IRANIAN JOURNAL OF CATALYSIS

Supramolecular catalysis

Compiled by Morteza Torabi

Morteza Torabi was born in 1995 in Hamedan, Iran. He received his B.Sc. in Applied Chemistry (2017) and M.Sc. in Organic Chemistry (2019) from Bu-Ali Sina University under the supervision of Professor Mohammad Ali Zolfigol. He is currently working towards his Ph.D. under the supervision of Professor Mohammad Ali Zolfigol at Bu-Ali Sina University. His research interest is the design, synthesis and characterization of acidic magnetic nanoparticles, magnetic ionic liquids, and urea based compound as catalysts and their applications in organic synthesis.

Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran

E-mail: torabimorteza74@yahoo.com

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

In the last decades supramolecular chemistry has been intruduced as one of the most attractive fields in chemistry domain. This field has been defined as ''chemistry beyond the molecule'' including systems based on molecular components that are held together by noncovalent intermolecular forces [1]. There are two Nobel Prize winners in this field firstly. Charles Pedersen, Donald J. Cram, and Jean-Marie Lehn's 1987 award for their development of crown ethers, carcerands, and cryptands, and secondary winners of the 2016 Nobel prizes Jean-Pierre Sauvage, Sir J. Fraser Stoddart, and Bernard L. Feringa for their introduction and advance of molecular machines [2]. Many applications have been reported for supramolecular chemistry. Host-guest chemistry, self-assembly, chemosensing, supramolecular materials, molecular machines and supramolecular catalysis are just a few of these applications [3-7]. Today, most of supramolecular chemistry extended to macrocyclic molecules and molecular cages that are at the heart of supramolecular chemistry and attracted considerable attention of investigators [8]. Molecular cages, can be defined as hollow structures with a three-dimensional cavity. The majority of molecular cages have been designed in a stepwise synthetic manner by the formation of comparably strong bonds, such as amides or C−C bonds [9]. In this way, supramolecular organocatalysis has been reported as a novel and popular research field in the domain of homogeneous catalysis. Especially, the use of functionalized organocage as supramolecular catalysts is highly innovative. These systems are oftentimes easily accessible and offer distinct advantages in catalysis. Macrocyclic catalysts can provide defined binding pockets, such as hydrophobic cavities. In addition, macrocycles can exhibit a harmonic arrangement of functional groups, such as binding sites or catalytically active groups. These systems are significantly similar to enzymes and their applications including Diels-Alder reaction, ester hydrolysis, decarboxylation inside the β-cyclodextrin, and so on [10-12]. Catalytic mechanism of supramolecular systems has been categorized as (i) encapsulation of a catalytic moiety, thereby shielding the reaction from undesired bulk side reactions and (ii) encapsulating only reactants and to rely on host–guest interactions to extend the reaction as do enzymes [13-14]. A historical viewpoint of important samples from thses systems are illustrated in **Scheme 1**.
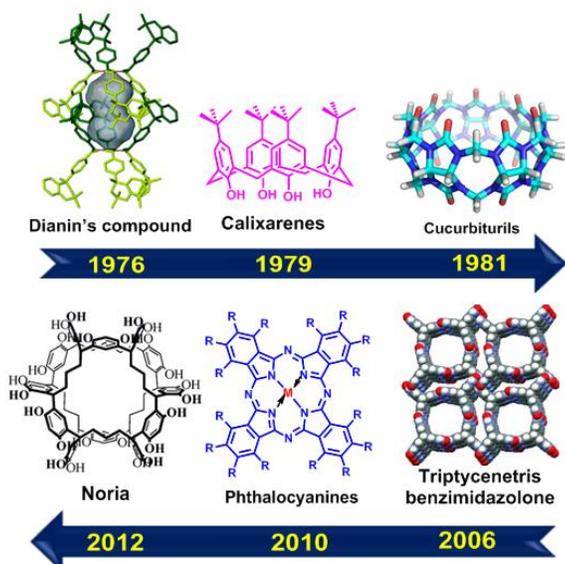
Scheme 1. The timeline of a number of most important supramolecules.

