

Ionic Conductive Silicate Organic Framework

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[Abstract] Ionic conductors generally based on polymers draw widespread academic attentions to figure out energy exchange issues such as solid state lithium batteries and thin film of diaphragm materials. However, the instinct boundedness of polymer materials enormously limited the ion-transitive spots. To break through the chain-dependence migration, a series of fast-ionic conductive anionic silicate organic frameworks (SiCOFs) depended on regularly crystalline porosity had been discussed. The synergistic effect which marks as a symbol of lowering the conductive activation energy (E_a) happens when the multi-ion migration between the high energy sites close to the anionic hexacoordinate Si-O and the low energy sites around the centre of the pores.¹ The stubborn covalent organic bonds and the pathway size of the frameworks supplied the ions immigration smoothly.² As a result of super high surface area at $1,634 \text{ m}^2\text{g}^{-1}$, undoubtedly increased the ion transportation space among the one-dimensional nanochannel networks of the SiCOFs.

[Introduction] Plenty of researches have been focused on looking for a suitable solid electrolyte interface (SEI) of Li-ion batteries (LIB). One of those acceptable facts among global researchers is producing solid state LIB. The ability of ion conductivity is a paramount generic of the solid state LIB. Compared with other ion conductive materials, poly (ethylene oxide) (PEO)-based electrolytes become the most famous one as a result of its flexible practical applications. However, solely depend on the chain direction of ion transportation could not follow the quick ion diffusion demands. Thus, a functional material with multi-ion concerted migration is a trend of future solid-state electrolytes.²

Covalent organic frameworks (COFs) are well-known of strong covalent bonds and manipulated topological structure. For the terms of minuting the energy barrier among the lattices to obtain much poor activity energy (E_a), creating higher and lower energy sites seems to be significant. In the case of Lithium ion migration, an anionic COF would provide a platform for the generation of synergistic effect. An up-to-date report of anionic silicate organic frameworks (SiCOFs) completely fulfilled with the potential barrier conditions and could serve as the infinite network for ion diffusion.^{3,4} Herein, it is essential to discuss the relationship between the anionic SiCOFs and the ionic conductivity.

[Methods] **9,10-dimethyl-2,3,6,7-tetramethoxyanthrance.** A cooled mixture of veratrole (12.8 ml, 0.1 mol), propanaldehyde (7.4ml, 0.1 mol) and CH_3CN (5.3 ml, 0.1 mol) was added dropwise to stirred H_2SO_4 (50 ml) maintained at $0\text{-}5^\circ\text{C}$ over 0.5h. The reaction mixture was then stirred at this temperature for 2 h and then poured onto ice. The resultant precipitate was filtered and washed with water and recrystallized from acetone to give yellow crystals.⁵

9,10-Dimethyl-2,3,6,7-tetrahydroxyanthracene. Under Nitrogen a Schlenk flask was sealed with 9,10-dimethyl-2,3,6,7-tetramethoxyanthrance (800 mg, 2.45 mmol). Anhydrous dichloromethane (20 ml) was added and 10.8 ml of 1.0 M boron tribromide solution in anhydrous dichloromethane (2.7 g, 10.8 mmol) was injected quickly to the suspension which immediately turned pink. After 4 h of stirring at room temperature the reaction mixture turned to brown. The solution was filtered and washed with water to give a yellow powder.⁶

Na-SiO₂-DMAn-COF. Add 9,10-dimethyl-2,3,6,7-tetrahydroxyanthrance (DMAn) (100 mg, 0.37 mmol), sodium methoxide (40 mg, 0.55 mmol), silica gel (SiO_2) (15 mg, 0.25 mmol) and anhydrous methanol (8.8 ml) sequencely to a 20 ml Teflon-lined steel autoclave. Sealed and

placed the autoclave in a 180 °C oven heating for five days. Filtration under inert atmosphere and collected the brown-yellow powder, washed with anhydrous acetone and evacuated at room temperature for 12 h (106 mg, 91%) ($\text{Na}_2[\text{Si}(\text{C}_{16}\text{H}_{10}\text{O}_4)_{1.5}]$).³

[Results and Discussion] Chart 1 and chart 2 showed the synthetic procedures of Na-SiO₂-DMAn-COF. Figure 1 give the information of extending the reaction to DMAn and the crystallographic unit cell of the fully eclipsed framework. Powder X-ray diffraction (PXRD) displayed in figure 2. Sharp reflections could not be denoted when starting monomer indicated the formation of a framework with a high level of crystallinity.

