Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting information

Lithium Cubane Clusters as Tetrahedral, Square Planar, and Linear Nodes for Supramolecular Assemblies

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Experimental details:

Materials and Methods. All reagent and solvent were commercially available and used as supplied without further purification. Gas sorption experiments were carried out on a Micromeritics ASAP 2020 surface area and pore size analyzer.

Synthesis of $Li_4(PyO)_4(MeOH)_4$ (HLiF-0). In a 20 mL vial, 25 mg of 4-pyridinol was dissolved in 5.018 g methanol and stirred for 10 minutes, then 0.3 mL of *t*-BuOLi (1.0 M solution in hexane) was added and stirred for another 10 minutes. The final clear solution was sealed and heated in a 100 °C oven for about 48 hours. Large amount of colorless crystals were obtained.

Synthesis of $Li_4(6\text{-}iQlO)_4(MeOH)_4$ (HLiF-1). In a 20 mL vial, 73 mg of 6-isoquinolinol was dissolved in 4.024 g methanol and stirred for 10 minutes, then 0.5 mL of *t*-BuOLi (1.0 M solution in hexane) was added and stirred for another 10 minutes. The final clear solution was sealed and heated in a 90 °C oven for about 24 hours. Large amount of colorless crystals were obtained.

Synthesis of $Li_4(6\text{-}QlO)_4(MeOH)_4$ (HLiF-2). In a 20 mL vial, 73 mg of 6-quinolinol was dissolved in a mixture of 0.525 g methanol and 2.525 g toluene to form a dark brown solution, after stirring for 10 minutes, 0.5 mL of *t*-BuOLi (1.0 M solution in hexane) was added, the turbid solution was stirred for another 10 minutes. The final solution was sealed and placed in a 70 °C oven for about 48 hours. Large amount of colorless crystals were obtained.

Synthesis of $Li_4(4\text{-}QlO)_4(MeOH)_4$ (HLiF-3). In a 20 mL vial, 72 mg of 4-quinolinol was dissolved in a mixture of 0.523 g methanol and 2.531 g toluene to form a clear solution, after stirring for 10 minutes, 0.5 mL of *t*-BuOLi (1.0 M solution in hexane) was added, the turbid solution was stirred for another 10 minutes. The final solution was sealed and placed in a 90 °C oven for about 48 hours. Large amount of colorless crystals were obtained.

Synthesis of $Li_4(5\text{-}QlO)_4(MeOH)_4$ (HLiF-4). In a 20 mL vial, 73 mg of 5-quinolinol was dissolved in 5.024 g methanol to form a clear solution, after stirring for 10 minutes, 0.5 mL of *t*-BuOLi (1.0 M solution in hexane) was added. After stirring for another 10 minutes, the final solution was sealed and heated in a 120 °C oven for about 24 hours. Large amount of colorless crystals were obtained.

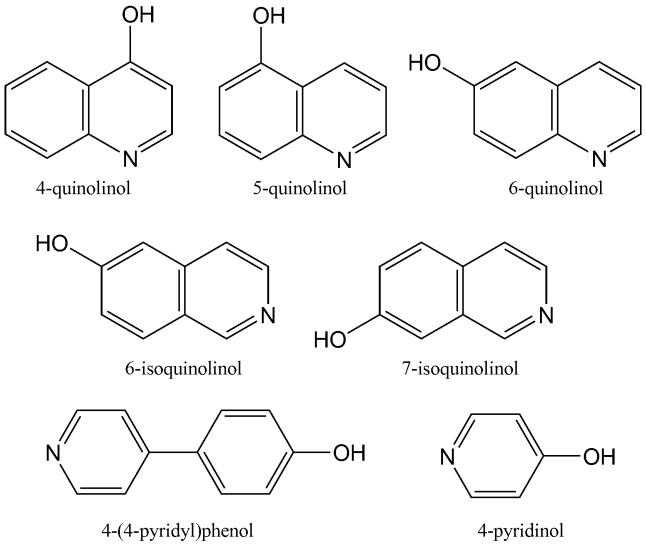
Synthesis of $Li_4(5\text{-}QlO)_4(MeOH)_4$ (HLiF-5). In a 20 mL vial, 73 mg of 6-quinolinol was dissolved in a mixture of 0.514 g methanol and 2.516 g toluene to form a dark brown solution, after stirring for 10 minutes, 0.5 mL of *t*-BuOLi (1.0 M solution in hexane) was added, the turbid solution was stirred for another 10 minutes. The final solution was sealed and placed in a 70 °C oven for about 48 hours. Large amount of colorless crystals were obtained.

