

Supporting Information

**PCU-Type Copper-Rich Open-Framework Chalcogenides:
Pushing Up the Length Limit of Connection Mode and the
First Mixed-Metal [Cu₇GeSe₁₃] Cluster**

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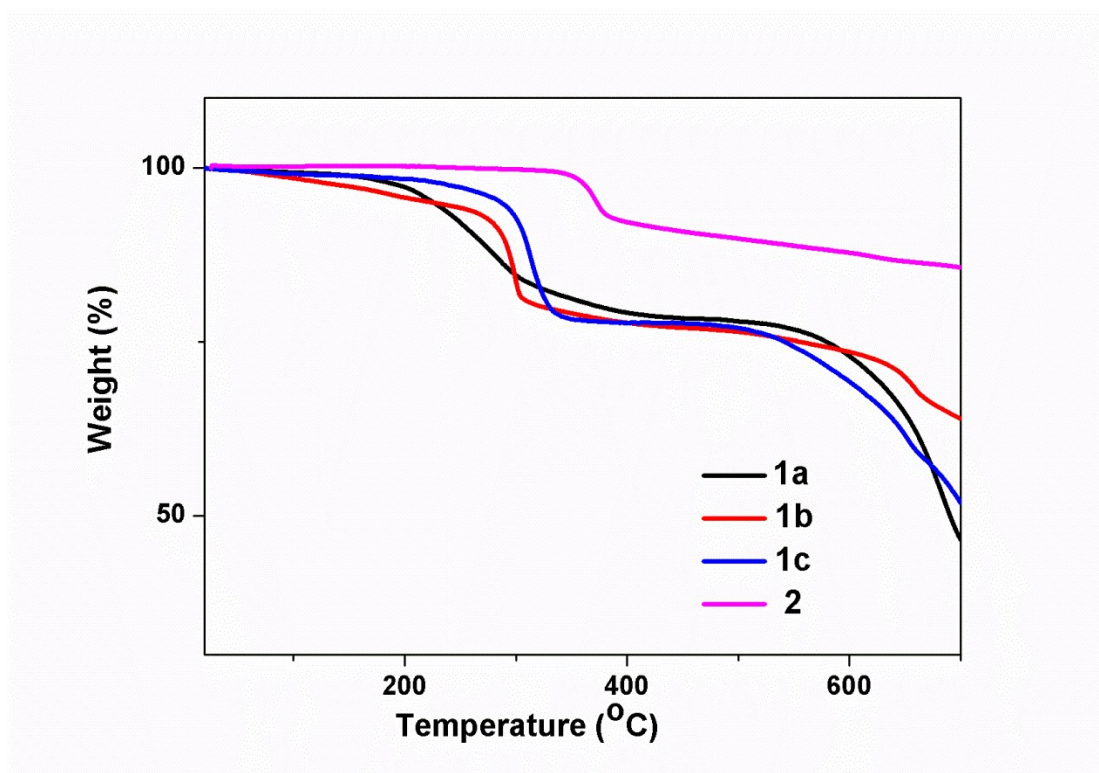


Figure S1. TGA curves for compounds **1a-1c** and **2**.

Compound **1a** undergoes the first step weight loss about 17% from room temperature to 310°C, which is in good agreement with the calculated value from the SCXRD analysis, corresponding to the loss of the piperidine molecules (Calcd. 17.43%). For compound **1b**, the first weight loss of 7% could be attributed to loss of water molecules (Calcd. 6.86%). On further heating, the second abrupt weight loss of around 12% occurs between 272-305°C, corresponding to the removal of the charge-balanced organic DABCO molecules (Calcd. 13.16%). Compound **1c** undergoes the first step weight loss about 21% from room temperature to 335°C, which could be correspond to the loss of the ethylenediamine molecules. Compound **2** undergoes the first step weight loss about 7.31% from room temperature to 390°C, corresponding to the removal of TAEA molecules (Calcd. 7.80%).