The goal of synthesis and designing of supramolecular catalysis is to create a micro- or nano-environment having features different from the bulk solution. In this situation, reactivity is different with normal conditions in solution, and thus the rate of the reaction, and further the products, can be different with the situation of classic catalysis [15]. Scientists try to developed new, efficient and selective supramolecular catalystic systems. The chemistry of supramolecular catalysis has been comprehensively reviewed [16-20]. In this spotlight, the catalytic performance of supramolecular catalysis in the synthetic organic methodologies were highlighted.

Abstracts

(A) In 2019, Gosh and coworkers reported a new and multifunctional macrocyclic organocatalyst which has bisamide and trisamine functional groups. These units act as hydrogen-bonding donors and have a good catalytic performance in a multi-component reaction between isatin, malononitril and toluidines. In the absence of a catalyst, synthesis of highly substituted pyrroloacridinone has little efficiency, while in the presence of macrocyclic catalyst (10 mol%), the yield of polycyclic product was significantly increased up to 91%. Moreover, the catalyst was dispersed in water or water/alcohol mixtures, where catalyst aggregates ranging were observed in size of 70-100 nm [21].
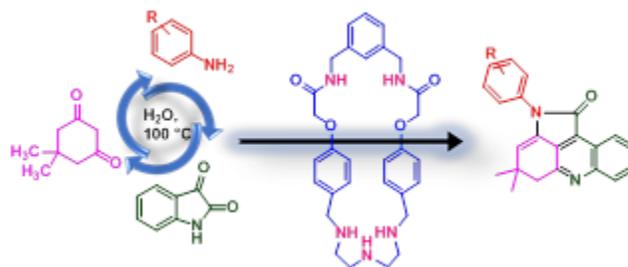
(B) In recent years, coordination cages have been increasingly developed as an important subclass of supramolecular chemistry. In 2006, Yoshizawa and coworkers described an aqueous organopalladium cage which created a hydrophobic reaction environment in aqueous solution. Due to the unique feature of this system, it can be used effectively in catalytic Diels-Alder reaction of anthracene and phthalimide guests. Interestingly, the reaction has been promoted at a terminal rather than central anthracene ring which have an unusual regioselectivity in the Diels-Alder reactions [22].
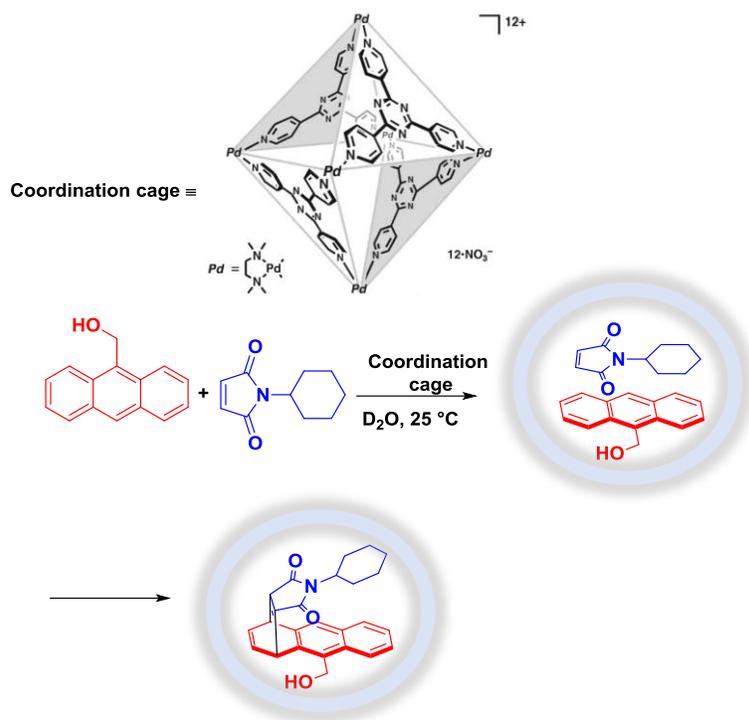
(C) So far, several catalytic applications of *β*-cyclodextrin have been reported [23]. For example, in 2015, Dipak and coworkers have used *β*-cyclodextrin as an effective supramolecular biodegradable and reusable catalyst in multi-component synthesis of dihydropyrano[2,3-c]pyrazole and spiro[indoline-3,4'-pyrano[2,3-c]pyrazole] in aqueous and neutral conditions [23].
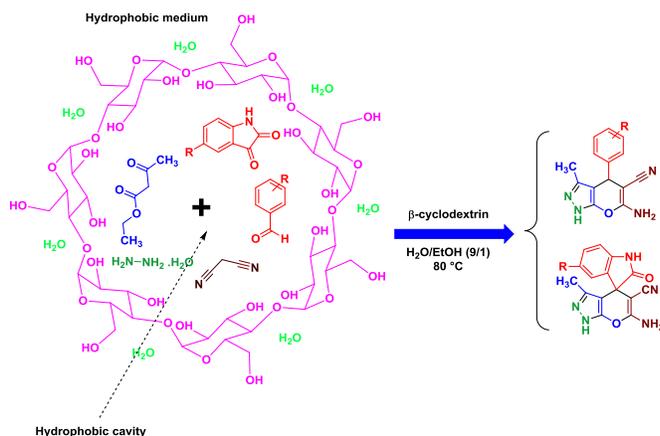