Synthesis of $Li_4(7\text{-}iQlO)_4(MeOH)_4$ (HLiF-6). In a 20 mL vial, 71 mg of 7-isoquinolinol was dissolved in a mixture of 1.045 g methanol and 1.609 g toluene to form a dark brown solution, after stirring for 10 minutes, 0.5 mL of *t*-BuOLi (1.0 M solution in hexane) was added, the turbid solution was stirred for another 10 minutes. The final solution was sealed and placed in a 70 °C oven for about 48 hours. Large amount of colorless crystals were obtained.

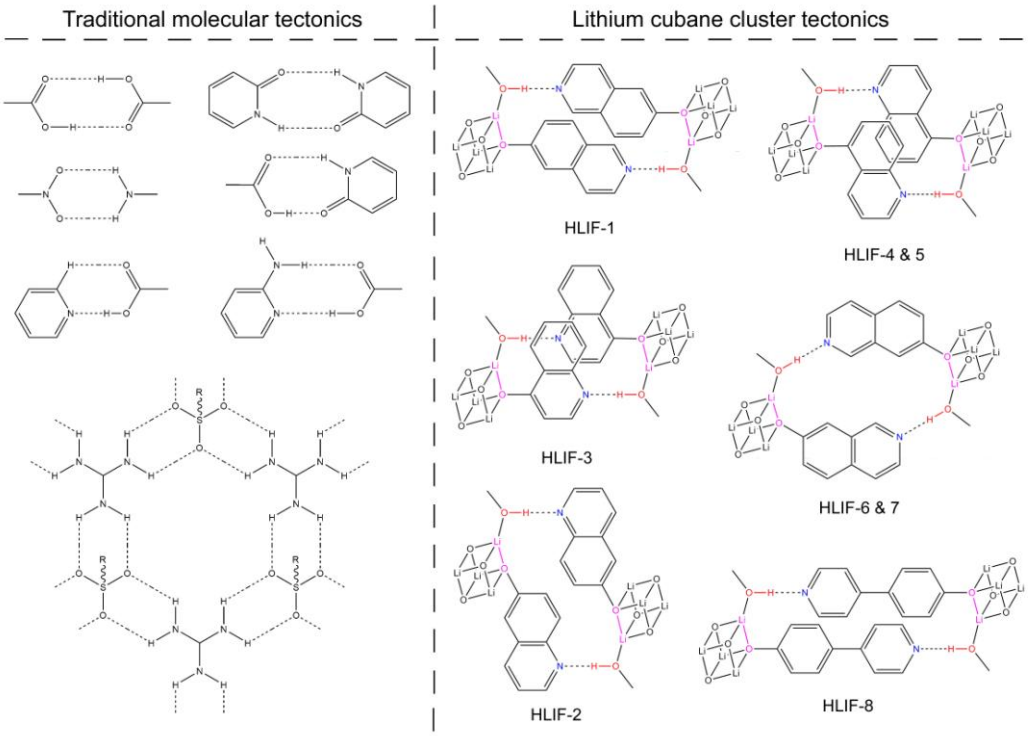
Synthesis of Li_4(7-*i*QlO)$_4$(MeOH)$_4$ (HLiF-7). In a 20 mL vial, 73 mg of 7-isoquinolinol was dissolved in 4.027 g methanol and stirred for 10 minutes, 0.5 mL of *t*-BuOLi (1.0 M solution in hexane) was then added and stirred for another 10 minutes. The final solution was sealed and placed in a 90 °C oven for about 24 hours. Large amount of colorless crystals were obtained.