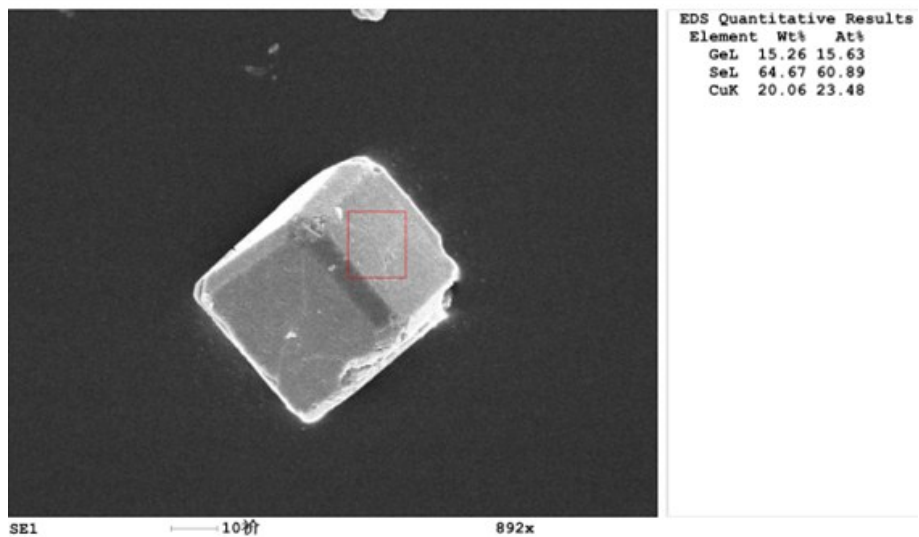


Figure S2. SEM image of compound 1a.

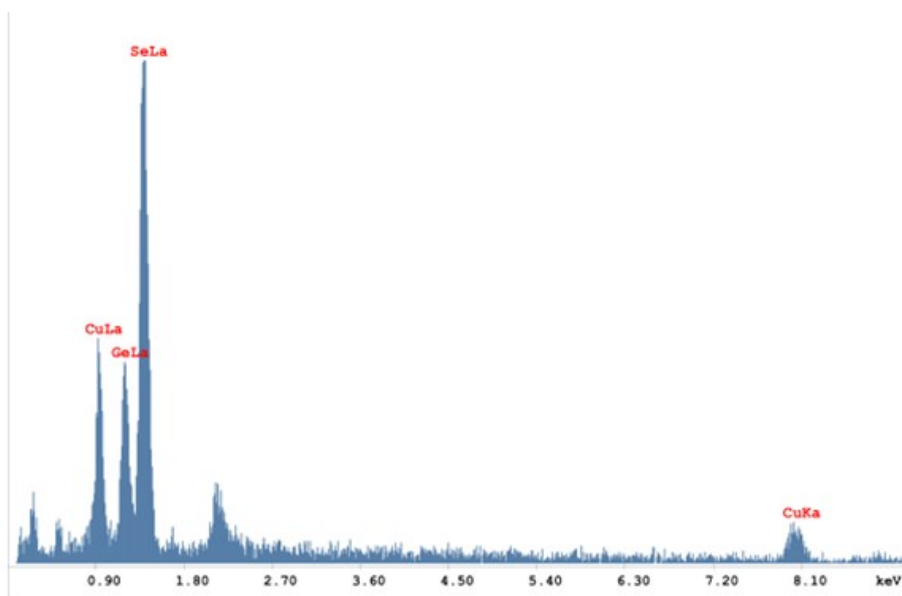


Figure S3. EDS of compound 1a.

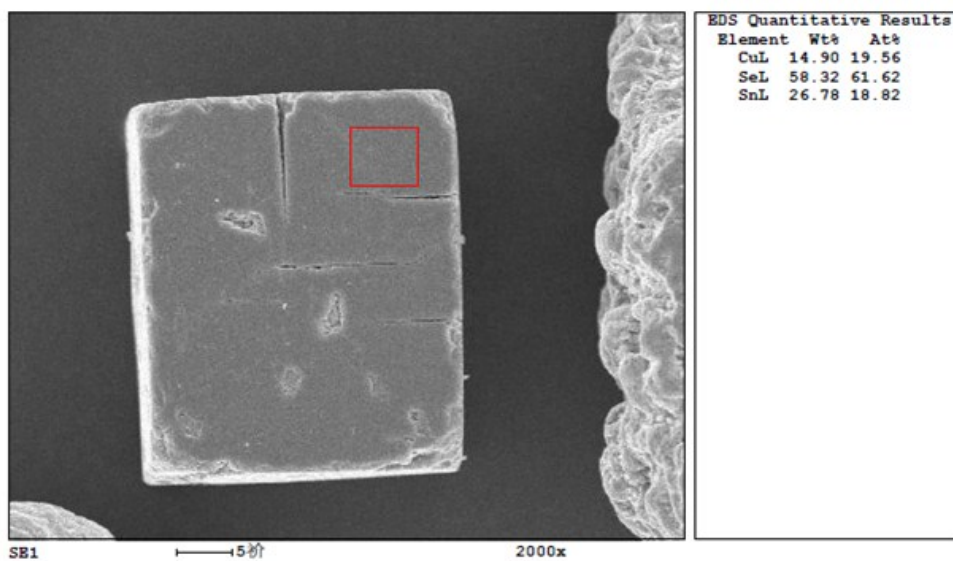


Figure S4. SEM image of compound 1b.

