Electronic Supplementary Information (ESI)

Construction of three-dimensional anionic molecular frameworks based on hydrogen-bonded metal-dithiolene complexes and the crystal solvent effect

So Yokomori,[a] Akira Ueda,*[a] Toshiki Higashino,[a] Reiji Kumai,[b] Youichi Murakami[b] and Hatsumi Mori*[a]

[a]*The Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 2778581, Japan. E-mail: a-ueda@issp.u-tokyo.ac.jp, hmori@issp.u-tokyo.ac.jp; Fax: +81 4 7136 3410; Tel: +81 4 7136 3410*

[b]*Condensed Matter Research Center (CMRC) and Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba, Ibaraki 3050801, Japan.*

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1. $(Ph_4P)[Au(catdt)_2]\cdot 0.5H_2O$, **3a**

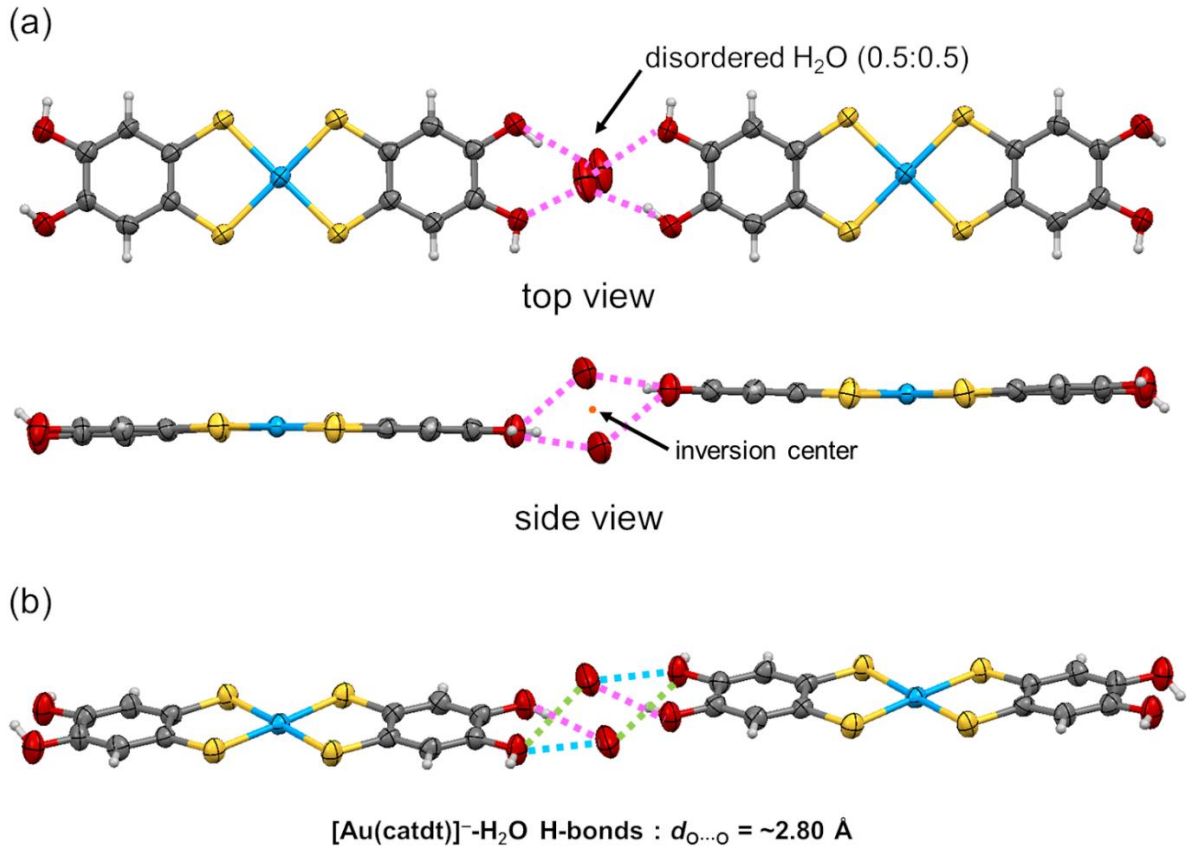

Fig. S1. Hydrogen-bonded motif positionally disordered H_2O molecules (0.5:0.5) and H-bonds between $[Au(catdt)_2]^-$ and H_2O in **3a**. (a) top view (top), side view (bottom) and (b) diagonal view. The thermal ellipsoids are scaled to the 50% probability level. Crystallographically equivalent H-bonds are shown in the same color dashed line in (b).