Synthesis of Li_4(PyPhO)$_4$(MeOH)$_4$ (HLiF-8). In a 20 mL vial, 42 mg of 4-(4-pyridyl)phenol was dissolved in 1.502 g methanol and 1.042 g toluene and stirred for 10 minutes, 0.1 mL of *t*-BuLi (2.5 M solution in hexane) was then added and stirred for another 10 minutes. The final solution was sealed and placed in a 70 °C oven for about 72 hours. Large amount of colorless crystals were obtained.

Single-Crystal X-Ray Crystallography. Single-crystal X-ray analysis was performed on a Bruker Smart APEX II CCD area diffractometer with nitrogen-flow temperature controller using graphite-monochromated Mo KR radiation (λ=0.71073 Å), operating in the ωand φscan mode. Raw data collection and refinement were done using SMART. Data reduction was performed using SAINT$^+$ and corrected for Lorentz and polarization effects.[1] The SADABS program was used for absorption correction. The structure was solved by direct methods, and the structure refinements were based on $|F^2|$ with anisotropic displacement using SHELX-97.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. All crystallographic calculations were conducted with the SHELXTL software suites. The crystallographic data and the structural refinement parameters were summarized in Table 1. CCDC-843789-843797 contain the supplementary crystallographic data, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB21EZ, U.K.; fax (t44) 1223-336-033; or deposit@ccdc.cam.ac.uk).



Scheme S1 Ligands used in this work



Scheme S2. Comparison of traditional molecular tectonics (left) and the novel lithium cubane cluster tectonics reported in this work (right).

Table S1 Summary of the hydrogen bond distances and π-π stacking distances in HLiFs.

Code	O-H···N distance (Å) (H···N distance) [a]	π-π stacking distance (Å) [b]
HLiF-1	2.717 (1.937)	3.93
HLiF-2	2.700 (2.164)	N/A[c]
HLiF-3	2.746 (2.005)	3.91
HLiF-4	2.685 (1.892)	4.00
HLiF-5	2.713 (1.897)	4.06
HLiF-6	2.675 (1.856), 2.691 (1.791), 2.696 (1.890), 2.714 (1.986)	N/A
HLiF-7	2.717 (1.930), 2.689 (1.943), 2.746 (2.014), 2.644 (2.048)	N/A
HLiF-8	2.754 (1.891)	4.11

[a] The hydrogen atoms are not directly observed and are placed at the calculated positions. [b] The ππ stacking distance reported here were measured based on the distance between the centers of corresponding aromatic rings. [c] In HLiF-2, although the two quinoline rings are parallel to each other, the ππdistance is about 5.18 Å. The ππinteraction is usually very weak at such distance and can be ignored.

