\right)_{2}(\mathrm{MeCN})_{2}\right] \mathrm{ClO}_{4}(0.077 \mathrm{~g}, 0.1 \mathrm{mmol}), \operatorname{Sn}(\mathrm{edt})_{2}(0.030 \mathrm{~g}, 0.1 \mathrm{mmol})(\mathrm{edt}=$ ethane-1,2-dithiolate) was added to give a yellow solution. After stirring at room temperature for 1 day, the solution was filtered to remove a little of precipitate. The yellow prismatic crystals of 2 were obtained by slow diffusion of diethyl ether into the filtrate in $56 \%$ yield (based on Cu ). Anal. Calcd for $\mathrm{C}_{87} \mathrm{H}_{90} \mathrm{Cl}_{8} \mathrm{Cu}_{4} \mathrm{O}_{9} \mathrm{P}_{4} \mathrm{~S}_{12} \mathrm{Sn}_{3}$ : C, 38.96; H, 3.38; S, 14.34. Found: C, 39.05; H, 3.48; S, 14.40. ${ }^{31} \mathrm{P} \operatorname{NMR}(202.3 \mathrm{MHz}, \mathrm{DMSO}, \mathrm{ppm}):-1.878\left(\mathrm{~s},-\mathrm{PPh}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}(500$ MHz, DMSO-d $\left.{ }^{6}, \mathrm{ppm}\right): \delta_{\mathrm{H}} 7.307-7.470\left(\mathrm{~m}, 60 \mathrm{H},-\mathrm{C}_{6} \mathrm{H}_{5}\right), 5.754\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right), 2.844-3.05(\mathrm{~m}$, $\left.24 \mathrm{H},-\mathrm{SCH}_{2} \mathrm{CH}_{2} \mathrm{~S}-\right)$. FT-IR( KBr pellet, $\mathrm{cm}^{-1}$ ): $3430 \mathrm{vw}, 3040 \mathrm{w}, 2925 \mathrm{w}, 1585 \mathrm{w}, 1500 \mathrm{~m}, 1435 \mathrm{~s}$, $1406 \mathrm{~m}, 1284 \mathrm{w}, 1269 \mathrm{w}, 1182 \mathrm{vw}, 1161 \mathrm{w}, 1093 \mathrm{vs}, 1028 \mathrm{~m}, 997 \mathrm{~m}, 920 \mathrm{w}, 843 \mathrm{w}, 825 \mathrm{vw}, 748 \mathrm{~s}$, $694 \mathrm{vs}, 621 \mathrm{~m}, 580 \mathrm{~s}, 525 \mathrm{vs}, 511 \mathrm{~s}, 490 \mathrm{~s}, 440 \mathrm{~m}, 428 \mathrm{~m}, 390 \mathrm{w}, 380 \mathrm{w}, 339 \mathrm{~m}, 322 \mathrm{~m}, 295 \mathrm{~m}, 285 \mathrm{~m}$, 274m, 229m, 218m. Raman (KBr pellet, $\mathrm{cm}^{-1}$ ): 3681(m), 3361(s), 3045(s), 2856(s), 2728(w), 2080(w), 1776(m), 1456(s), 634(m), 538(m), 318(w).

## 3. Supporting Tables and Figures

Table S1. Crystal data collection and structural refinement parameters for 2.