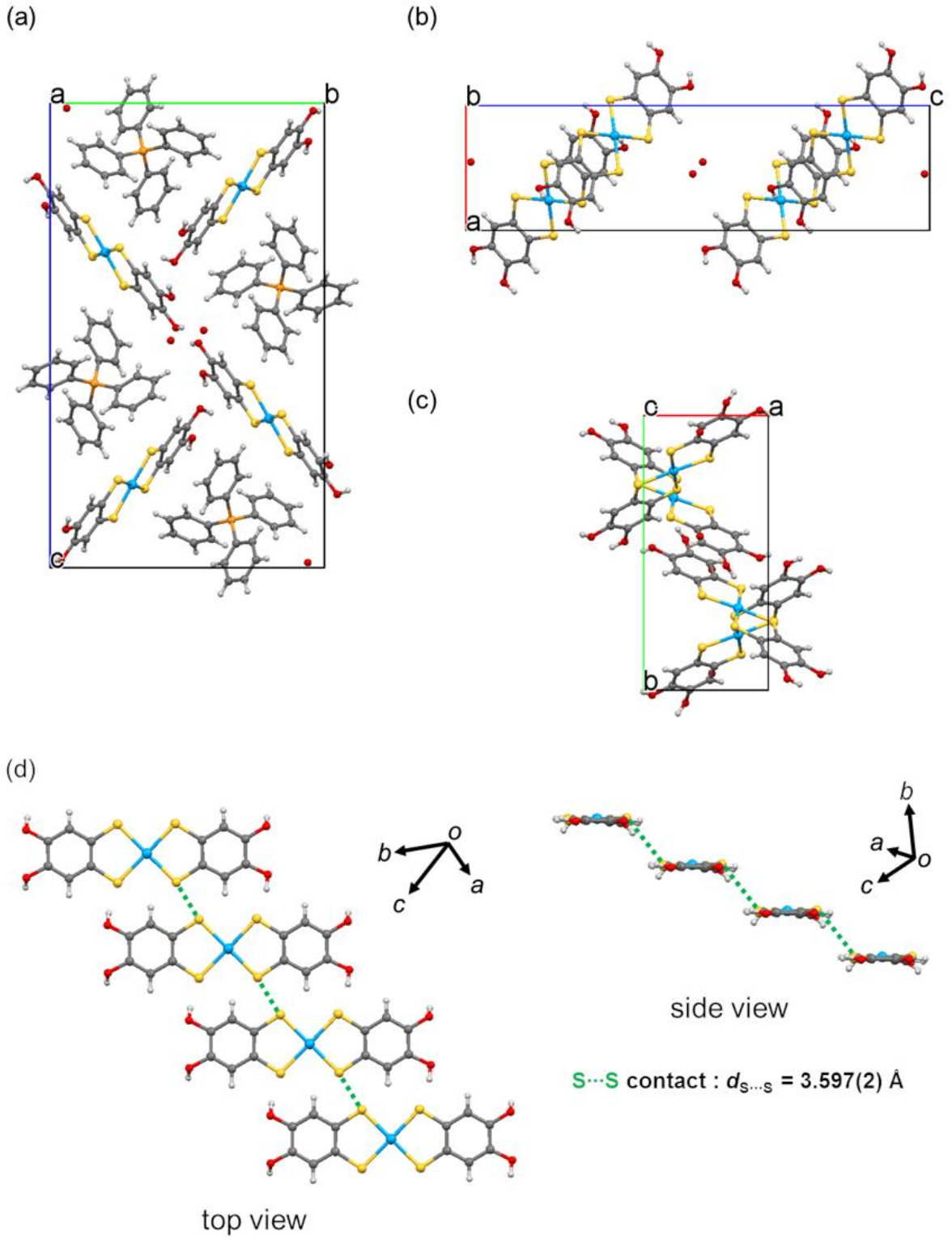

Fig. S2. Molecular arrangements in the unit cell of **3a**, viewed along the (a) *a*, (b) *b* and (c) *c* axis, respectively. Ph_4P^+ cations are omitted in (b) and (c) for clarify. (d) Top view (left) and side view (right) of $[Au(catdt)_2]^-$ molecules in 2D sheet on 3D framework.