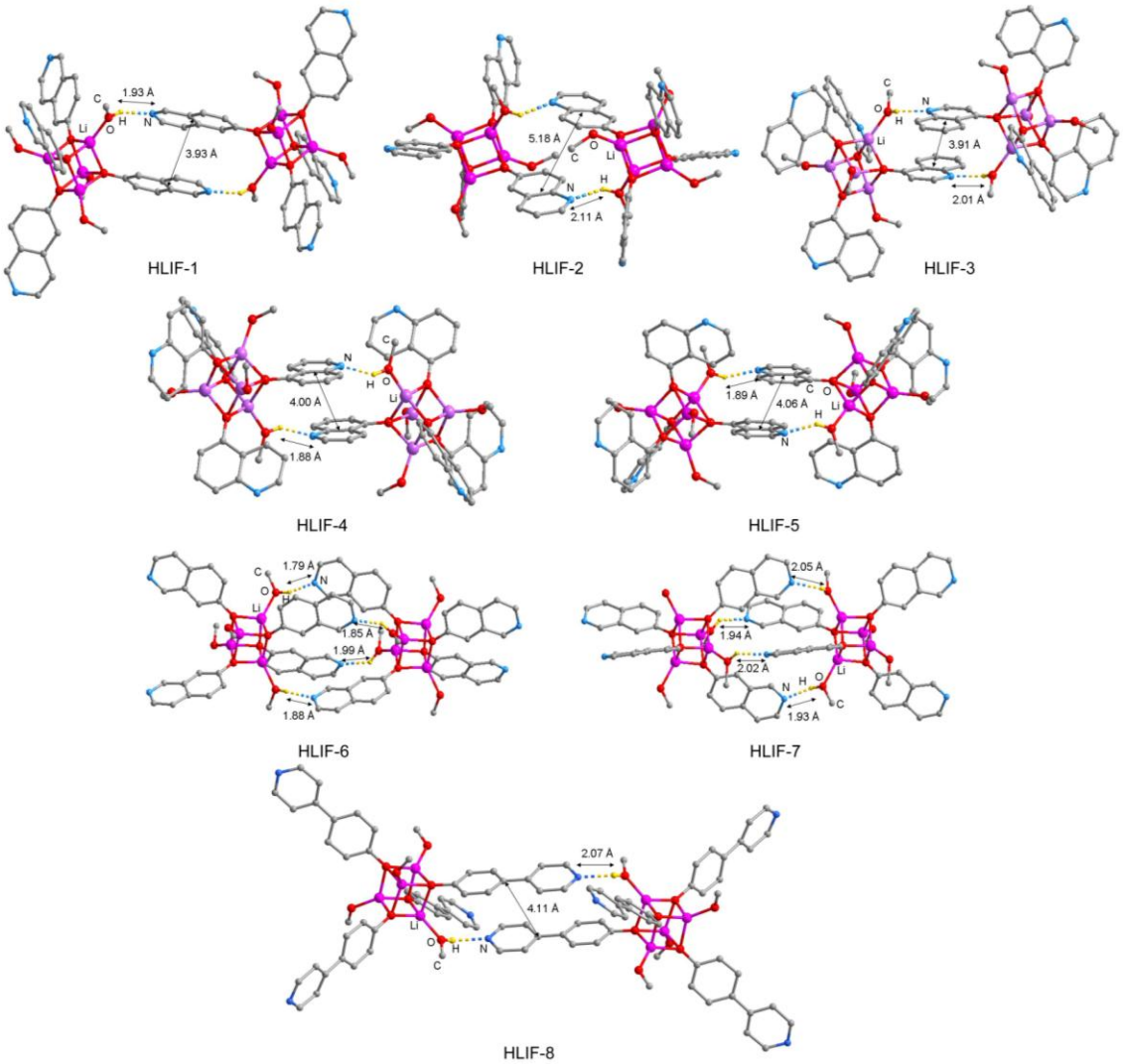


Figure S1 The connection between adjacent lithium cubane cluster in all HLiFs. H-bonding distance and ππdistances are given. (purple: Li; red: O; blue: N; grey: C; yellow: H, only part of the hydrogen atoms are shown, others are omitted for clarity)

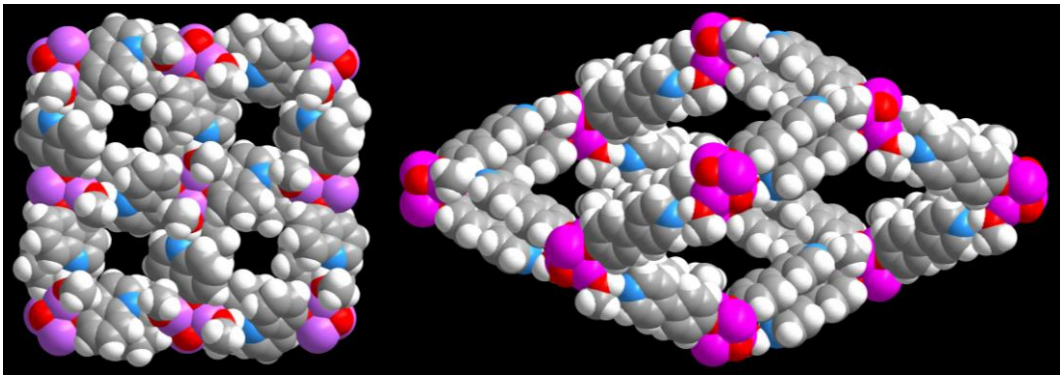


Figure S2. Space filling diagram of the HLiF-5 (left) and a single diamond net in HLiF-8 (right) (Li: purple, O: red, N: blue, C: grey and H: white).

