

Electron-catalysed molecular recognition

J. Fraser Stoddart, William A. Goddard III et al. Nature, 603, 265-270 (2021)

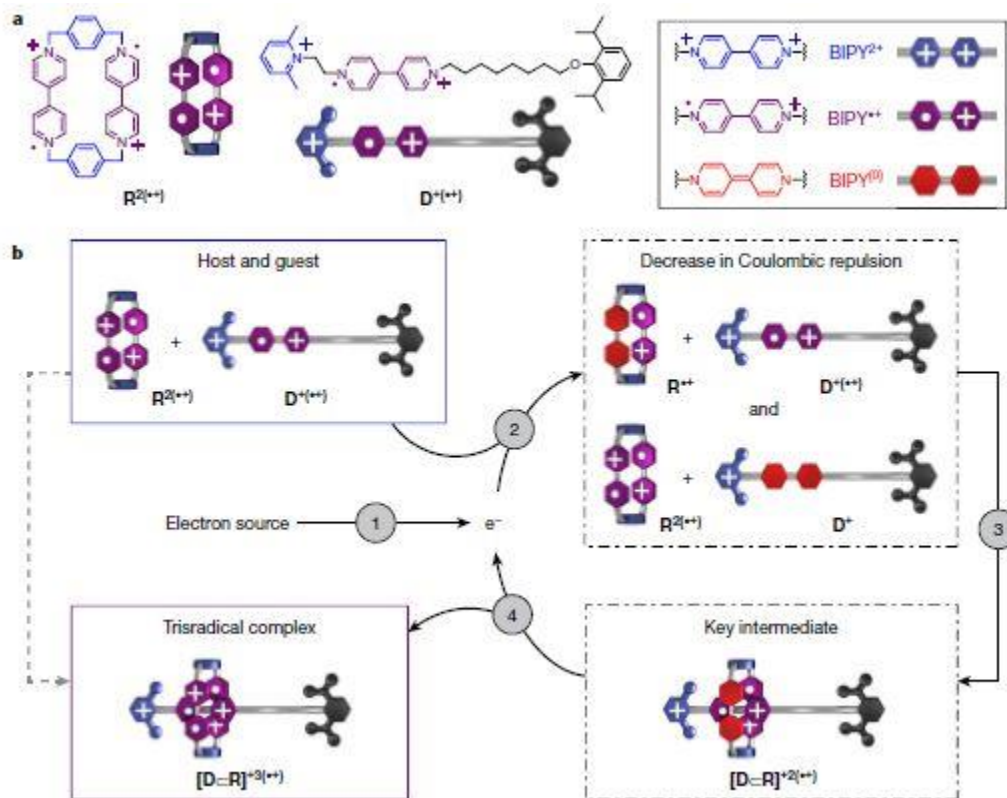


Figure 1: Design of an electron-catalysed molecular recognition process. *a*, Structural formulae and graphical representations of the host-guest system, which includes a macrocyclic host, $R^{2(2+)}$ and a dumbbell-shaped guest, $D^{+(2+)}$. *b*, Proposed mechanism for an electron-catalysed molecular recognition process. The direct (grey dashed arrow) formation of a $[D-CR]^{3(2+)}$ trisradical complex from $R^{2(2+)}$ and $D^{+(2+)}$ is all but kinetically forbidden. The catalytic (black solid arrows) complexation comprises four steps, including one initiating step and three propagating steps.

Who are the corresponding authors and what are their research areas?

J. Fraser Stoddart (Northwestern University, Evanston, IL, USA), William A. Goddard III (California Institute of Technology, Pasadena, CA, USA).

Stoddart has pioneered the development of the use of molecular recognition and self-assembly processes in template-directed protocols for the syntheses of two-state mechanically interlocked molecules (MIMs), i.e., bistable catenanes and rotaxanes, that have been employed as molecular switches in the development of artificial molecular machines (AMMs). It was for this research that he was awarded the 2016 Nobel Prize in Chemistry.

The Goddard's research is focus on the description of the properties of chemical, biological, and materials systems directly from first principles (without the necessity of empirical data). To accomplish this the

group has been developing new theory, new methods, and new software. The group's approach builds from Quantum Mechanics (QM) using different methods including molecular dynamics (MD), mesoscale dynamics, and macroscopic dynamics.

What is the main claim of the article?

In this paper they developed a simple and efficient strategy to facilitate molecular recognition by extending electron catalysis, which is widely applied in synthetic covalent chemistry, into the field of supramolecular chemistry. They showed that the formation of a trisradical complex between a macrocyclic host and a dumbbell-shaped guest (process which is kinetically forbidden under ambient conditions) can be accelerated upon the addition of catalytic amounts of a chemical electron source (CoCp₂). It is, therefore, electrochemically possible to temporally control the molecular recognition.

How is it demonstrated?

The molecular recognition event was monitored by UV/Vis/IR spectroscopy. Then, fitting the data with a kinetic model they observed that the rate constant of this supramolecular process in the presence of 4 mol% CoCp₂ is 640-fold larger than the rate constant recorded in absence of CoCp₂.

Comparison between the different kinetic constants at different amount of CoCp₂ reveals the catalytic nature of the process.

What are the typical experimental conditions?

MeCN as a solvent, catalytic amount of CoCp₂, micromolar concentration range.

Which are the key related papers?

1. Studer, A. & Curran, D. P. *Nat. Chem.* 6, 765–773 (2014).
2. Frasconi, M. J. Fraser Stoddart et al. *J. Am. Chem. Soc.* 137, 11057–11068 (2015).