Anion-encapsulating sodium alkoxide clusters (X@RONa): structure and function as multi-functional Lewis acid catalysts

([1]*School of Physical Science and Technology, ShanghaiTech University*) ○Zhi Li[1]

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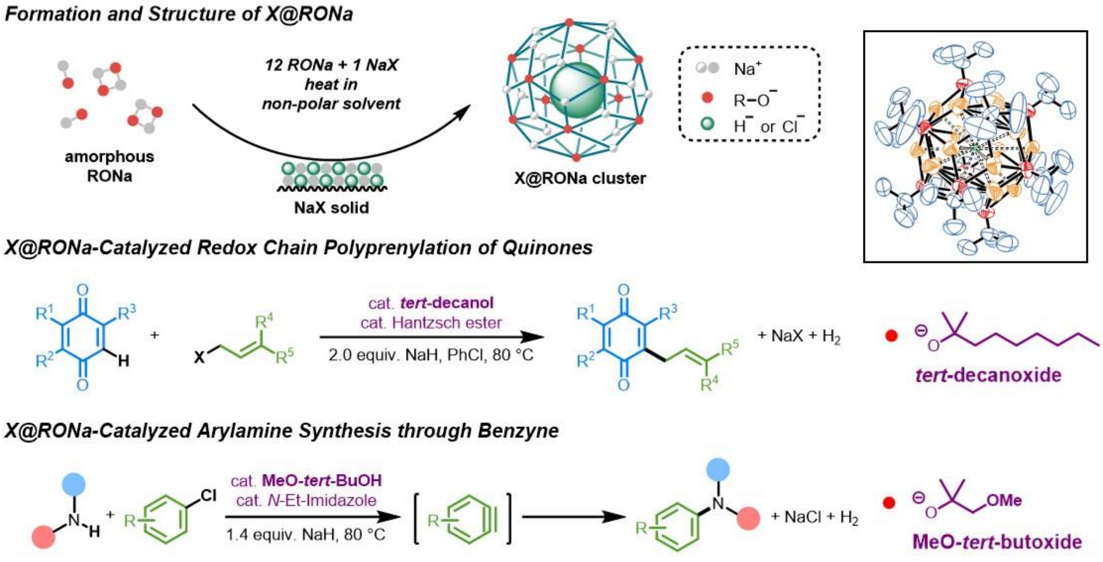
Sodium salts are able to aggregate into various types of polymeric or molecular substances depending on anions. We discovered that sodium *tert*-butoxide formed thermodynamically favored dodecameric anion-encapsulating molecular clusters $(NaO\textit{t}\text{-}Bu)_{12}NaX$, or X@*t*-BuONa, where X is the encapsulated anion. The synthesis could be as simple as heating NaO*t*-Bu and fine powder of NaCl together in a non-polar solvent. The structures of these substances were studied by X-ray crystallography and NMR. Unlike their well-known oligomeric clusters or amorphous ionic polymers, its structure consists of 12 alkoxide anions located at vertices of an icosahedron, a halide or other anion at the center, and 13 sodium cations dynamically distributed at 13 of the 20 faces.

The multi-level composition of these clusters allowed us to design clusters by changing the *tert*-butoxide to other alkoxide ligand RO as X@RONa, thus enabling their catalytic activities. The RO ligand, encapsulated X, and substrates coordinated to Na were all Lewis basic ligands that interacting with the cluster as well as each other, thus we consider the X@RONa as a new type of Lewis acid catalyst. The catalytic activity will be illustrated in the following two cases.

First, X@RONa was able to promote transition-metal-free polyprenylation of quinones through redox chain mechanism we discovered earlier.[1] Many biologically important polyprenylquinones were synthesized from corresponding parent quinone and polyprenyl halide as precursors and NaH as base in one step and high yield.

Second, X@RONa was applied in catalytic transition-metal-free C-N bond formation. Aryl amines are usually synthesized from transition metal-catalyzed cross coupling or C-H activations from aryl halides, triflates, or arenes. Although these methods are effective, the costs of precursors, reagents and catalysts are often too high for them to be applied in large scale synthesis. We recently discovered that X@RONa was capable of catalytically promoting benzyne formation from simple aryl chlorides, as well as the subsequent arylation of amines. From very simple and cheap aryl chlorides, alkyl amines and NaH, aryl amines can be easily synthesized in large scale. This is also a very rare case of large-scale application of benzyne.



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