2. $(Ph_4P)[Au(catdt)_2]\cdot Et_2O\cdot n(solv)$, **3b**

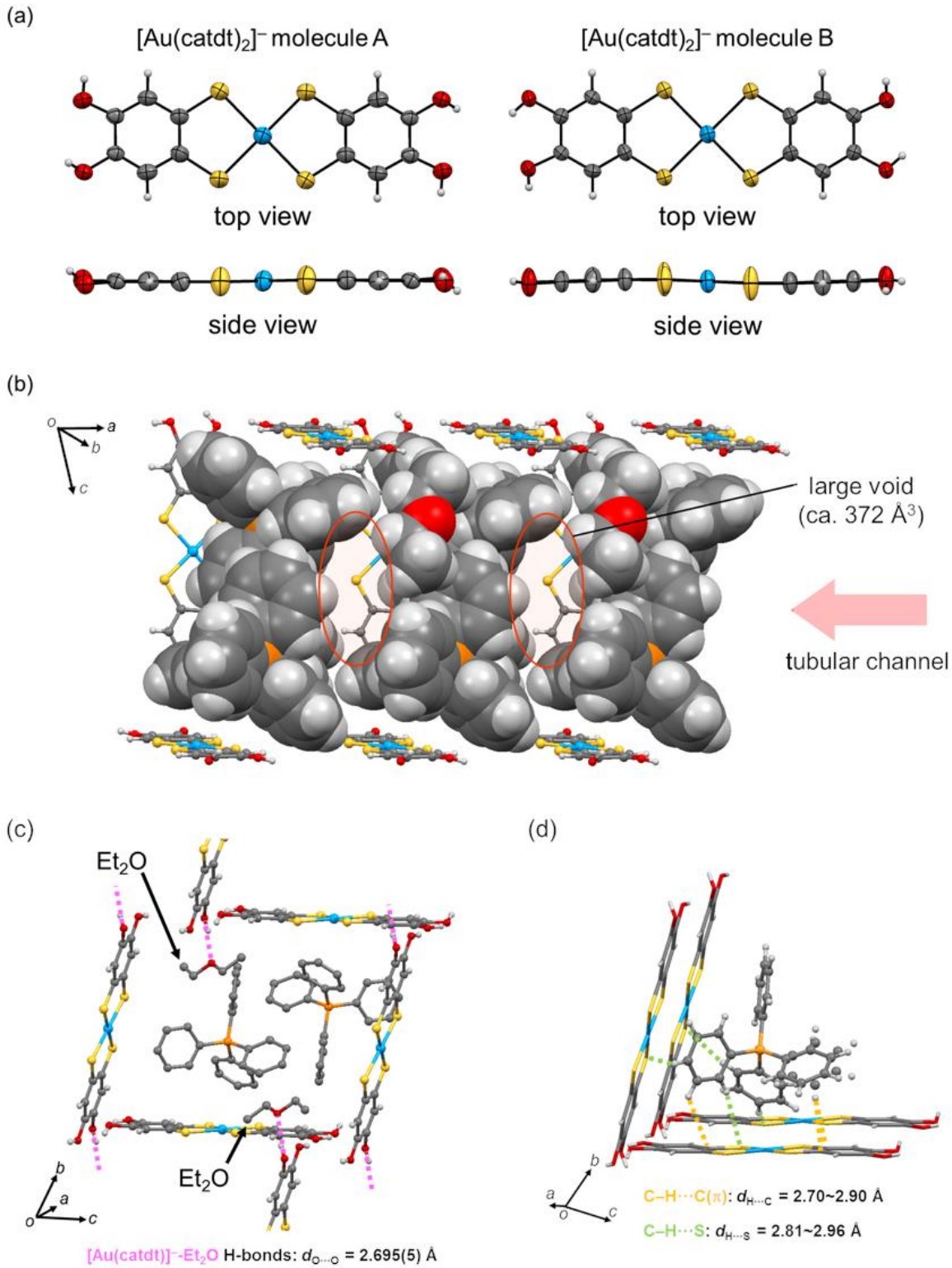

Fig. S3. (a) ORTEP drawings of two kinds of $[Au(catdt)_2]^-$ molecules in **3a**; top view (top), side view (bottom). The thermal ellipsoids are scaled to the 50% probability level. (b) Voids formed between

Ph_4P^+ and Et_2O molecules in the 1D channel. The volume of each void was calculated to be about 370 $Å^3$ by the Platon/SQUEEZE program[S1]. According to the crystal structure data, there should be solvent molecules in these voids; however, they are highly disordered and not to be determined. Thus their electron densities were removed by the Platon/SQUEEZE program. (c) Intermolecular H-bonds between $[Au(catdt)_2]^-$ and Et_2O in the tubular channel of the framework. Hydrogen atoms on Ph_4P^+ and Et_2O molecules are omitted in (c) and disordered phenyl group is omitted in (b) and (c) for clarify. (d) Intermolecular short contacts between $[Au(catdt)_2]^-$ (framework) and Ph_4P^+.

