

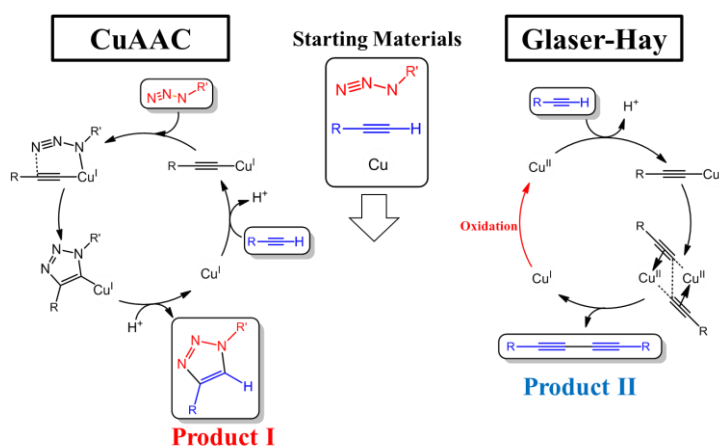
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~Introduction~

The system converting an electric signal into a molecular framework can be a basic nanoscale tool to construct a selected structure at a desired position in molecular scale. We aimed to construct such a system from a redox-active catalyst which undergoes different coupling reactions depending on its oxidation state. There are two reactions of terminal alkyne with

copper catalysts. Glaser-Hay Coupling is an oxidative reaction which affords 1,3-diynes by the homocoupling of terminal alkynes, and a Cu(II)/Cu(I) re-oxidation step by oxygen complete the catalytic cycle. Azide-Alkyne Cycloaddition is the reaction which affords 1,2,3-triazole from terminal alkynes and azides, without any oxidant. Thus, Glaser-Hay Coupling or CuAAC process can be selected from the same solution if we switch the oxidation process (**Scheme 1**).

Scheme 1. Glaser-Hay Coupling and CuAAC



~Experimental and Results~

The solution containing phenylacetylene, benzylazide (0.73 equiv.), copper(tmeda) complex (0.8 mol%) and TMEDA (= *N,N,N',N'*-tetramethylethylenediamine) under oxygen atmosphere formed diyne, however, a subproduct also formed through the oxidation of an intermediate from the CuAAC catalytic cycle. Decreasing the additional TMEDA from 18 mol% to 0.8 mol% resulted in suppression of the formation of the subproduct. Furthermore, the formation of diyne or triazole can be switched several times in presence or absence of oxygen, respectively (**Figure 1**).

In the formation process of 1,3-diyne, the

oxidation process by oxygen could be replaced with anodic oxidation. The reaction proceeded with almost quantitative current efficiency, but it decelerated in the course of the reaction, due to a disproportionation of the solution within the separated electrolysis cell. The application of the anodic oxidation to switch the dual-reactivity is now under investigation.

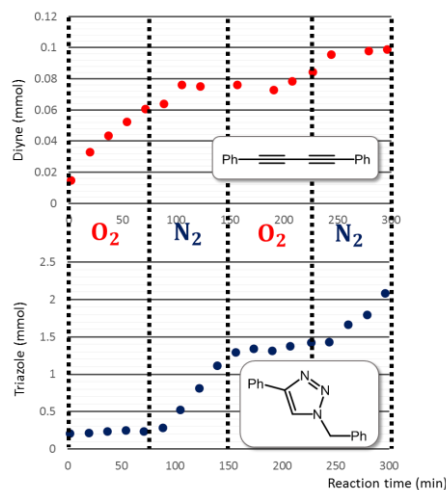


Figure 1. Product formation profile from a solution containing 0.8 mol% CuCl₂(tmeda), 0.8 mol% TMEDA, DME:MeOH(1:1), phenylacetylene, 0.73 eq. benzylazide, *o*-terphenyl as standard, under O₂ or N₂ atmosphere.