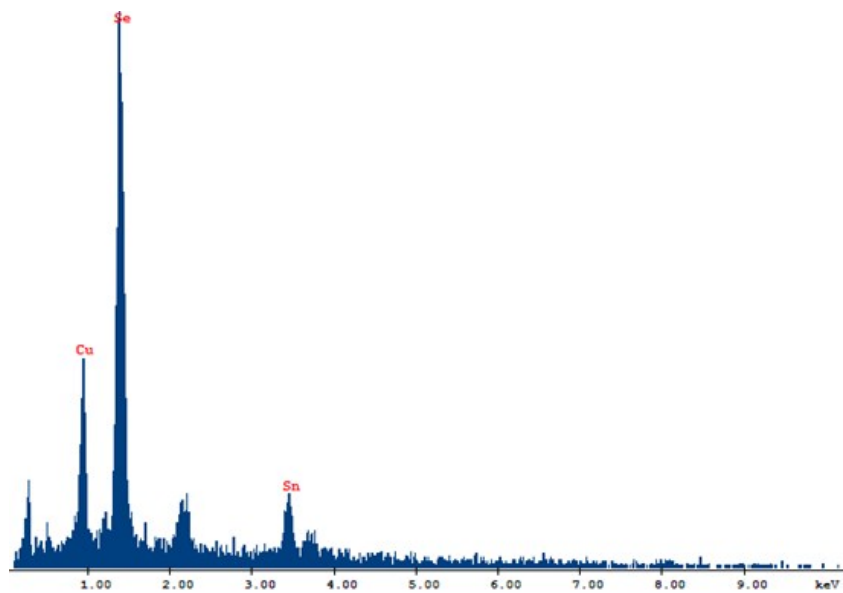


Figure S5. EDS of compound **1b**.

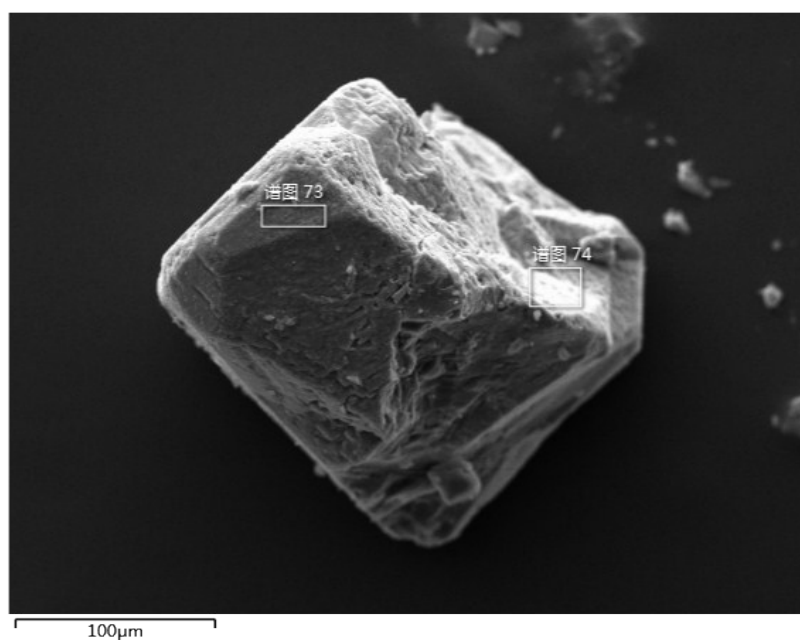


Figure S6. SEM image of compound **1c**.

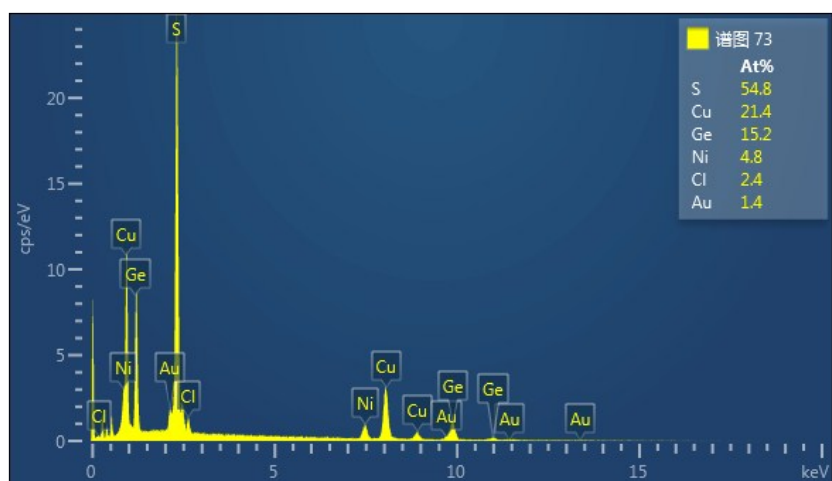


Figure S7. EDS of compound **1c**.