(D) The first calixarene has been reported in 1979. Literature surveys shows that many calixarene derivatives have been reported up to now [24]. In 2013, Fernandes and coworkers have described the tetrasulfonated calix[4]arene as an organocatalyst for the Povarov reaction. 4-Bromoaniline, formaldehyde and styrene were reacted *via* a three-component reaction to yield julolidine-derivatives. They investigated several inorganic and organic acids but only sulfuric acid gave a moderate yield of 60% with a little diastereoselectivity (12% de). In contrast, the calix[4]arene provided the product in 70% yield and 74% de. Indeed, calix[4]arene has shown good activity and stereoselectivity [25].
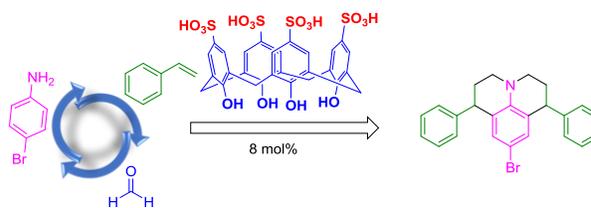
(E) The hexameric resorcinarene capsule has been reported by Atwood in 1997. This capsule has an exceptional catalytic performance. It's inner cavity can provide a unique environment which efficiently catalyzed organic reactions [26]. There are different abilities for hexameric resorcinarene capsule. This capsule has a good substrate selectivity and can stabilize the transition states and the intermediates by secondary interactions. Finally, it's ability has been considered in hydrogen bonding catalysts [26]. For example, the intramolecular hydroalkoxylation of hydroxyolefins has been investigated in the presence of hexameric resorcinarene capsule or TfOH. In the presence of capsule, high selectivity and conversion (92%) has been obtained. While, the larger alcohol showed a lower conversion (8%) [27].
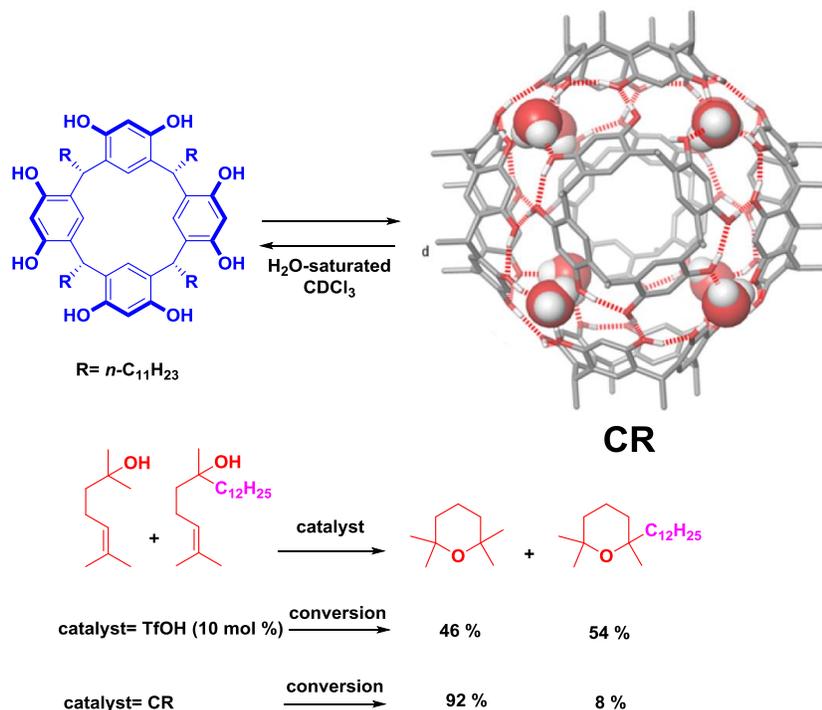
(F) In 2019, Yang and coworkers reported a water-soluble calix[4]carbazole which represents a unique property for the selective formation of hydrazone bond. It has a large hydrophobic cavity so that it is capable of encapsulating specific guests either in 1,3-alternative or in cone conformation. In this work, bishydrazone has been synthesized under physiological conditions using calix[4]carbazole and ratified a folded geometry and exhibited an intramolecular excimer emission. This molecule could serve as an AT-DNA selective ratiometric sensor [28].
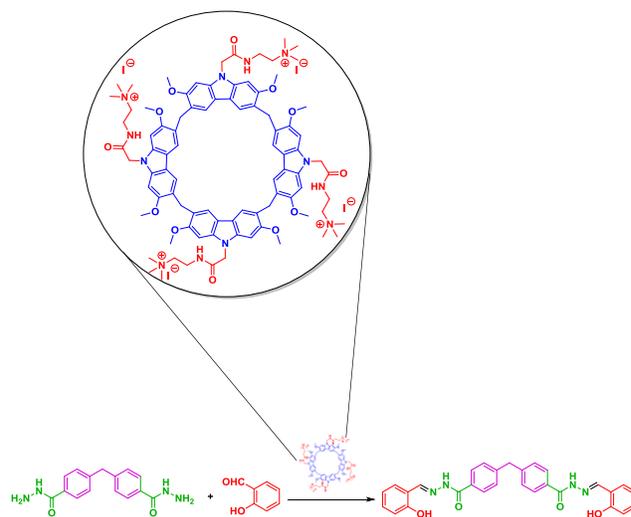
(G) Most of Diels-Alder reactions have endo-selectivity due to secondary π-intractions. Nevertheless, supramolecular catalysis can provide a situation for exo-selectivity. Sanders and coworkers reported the trimeric porphyrin host that bimolecular Diels-Alder reaction has been substantially performed in its cavity. There is high stereoselectively by binding diene and dienophile within the cavity of a cyclic metalloporphyrin trimer. When two or three pyridine ligands are bound within the cavity host, their effective concentration is dramatically increased. In this case, exo-seletive Diels-Alder reaction has been accelerated which transition-state geometry matches the relative orientation of bound ligands [29].