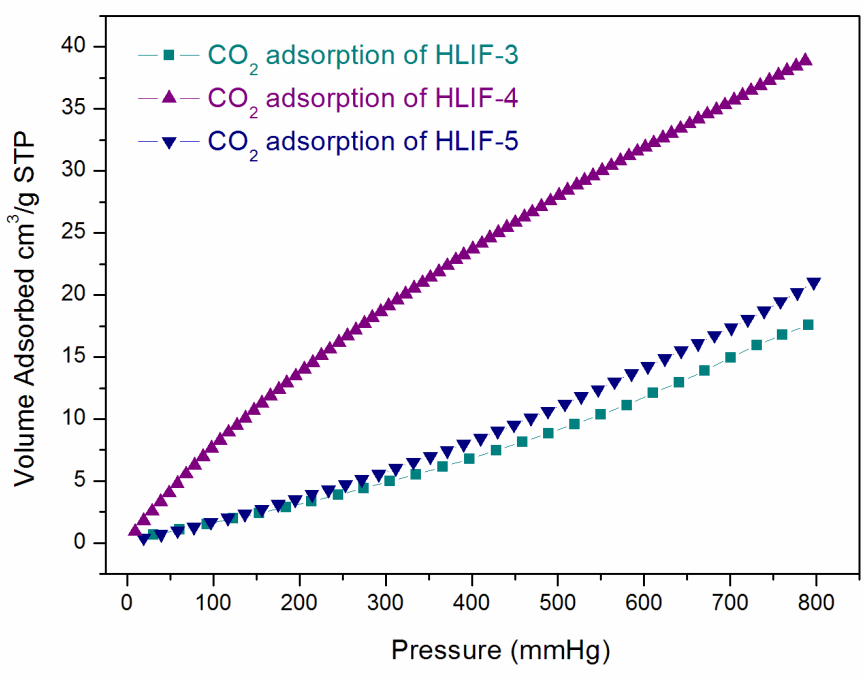


Figure S3. CO_2 adsoption isotherms of HLiF-3, HLiF-4 and HLiF-5 (at ~273 K).

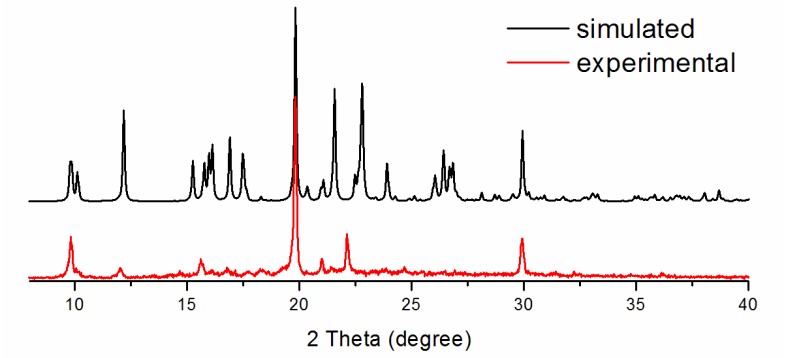


Figure S4. Experimental and simulated powder XRD pattern of HLiF-2.