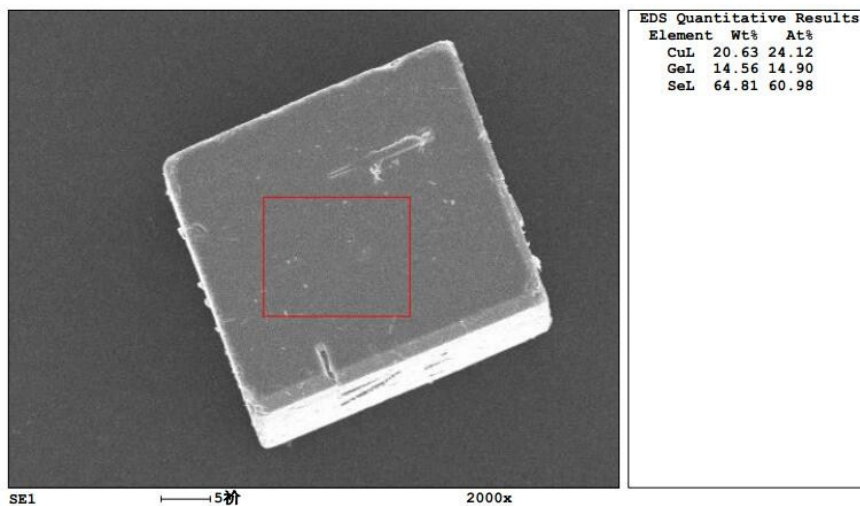


Figure S8. SEM image of compound 2.

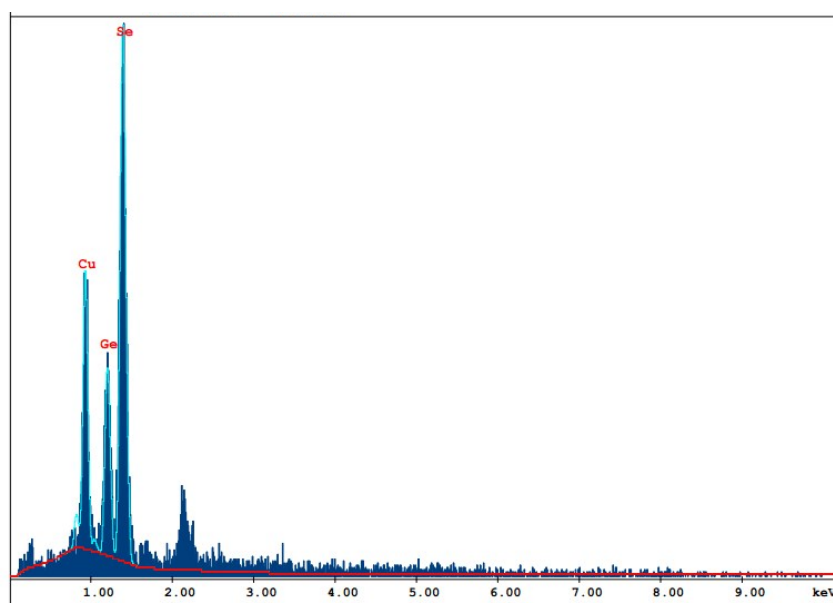


Figure S9. EDS of compound 2.

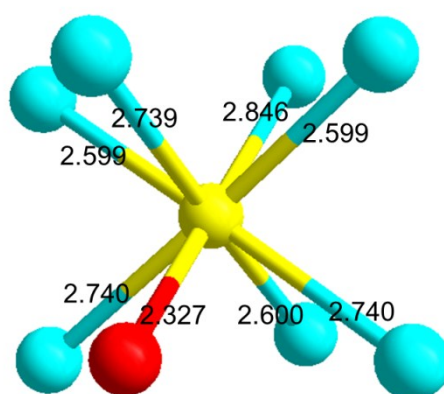


Figure S10. The Cu-Se (central) bond length and Ge-Se bond length in compound 2.