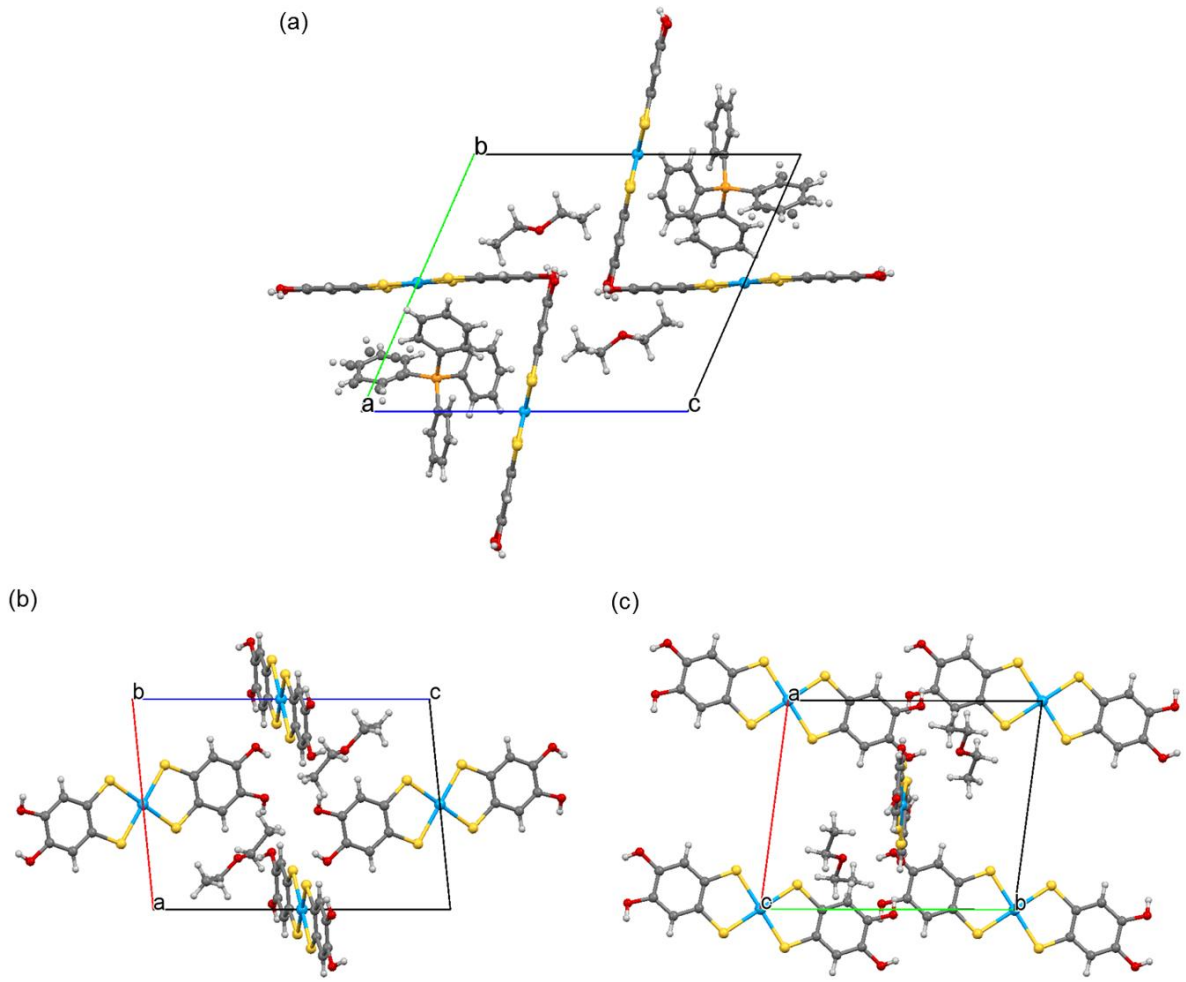

Fig. S4. Molecular arrangements in the unit cell of **3b**, viewed along the (a) *a*, (b) *b* and (c) *c* axis, respectively. Ph_4P^+ cations are omitted in (b) and (c) for clarify.