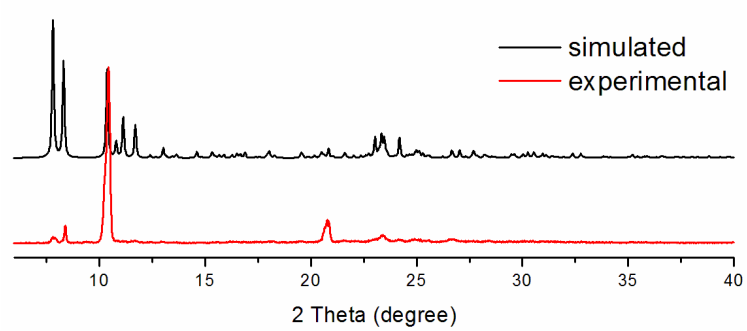


Figure S5. Experimental and simulated powder XRD pattern of HLiF-4.

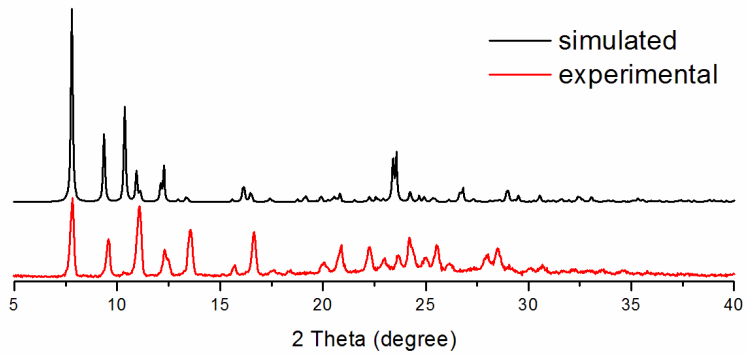


Figure S6. Experimental and simulated powder XRD pattern of HLiF-5.

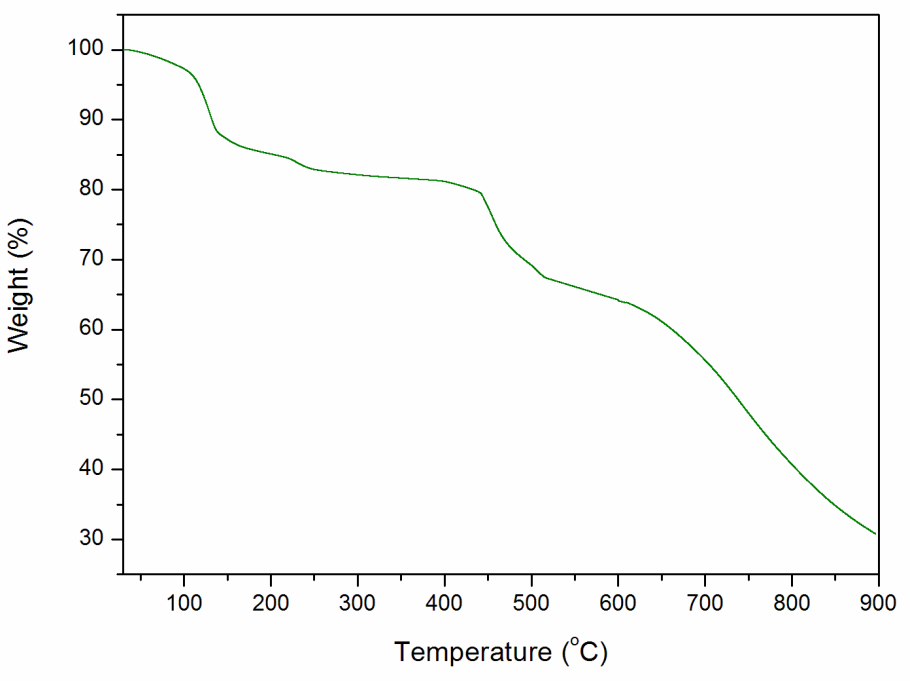


Figure S7. TG curve of HLiF-3. Conditions: temperature range from 30 °C to 900 °C at 10 °C/min under flow of N_2 gas.