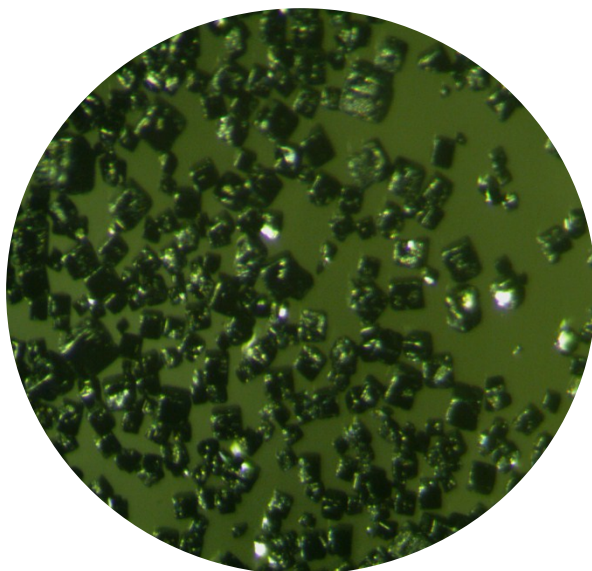


Figure S11. The crystal photo of compound **1a**.

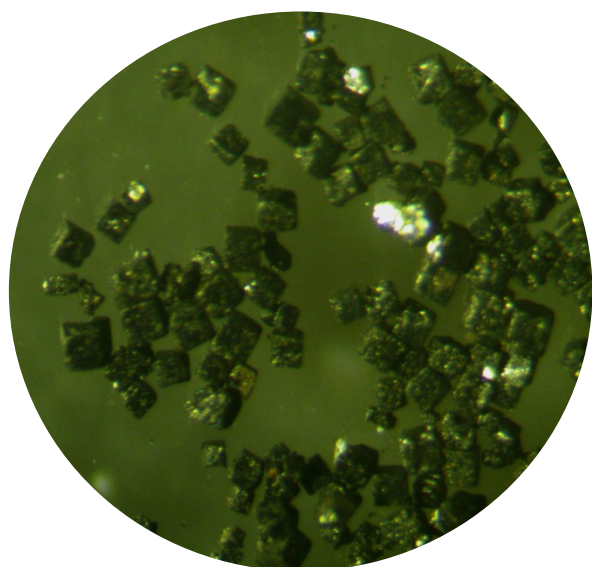


Figure S12. The crystal photo of compound **1b**.

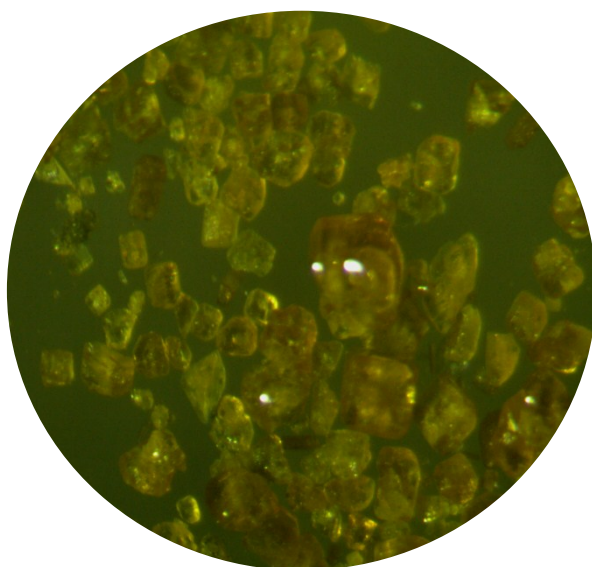


Figure S13. The crystal photo of compound **1c**.

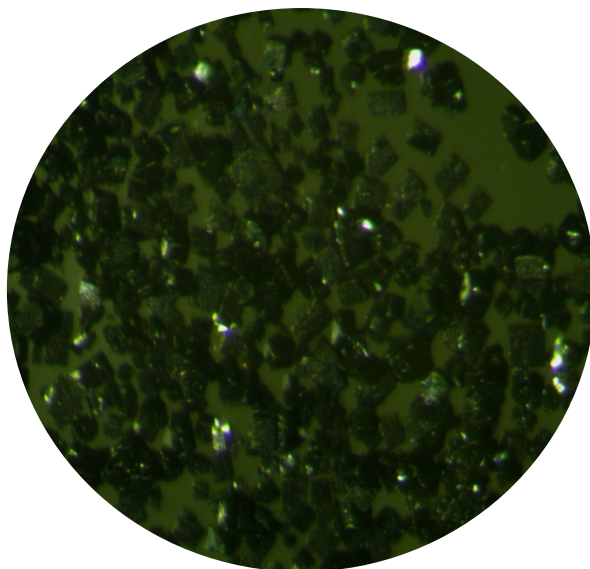


Figure S14. The crystal photo of compound **2**.

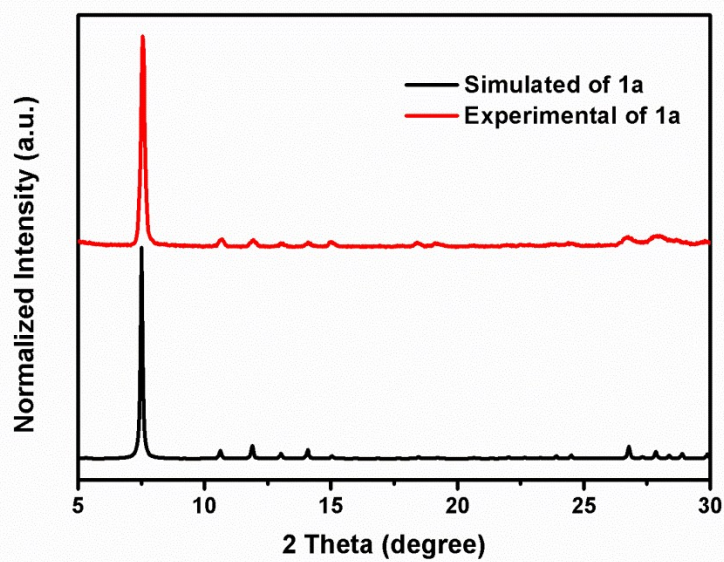


Figure S15. The simulated and experimental PXRD patterns of compound **1a**.

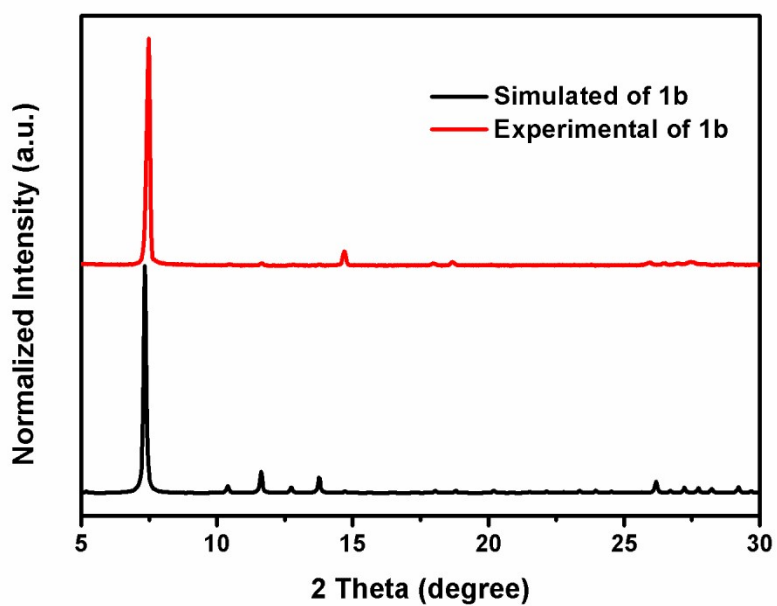


Figure S16. The simulated and experimental PXRD patterns of compound **1b**.

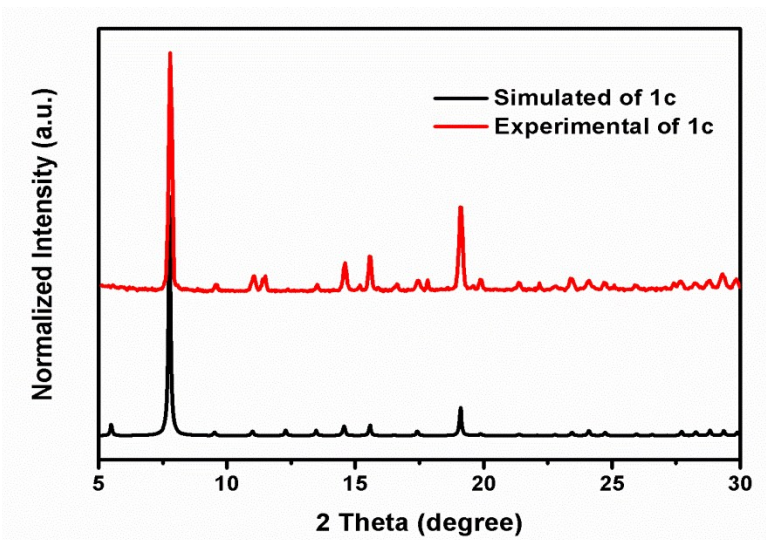


Figure S17. The simulated and experimental PXRD patterns of compound 1c.

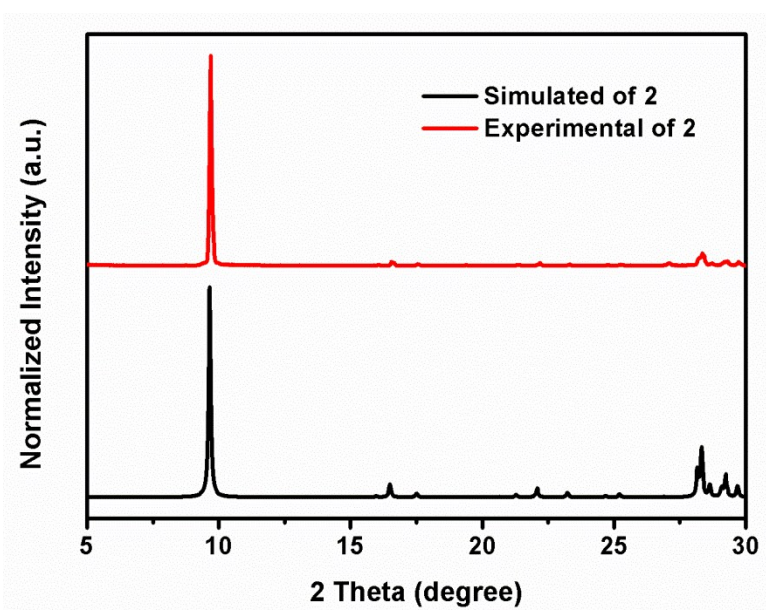


Figure S18. The simulated and experimental PXRD patterns of compound 2.

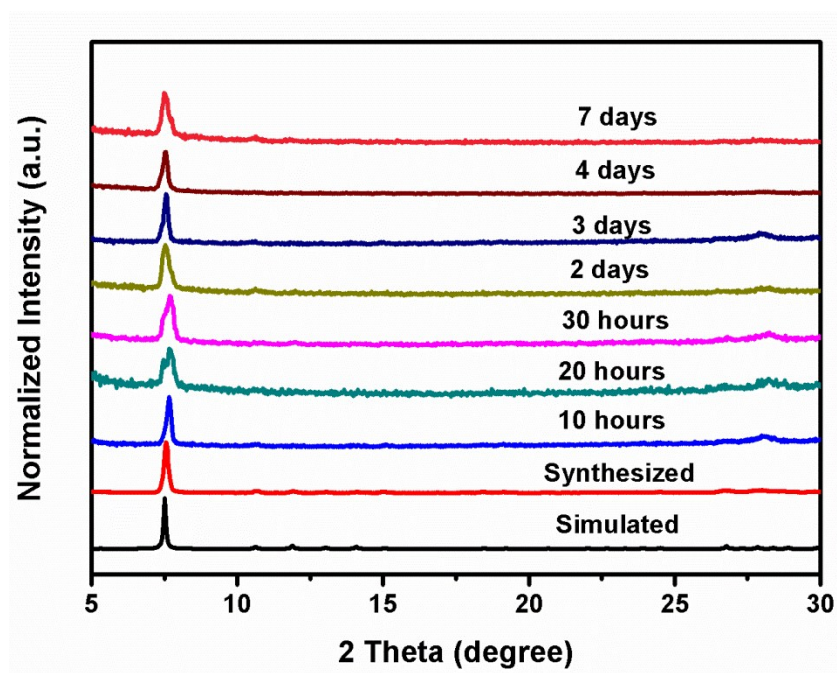


Figure S19. The structural stability of compound 1a in air.

