

Supporting Information I

What molecular assembly can learn from catalytic chemistry

Yu Wang,^{ab} Hai-Xin Lin,^b Liang Chen,^b Song-Yuan Ding,^{ab} Zhi-Chao Lei,^b De-Yu Liu,^b Xiao-Yu Cao,^{*b} Hao-Jun Liang,^{ac} Yun-Bao Jiang,^{ab} and Zhong-Qun Tian^{*ab}

^a Collaborative Innovation Center of Chemistry for Energy Materials, Xiamen University, Xiamen 361005, China.

^b State Key Laboratory of Physical Chemistry of Solid Surfaces and College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.

^c CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, China

To whom correspondence should be addressed. Email: zqtian@xmu.edu.cn; xcao@xmu.edu.cn

Why catassembly needs to be considered apart from catalysis.

The term “catassembly” can explicitly describe the corresponding phenomenon in this review, and two reasons necessitate its creation:

Reason I: catassembly needs to be considered apart from catalysis because they are essentially different.

Catassembly refers to molecular assembly and catalysis refers to chemical reaction, they are distinctively different:

(a) Molecular assembly involves mainly noncovalent interactions, but chemical reactions focus on the formation and cleavage of covalent bonds. Noncovalent interactions, such as hydrogen bonding, $\pi-\pi$ stacking, hydrophobic effects, weak coordination, etc., are more labile and more diverse. In addition, noncovalent interactions in assembly process usually function at multiple sites, exhibiting effects as multivalency or cooperativity which greatly increase the complexity of noncovalent interactions.

(b) Building blocks for assembly range from small molecules to macromolecules to nanoparticles. Thus, molecular assembly exhibits complexity at different levels, as shown in Fig S1. At level 1, assembly involves relatively simple noncovalent interactions between one or two kinds of molecules; at level 2, hierarchical assembly involves multi-components and complex interactions; and at higher levels, supramolecular systems involve multiple associated assembly processes at multiple time and space scales. By contrast, chemical reactions usually deal with simple molecular segments.

Therefore, it is inappropriate to use a simple phase “chemical reaction” to describe both chemical reactions and all these complex molecular assembly processes without distinguishing their differences.

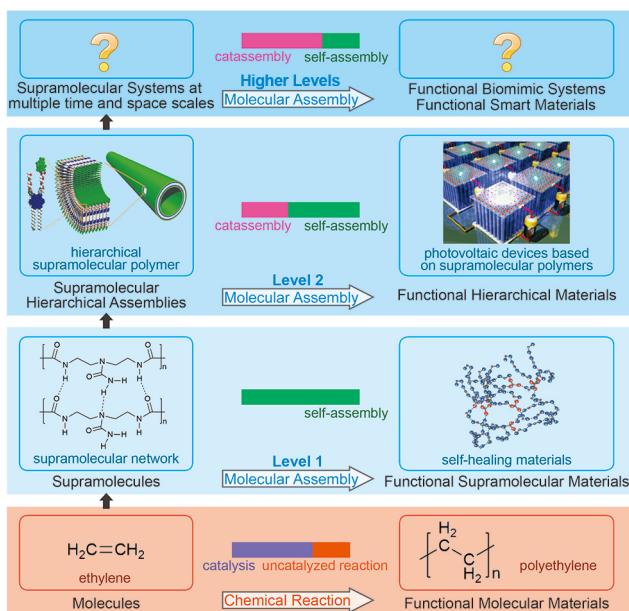


Fig S1. Fabrication of functional materials through chemical reaction and molecular assembly with complexity at different levels.

Besides, catassembler interacts noncovalently with building blocks at multiple sites, whereas catalyst covalently with substrates at one or two sites. When the system becomes more complex at level 2 and higher levels, diversification of catassemblers is an inevitable trend, and several catassemblers would be needed to work cooperatively. And they fall into builder-like catassembler and porter-like catassembler.

Table S1. Comparison among catalyst, supramolecular catalyst, and catassembler

	Catalyst	Supramolecular Catalyst	Catassembler
Region of applicability	Chemical reaction	Chemical reaction	Molecular assembly
Interactions	Covalent	Noncovalent	Noncovalent
Active sites	One or two	Several/Multiple	Several/Multiple

Therefore, catassembler and catalyst have different regions of applicability, and their features are dramatically different, as shown in Table S1. It is inappropriate to use “catalysis” and “catalyst” to describe “catassembly” and “catassembler,” because they essentially different.

Reason II: even if one could consider catassembly as a type of catalysis, the catalysed assembly phenomenon should have its specialized term to distinguish from other catalysis phenomena, such as organometallic catalysis, organocatalysis and supramolecular catalysis.

This term can be a combined phrase or a coined word, and “catalysed-assembly” appears to be more acceptable than “catassembly”. However, the term of the “helper” in a catalysed-assembly process would be difficult to define. “Catalyst” is too general; while combined terms of “assembly catalyst” and “assembling catalyst” easily cause confusions with “supramolecular catalyst,” which

has been explicitly defined as a substance that accelerates a chemical reaction, instead of an assembly process.

Catassembly can be considered as the abbreviation of catalysed-assembly, combining the Greek root cata- (before a vowel cat-¹) of catalysis with assembly. One can also easily find the inference with self-assembly and co-assembly in terminology. The noun form could be defined as catassembler, which can completely avoid the confusion with supramolecular catalyst and noncovalent catalyst. In addition, the verb and adjective forms can be defined as catassemble, and catassembled. All these terms identifiably suggest they reflect the “catalyzed” phenomenon at molecular assembly level.

Therefore, “catassembly”, “catassembler”, and “catassemble” are superior to “catalysed-assembly”, “assembly-catalyst”, and “catalyse” in terminology.

¹ <http://dictionary.reference.com/browse/cata?s=t>