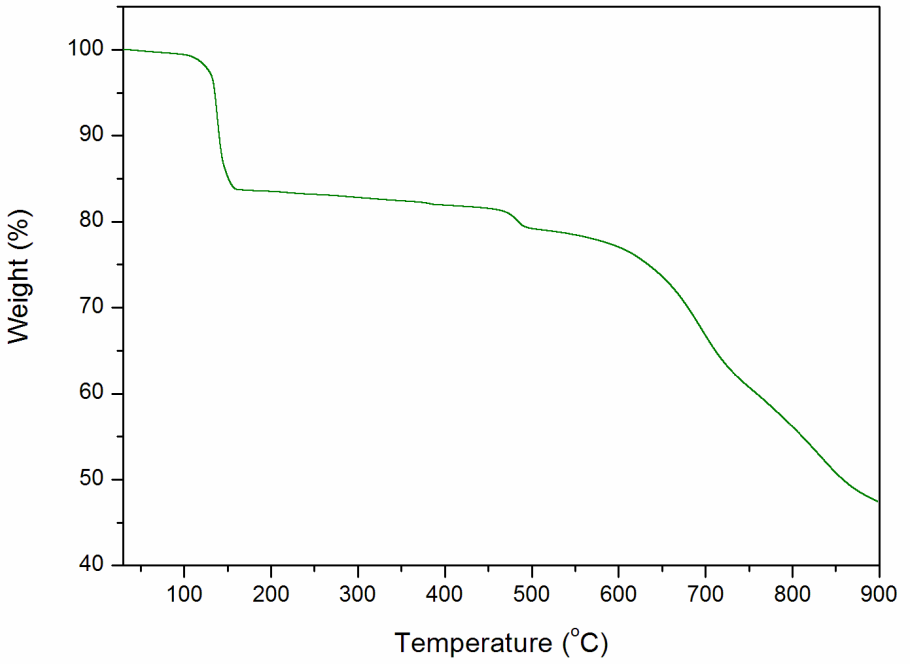


Figure S8. TG curve of HLiF-4. Conditions: temperature range from 30 °C to 900 °C at 10 °C/min under flow of N_2 gas.

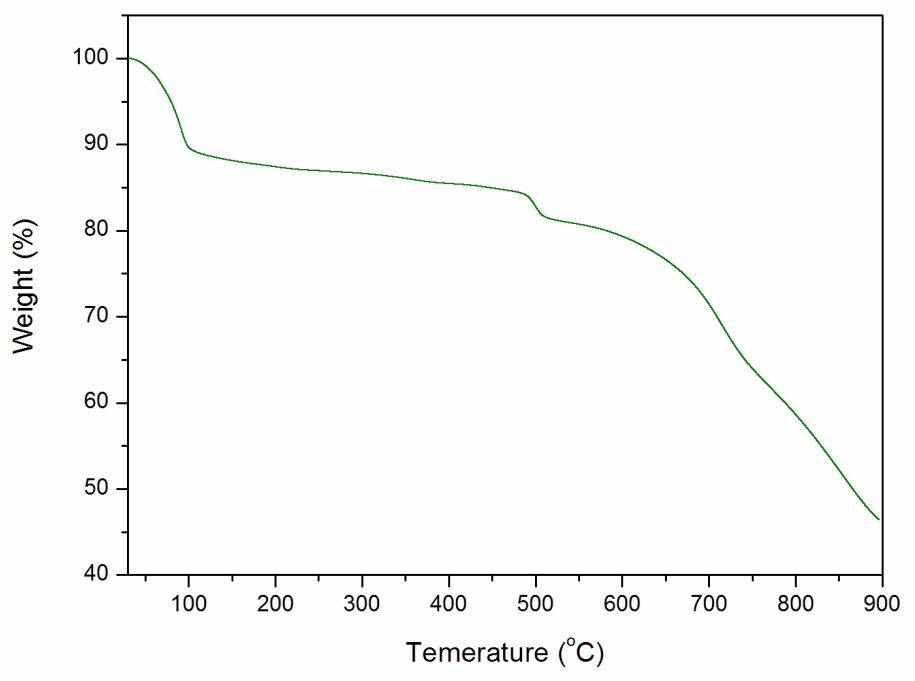


Figure S9. TG curve of HLiF-6. Conditions: temperature range from 30 °C to 900 °C at 10 °C/min under flow of N_2 gas.