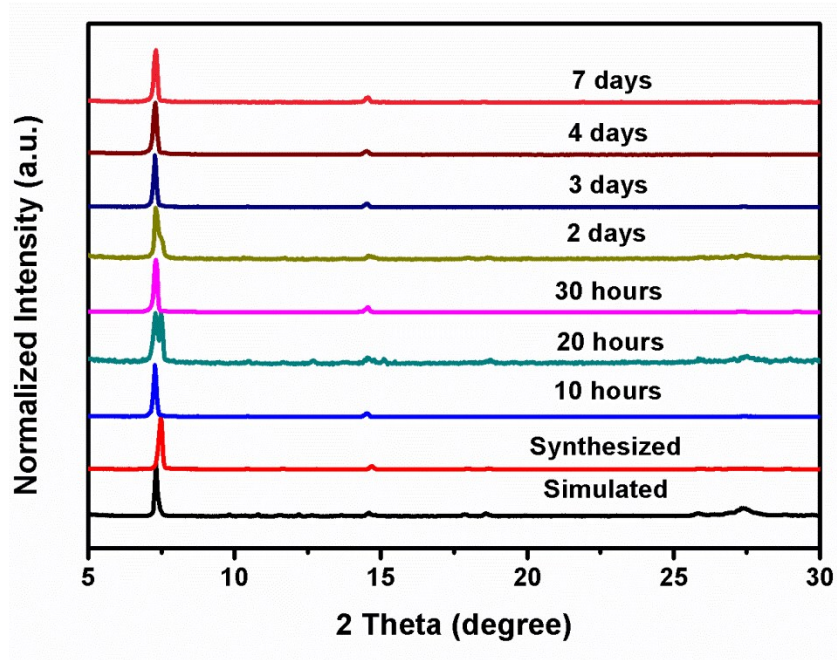


Figure S20. The structural stability of compound **1b** in air.

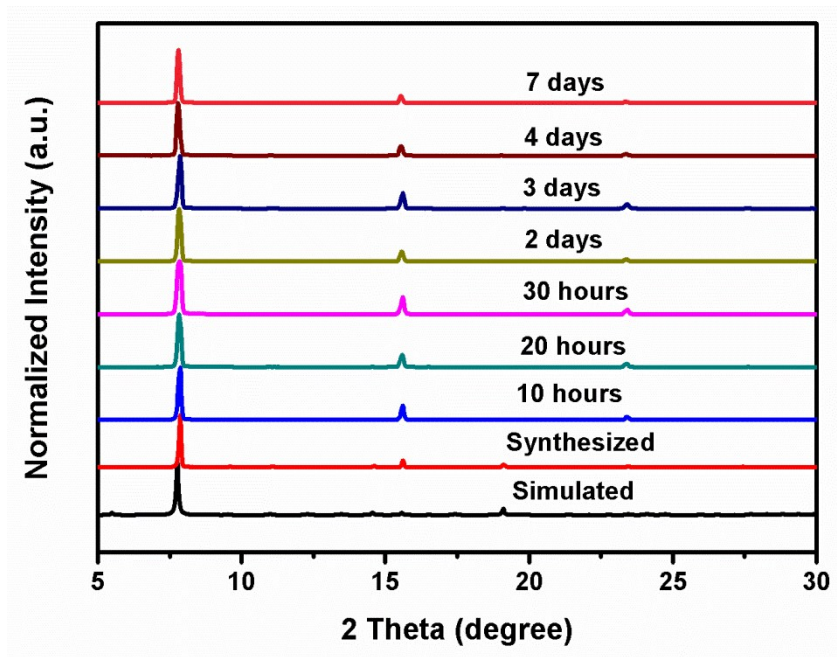


Figure S21. The structural stability of compound **1c** in air.

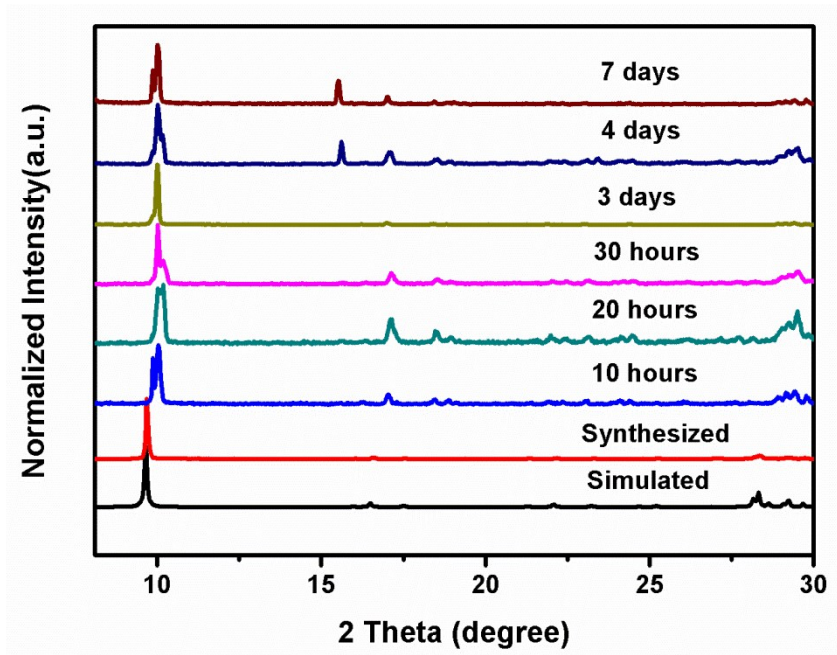


Figure S22. The structural stability of compound 2 in air.