Transition state
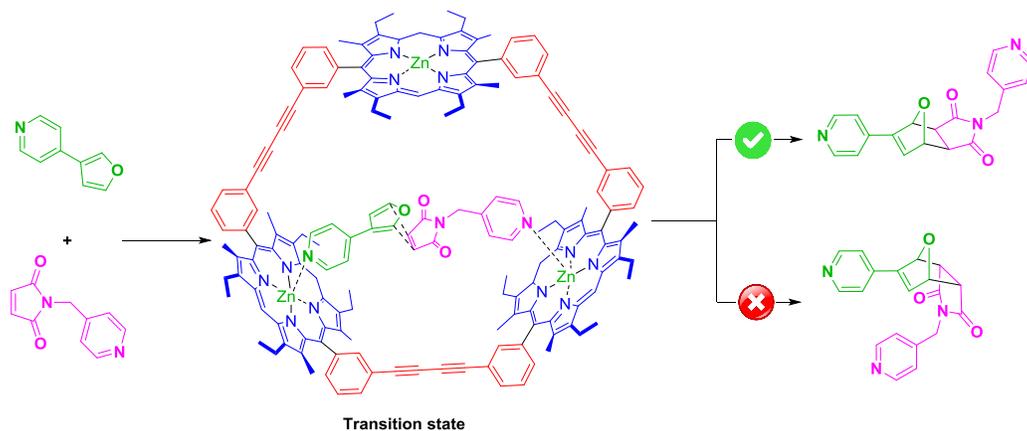
(H) Yilmaz and coworkers developed calix[4]arene based organocatalysts which have two proline-units with hydrazone-linkages. They have investigated the aldol reaction of cyclohexanone with different aldehydes that could be carried out in water at room temperature. When calix[4]arene is used as a catalyst, excellent stereoselectivities is observed (up to 93% ee). In this study, the monomeric analogue has been shown significantly to lower stereoselectivity. This confirms that each of hydrophobic calixarene pocket or the bi-functional nature of catalyst has a significant effect in excellent stereo-induction [30].
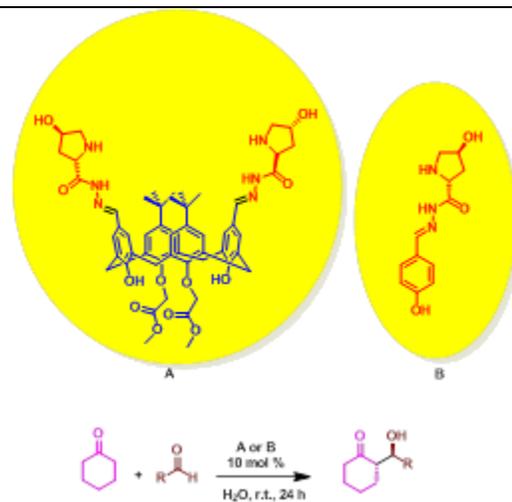
(I) In 2002, Rebek and coworkers have reported a self-assembled cage with hydrogen-bonding and they applied the prepared structure as a catalyst for a 1,3-dipolar cycloaddition of phenylacetylene and phenyl azide. This cage is an encapsulated two guest molecules in a edge-toedge fashion. Efficiently, this self-assembling accelerates the cyclo-addition reactions in synthesis of triazoles. The observed rate acceleration can be attributed to the effective concentration within the cavity. Moreover, there is size-selectivity in this situation and for larger azides, good results are not observed [31].