3. $(Ph_4P)[Au(catdt)_2]\cdot 2THF$, **3c**

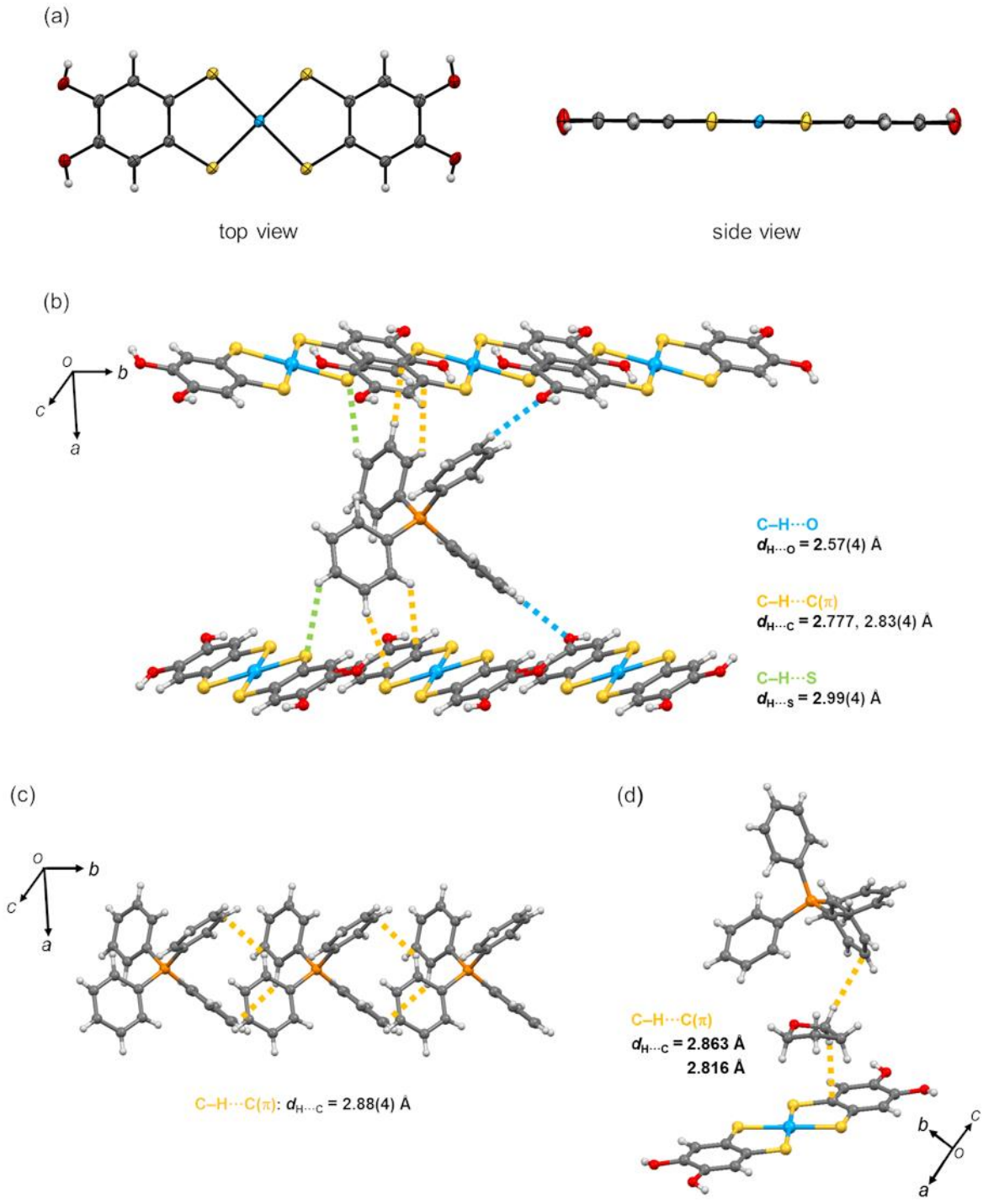

Fig. S5. (a) ORTEP drawings of $[Au(catdt)_2]^-$ in **3c**; top view (left), side view (right). The thermal ellipsoids are scaled to the 50% probability level. (b) Intermolecular short contacts between $[Au(catdt)_2]^-$ and Ph_4P^+. (c) Intermolecular short contacts between Ph_4P^+ cations. (d) Intermolecular short contacts between THF and $[Au(catdt)_2]^-$ and between THF and Ph_4P^+.

