

Metal-carbene unit: a universal tool towards high-efficient photochemical reaction in solution

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Topochemically-controlled stereoselective [2+2] photocycloadditions are now well-established in the literatures. The construction of cyclobutane rings has attracted considerable attention due to the existence of this structural motif in natural products and synthetic medicines. Furthermore, cyclobutane derivatives appended with pyridyl or carboxylic groups exhibit intriguing properties in some advanced formation of metallo-supramolecular assemblies and materials. Generally, the photochemical [2+2] cycloaddition reactions are reported to take place in the solid state. Among several known methods, the photocycloaddition of olefins is recognized as one of the most promising strategies for the synthesis of cyclobutane rings. In this field, significant efforts have been devoted to exploring the structural transformations induced by photochemical [2+2] cycloaddition in the solid state [1].

Unlike the photochemistry in the solid state, it is significantly difficult to control the outcomes of photochemical reactions in solution, because photolysis of olefin-containing substrates in solution usually leads to the *trans-cis* photoisomerization prior to the formation of cyclobutanes. Recently, Han and co-workers [2,3] in Northwest University (Xi'an, China) have made significant progress in the supramolecular control of photocycloaddition in solution. They

have developed a series of novel metal-carbene units for the highly efficient photochemical reactions in homogeneous solutions, which represent an important step to achieve topochemical controls in solution similar to those in the solid state.

In a recent communication, Han and co-workers [4] reported a new family of supramolecular metallacycles capable of undergoing photochemical reactions in solution (Figure 1). The molecular metallacycles were readily obtained by using dinuclear metal-carbene organometallic clips and olefin-functionalized bridging ligands via the coordination-driven self-assembly. Preorganization of the components at the metal-carbene template allowed the precise control of the stereochemistry of the photoproducts upon photolysis. The pure cyclobutane derivatives with the readily-functionalized appended groups can be freely released *in situ*. This exciting research demonstrates that the metal-carbene units enable precision control of the functional olefin ligands to form different targeted cyclobutanes. This work is a breakthrough for the photochemical [2+2] cycloaddition in solution. This novel approach is anticipated to be applicable in preparing new types of functionalized cyclobutanes such as [2.2] paracyclophane and [n]ladderane derivatives.

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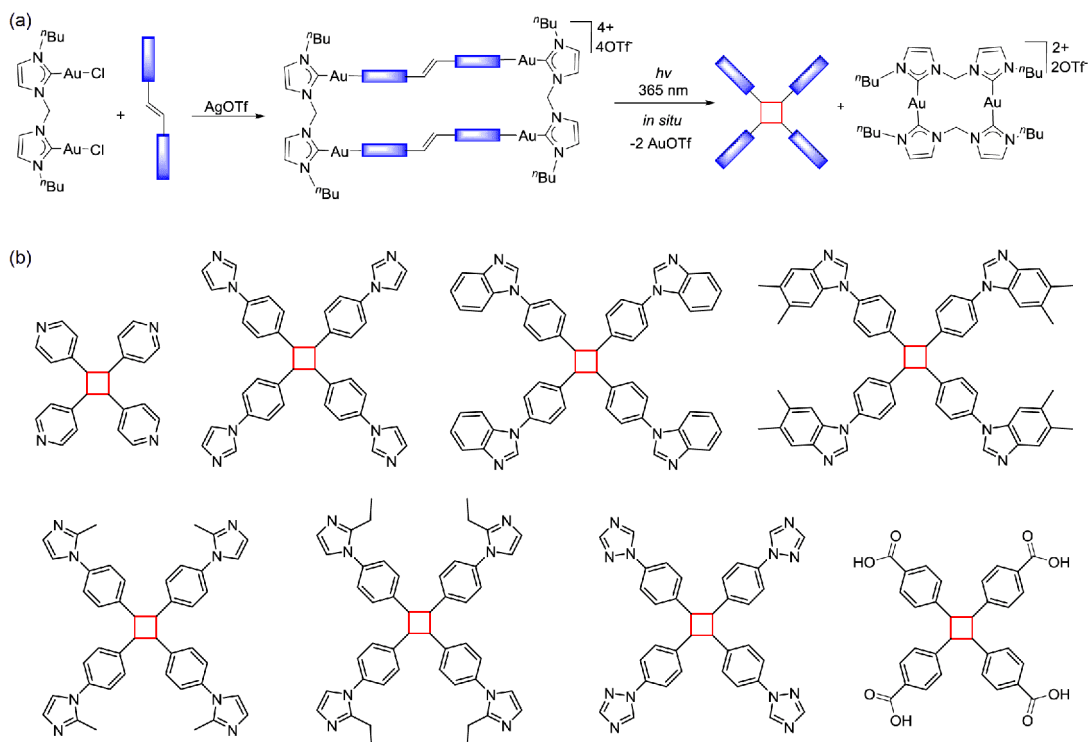


Figure 1 (a) Coordination-driven self-assembly of organometallic metallacycles and their photolytic transformation to afford cyclobutane derivatives. (b) The structures of cyclobutane derivatives. Adapted from Ref. [4], copyright Wiley Publishing Group (color online).

Conflict of interest The authors declare that they have no conflict of interest.

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