203

(J) In 2018, Rebek and coworkers investigated the acid-functionalized resorcinarene. Cyclohexane-carboxylic acid is linked to resorcinarene-backbone and this system has been applied for the catalytic cyclization of epoxy-alcohols. Activation of epoxide by the carboxylic acid lead to intramolecular cyclization to the corresponding furane. The speed of reaction in mesitylene as a solvent is better than CH_2Cl_2. In the presence of 10 mol% CH_2Cl_2, there is a competing guest for the resocinarene cavity and this slows down the reaction [32].
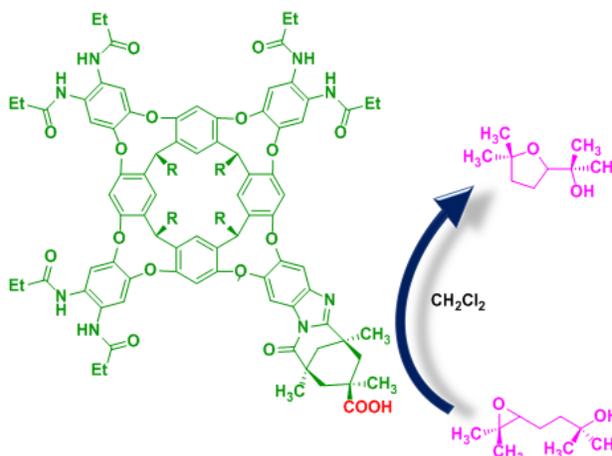
References

[1] J. M. Lehn, Chem. Soc. Rev., 36 (2007) 151-160.

[2] I. V. Kolesnichenko, E. V. Anslyn, Chem. Soc. Rev., 46 (2017) 2385-2390.

[3] B. A. Moyer, J. F. