Metal-Quinone Framework To Capture CO_2

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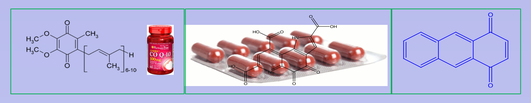
Need for the Study

1. MOFs: well-defined nanomaterials with super large surface area;
2. Sophisticated off-line analyses are often used to show MOFs' absorption;
3. Online detection of such a capture with a direct change in color is rare;
4. Naked metal centers in MOF has minimum selectivity to CO_2.

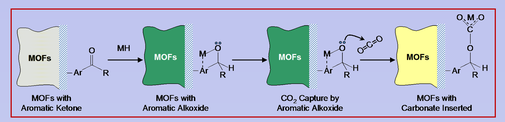
Concept

1. Quinone: conjugated cyclic dione structure; classified into 1,4; 1,2; or 9,10-quinone.



Co-enzyme Q10 PPQ 1,4-anthraquinone

2. Covalent binding will be used for CO_2 capture

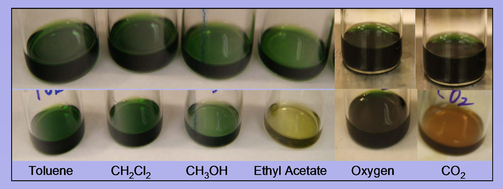


- Aromatic ketone in MOFs will generate aromatic alkoxide after reacting with metal hydride (MH);
- Charge transfer between M (metal center) and Ar (aromatic moiety) will impart a deep color to MOFs;
- After CO_2 capture on MOF surfaces, color will quickly fade away due to enlarged distance between M and Ar.

Experimental Method

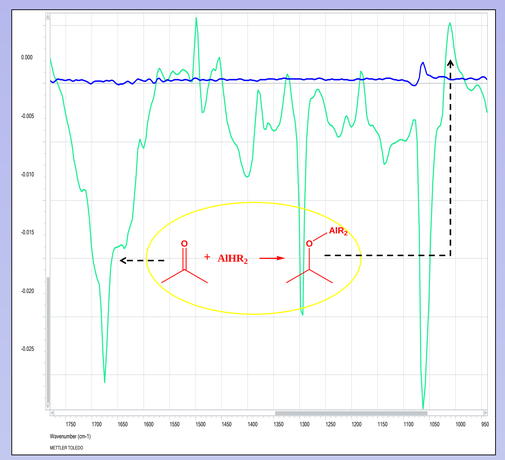
- 6,13-pentacenequinone and 1,4-anthracenequinone were selected as first quinones of interest;
- Diisobutylaluminum Hydride (DIBAL) was chosen as the reduction reagent and metal source;
- React-IR was utilized to track the reaction kinetics online.

Colorful Aromatic Alkoxide



- In one minute, ethyl acetate or CO_2 brought about color change;
- Preliminary reactions showed selectivity.

Spectroscopic Analysis

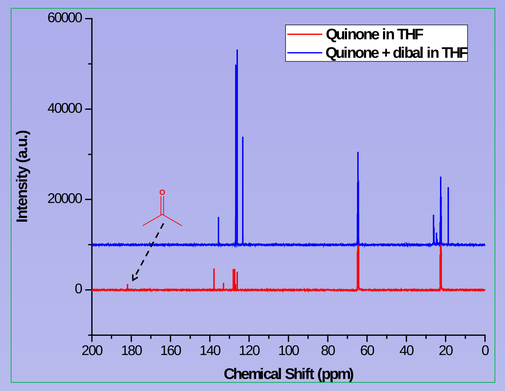


- Depletion of peak at 1674 cm^{-1} and build-up of peak at 1011 cm^{-1} indicate the consumption of carbonyl and formation of Al-O-C functionalities, respectively.

Reaction Kinetics

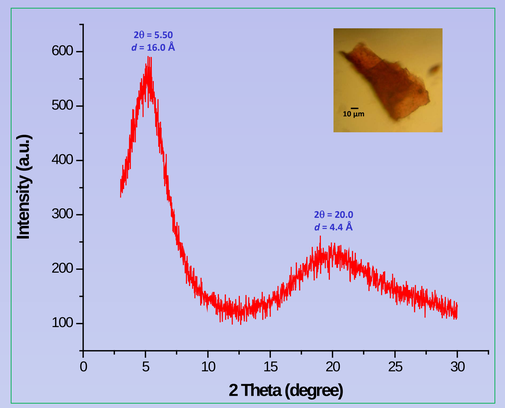
- In-situ IR analysis discloses the descending trend of carbonyl group and the ascending trend of Al-O-C group;
- The reaction of the quinone with DIBAL is slow.

^{13}C-NMR Analysis



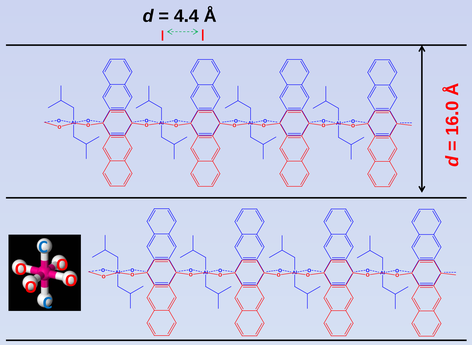
- NMR detected no peaks from the staring quinone or resulted alkoxide, suggesting an insoluble intermediate after 30 min.

Flake-like Framework



- The framework displays a layer- or flake-like structure, where XRD analysis indicates a *d*-spacing of 16.0 Å.

Structural Model



- Al adopts an octahedral coordination with 6 neighbors;
- Many chains align to each other, forming a planar structure, and further 3-D framework.

Results

- 1,4-anthraquinone showed fast complexation to form the framework;
- The framework is insoluble in common organic solvents or H_2O; 1< density < 1.33 gm/cm^3;
- The framework adopts a lamellar structure, *d* = ~16 Å;
- The colorful Aluminum Alkoxide solution can detect $CO_2$with selectivity;
- **BONUS**: The pre-fromework traps tremendous amount of organic solvents.

Future Work

- Al-NMR to confirm Al's coordination state;
- Test the framework's capability to absorb multiple carbon sources;
- Perform theoretical simulation to reveal structural-performance relationship;
- Investigate other quinones with a broader perspective.

References

- Anne Boutin and Alain H. Fuchs, J. Phys. Chem. C, 2010, 114, 22237–22244;
- J. Derouault, P. Granger and M. T. Forelza, Inorganic Chemistry, 1977, 16, 3214-3218.

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