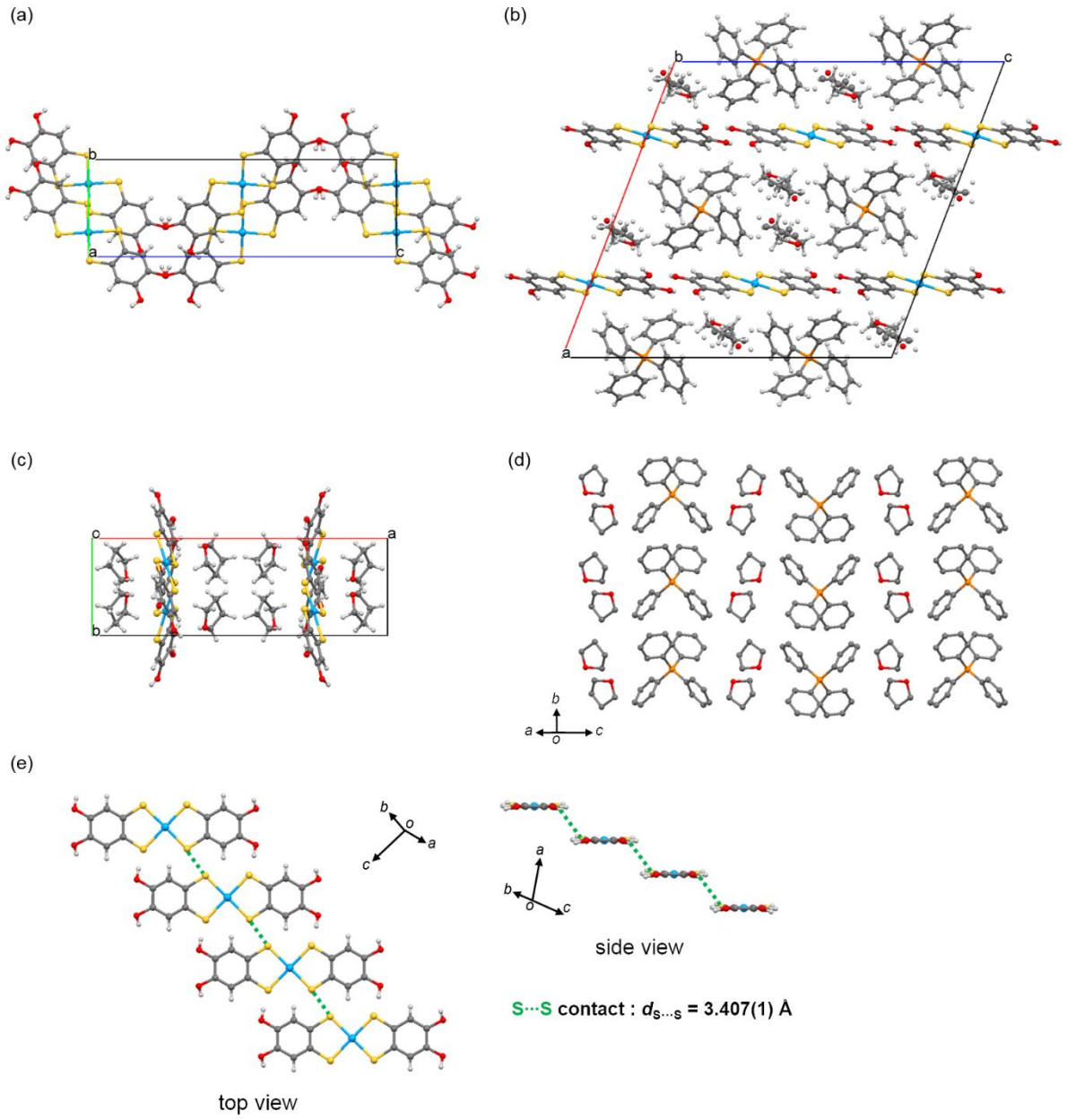

Fig. S6. Molecular arrangements in the unit cell of **3c**, viewed along the (a) *a*, (b) *b* and (c) *c* axis, respectively. For clarify, Ph_4P^+ cations and THF molecules are omitted in (a) and Ph_4P^+ cations are omitted in (c). (d) Top view of Ph_4P^+ and THF layer seen from vertical direction to 2D layer of $[Au(catdt)_2]^-$ (the same direction as Fig.10a). Hydrogen atoms are omitted in (d) for clarify. (e) Top view (left) and side view (right) of $[Au(catdt)_2]^-$ molecules of 2D layer.