| Formula | $\mathrm{C}_{87} \mathrm{H}_{90} \mathrm{Cl}_{8} \mathrm{Cu}_{4} \mathrm{O}_{9} \mathrm{P}_{4} \mathrm{~S}_{12} \mathrm{Sn}_{3}$ | $\mu\left(\mathrm{~mm}^{-1}\right)$ | 2.077 |
| :--- | :--- | :--- | :--- |
| $F w$ | 2682.02 | $T(\mathrm{~K})$ | 130.15 |
| $a(\AA)$ | $18.156(2)$ | $\theta_{\text {min }}\left({ }^{\circ}\right)$ | 3.17 |
| $b(\AA)$ | $18.156(2)$ | $\theta_{\text {max }}\left({ }^{\circ}\right)$ | 27.49 |
| $c(\AA)$ | $54.495(10)$ | Total reflections | 39919 |
| $\alpha($ deg $)$ | 90 | Independent reflections | 7923 |
| $\beta($ deg $)$ | 90 | Observed reflections $(I>2 \sigma(I))$ | 7653 |
| $\gamma($ deg $)$ | 120 | $R_{\text {int }}$ | 0.0365 |
| $V\left(\AA^{3}\right)$ | $15558(4)$ | Parameters refind | 401 |
| $Z$ | 6 | $R{ }^{\text {a }}$ | 0.0496 |
| Crystal system | trigonal | $R w^{\text {b }}$ | 0.1042 |
| Space group | $R-3$ | GOF | 1.114 |
| Crystal size $(\mathrm{mm})$ | $0.38 \times 0.30 \times 0.25$ | Max/mean shift in final cycle | $0.001 / 0.000$ |
| $\lambda(\AA)$ | 0.71073 | Max/min. $\Delta \rho\left(\mathrm{e} / \AA^{3}\right)$ | $4.638 /-1.360$ |
| $\rho\left(\mathrm{~g} / \mathrm{cm}{ }^{3}\right)$ | 1.718 | Max./min. transmission | 0.8005 to 1.000 |

a. $\quad R=\Sigma\left(\left\|F_{o}|-| F_{c}\right\|\right) / \Sigma\left|F_{o}\right|$,
b. $\quad R w=\left\{\Sigma w\left[\left(F_{o}{ }^{2}-F_{c}{ }^{2}\right)\right]^{2} / \Sigma w\left[\left(F_{o}{ }^{2}\right)^{2}\right]\right\}^{1 / 2}, w=1 /\left[\sigma^{2}\left(F_{o}{ }^{2}\right)+(0.0267 P)^{2}+242.2413 P\right], P=\left(F_{o}{ }^{2}+2\right.$ $\left.\left.F_{c}{ }^{2}\right) / 3\right]$

Table S2. Selected bond distances $(\AA)$ of the nonhydrogen atoms.

| Bond | Dist. | Bond | Dist. |
| :--- | :--- | :--- | :--- |
| $\mathrm{Sn}(1)-\mathrm{O}(1)$ | $2.0626(6)$ | $\mathrm{Cu}(2)-\mathrm{P}(2)$ | $2.2500(19)$ |
| $\mathrm{Sn}(1)-\mathrm{S}(3)$ | $2.4367(12)$ | $\mathrm{Cu}(2)-\mathrm{S}(1) \# 1$ | $2.3032(12)$ |
| $\mathrm{Sn}(1)-\mathrm{S}(1) \# 1$ | $2.4940(12)$ | $\mathrm{Cu}(2)-\mathrm{S}(1) \# 2$ | $2.3032(12)$ |
| $\mathrm{Sn}(1)-\mathrm{S}(2)$ | $2.5869(10)$ | $\mathrm{Cu}(2)-\mathrm{S}(1)$ | $2.3032(12)$ |
| $\mathrm{Sn}(1)-\mathrm{S}(4)$ | $2.6080(13)$ | $\mathrm{S}(1)-\mathrm{Sn}(1) \# 2$ | $2.4941(12)$ |
| $\mathrm{Sn}(1)-\mathrm{S}(4) \# 1$ | $2.6152(13)$ | $\mathrm{S}(2)-\mathrm{Cu}(1) \# 1$ | $2.3046(10)$ |
| $\mathrm{Cu}(1)-\mathrm{P}(1)$ | $2.2303(11)$ | $\mathrm{S}(4)-\mathrm{Sn}(1) \# 2$ | $2.6152(13)$ |
| $\mathrm{Cu}(1)-\mathrm{S}(2)$ | $2.2806(10)$ | $\mathrm{O}(1)-\mathrm{Sn}(1) \# 1$ | $2.0626(7)$ |
| $\mathrm{Cu}(1)-\mathrm{S}(2) \# 2$ | $2.3046(10)$ | $\mathrm{O}(1)-\mathrm{Sn}(1) \# 2$ | $2.0626(6)$ |

Symmetry transformations used to generate equivalent atoms: \#1-x+y+1, -x+1, z; \#2-y+1, x-y, Z

Table S3. Selected bond angles $\left({ }^{\circ}\right)$.

| Angle | $\left({ }^{\circ}\right)$ | Angle | $\left({ }^{\circ}\right)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{O}(1)-\mathrm{Sn}(1)-\mathrm{S}(3)$ | $168.03(11)$ | $\mathrm{S}(1) \# 1-\mathrm{Sn}(1)-\mathrm{S}(4) \# 1$ | $83.01(4)$ |
| $\mathrm{O}(1)-\mathrm{Sn}(1)-\mathrm{S}(1) \# 1$ | $99.23(12)$ | $\mathrm{S}(2)-\mathrm{Sn}(1)-\mathrm{S}(4) \# 1$ | $88.67(3)$ |
| $\mathrm{S}(3)-\mathrm{Sn}(1)-\mathrm{S}(1) \# 1$ | $91.93(4)$ | $\mathrm{S}(4)-\mathrm{Sn}(1)-\mathrm{S}(4) \# 1$ | $154.54(3)$ |
| $\mathrm{O}(1)-\mathrm{Sn}(1)-\mathrm{S}(2)$ | $83.52(12)$ | $\mathrm{P}(1)-\mathrm{Cu}(1)-\mathrm{S}(2)$ | $132.04(4)$ |
| $\mathrm{S}(3)-\mathrm{Sn}(1)-\mathrm{S}(2)$ | $86.17(4)$ | $\mathrm{P}(1)-\mathrm{Cu}(1)-\mathrm{S}(2) \# 2$ | $120.10(4)$ |
| $\mathrm{S}(1) \# 1-\mathrm{Sn}(1)-\mathrm{S}(2)$ | $170.41(4)$ | $\mathrm{S}(2)-\mathrm{Cu}(1)-\mathrm{S}(2) \# 2$ | $104.29(4)$ |
| $\mathrm{O}(1)-\mathrm{Sn}(1)-\mathrm{S}(4)$ | $77.58(3)$ | $\mathrm{P}(2)-\mathrm{Cu}(2)-\mathrm{S}(1) \# 1$ | $111.22(3)$ |
| $\mathrm{S}(3)-\mathrm{Sn}(1)-\mathrm{S}(4)$ | $96.98(5)$ | $\mathrm{P}(2)-\mathrm{Cu}(2)-\mathrm{S}(1) \# 2$ | $111.22(3)$ |
| $\mathrm{S}(1) \# 1-\mathrm{Sn}(1)-\mathrm{S}(4)$ | $96.41(4)$ | $\mathrm{S}(1) \# 1-\mathrm{Cu}(2)-\mathrm{S}(1) \# 2$ | $107.67(3)$ |
| $\mathrm{S}(2)-\mathrm{Sn}(1)-\mathrm{S}(4)$ | $93.15(3)$ | $\mathrm{P}(2)-\mathrm{Cu}(2)-\mathrm{S}(1)$ | $111.22(3)$ |
| $\mathrm{O}(1)-\mathrm{Sn}(1)-\mathrm{S}(4) \# 1$ | $77.41(3)$ | $\mathrm{S}(1) \# 1-\mathrm{Cu}(2)-\mathrm{S}(1)$ | $107.67(3)$ |
| $\mathrm{S}(3)-\mathrm{Sn}(1)-\mathrm{S}(4) \# 1$ | $108.49(5)$ | $\mathrm{S}(1) \# 2-\mathrm{Cu}(2)-\mathrm{S}(1)$ | $107.67(3)$ |

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


Figure S1. ORTEP drawing of the complex cation of $\mathbf{2}$ with atom labeling scheme showing $30 \%$ themal ellipsoids. Phenyl rings on the phosphorous atoms, three dichloromethane solvent molecules and one perchlorate anion are omitted for clarity. Symmetry codes: A: $1-\mathrm{x}+\mathrm{y}, 1-\mathrm{x}, \mathrm{z}$;

B: 1-y, x-y, z.


Figure S2. XRD patterns of experimental (red line) and that of simulated from single crystal data (black line).


Figure S3. ${ }^{1}$ H NMR spectrum for compound 2 in DMSO-d ${ }^{6}$ using TMS as an internal reference.


Figure S4. ${ }^{31} \mathrm{P}$ NMR spectrum for compound $\mathbf{2}$ in DMSO solvent using $85 \% \mathrm{H}_{3} \mathrm{PO}_{4}$ as external standard.


Figure S5. IR spectrum for 2.


Figure S6. Raman spectrum for compound 2


Figure S7. Low-frequency infrared spectrum for compound 2