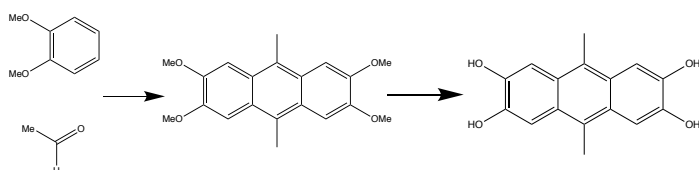


Chart 1. Synthesis route for 9,10-Dimethyl-2,3,6,7-tetrahydroxyanthracene.

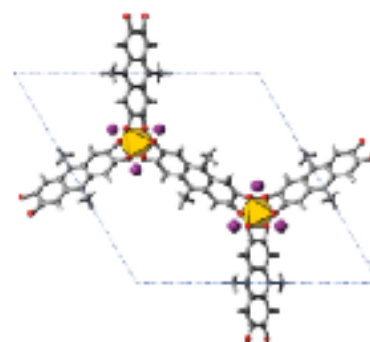


Figure 1. J. Crystallographic unit cell of the fully eclipsed framework ($a = 21.25(2) \text{ \AA}$, $c = 4.620(10) \text{ \AA}$, space group $P31m$).

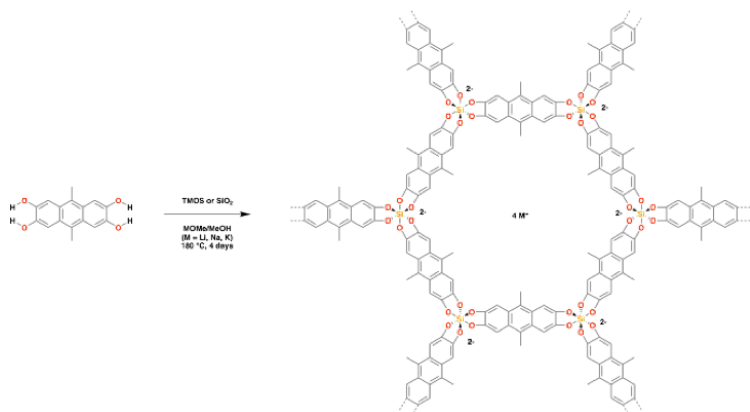


Chart 2. Synthesis route for Na-SiO₂-DMAn-COF.

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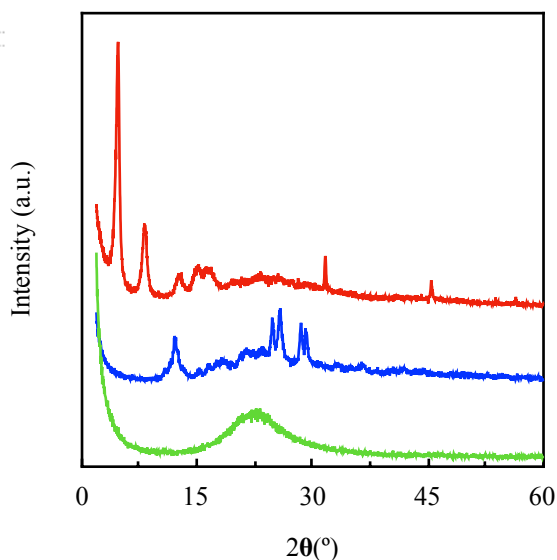


Figure 2. PXRD patterns of Na-SiO₂-DMAn-COF (red), DMAn (blue) and SiO₂ (green).