4. $(Ph_4P)_3[Au(catdt)_2]\cdot Br_nCl_{2-n}$, **2**

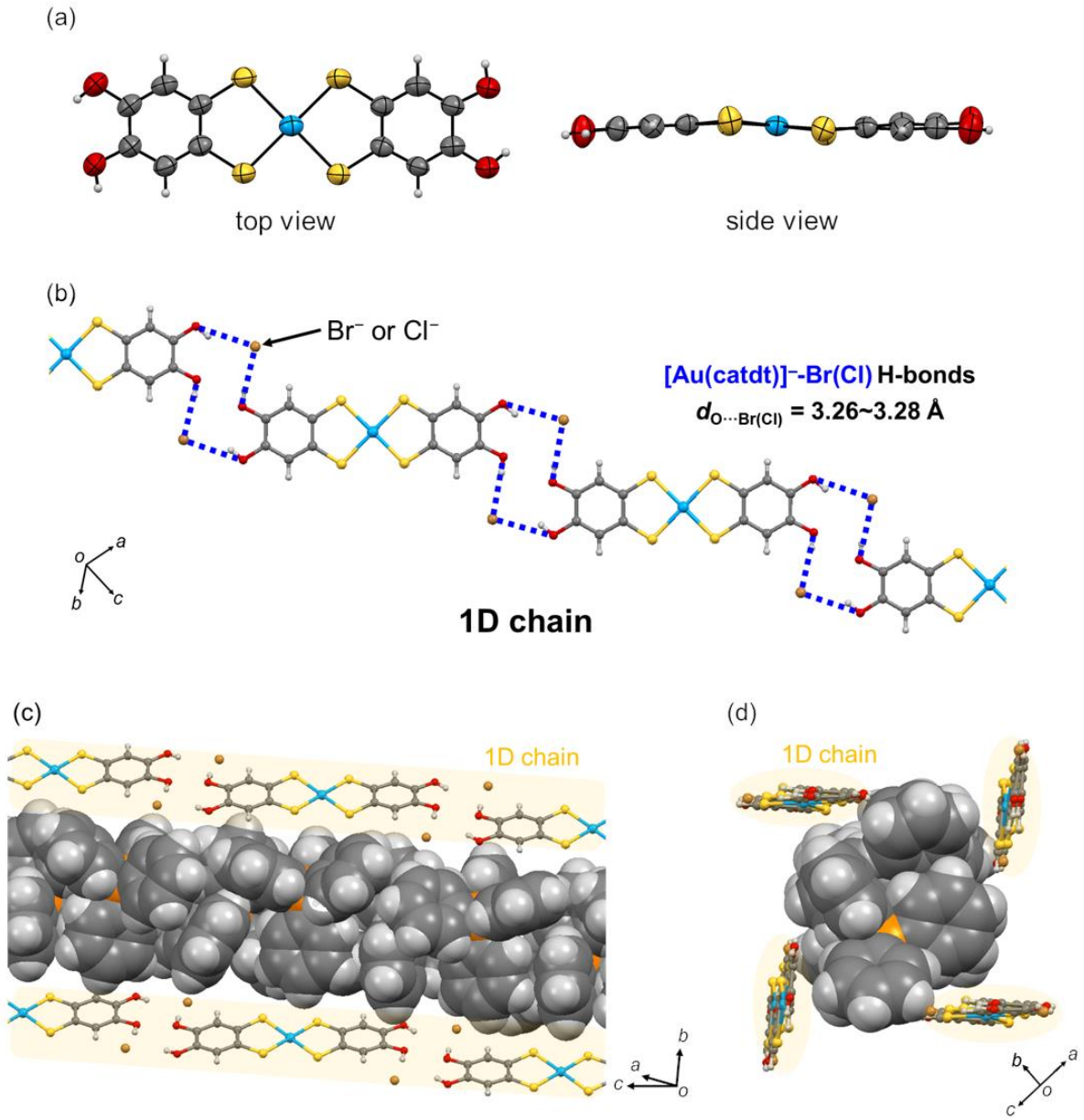

Fig. S7. The crystal structure of anion salt **2**. (a) ORTEP drawings of $[Au(catdt)_2]^-$; top view (left), side view (right). The thermal ellipsoids are scaled to the 50% probability level. (b) The 1D chain structure formed through intermolecular H-bonds between $[Au(catdt)_2]^-$ and Br^- (or Cl^-). (c) Arrangement manner of the 1D chain structures separated by Ph_4P^+ cations, viewed along the (c) parallel and (d) vertical direction to the chain. (d) Cl^- anions are omitted for clarify in (b), (c) and (d).

5. References

S1. (*a*) P. v. d. Sluis and A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 194–201; (*b*) A. L. Spek, *Acta Crystallogr., Sect. D: Biol. Crystallogr*., 2009, **65**, 148–155. (c) A. L. Spek, *Acta Crystallogr. Sect.* C 2015, **71**, 9.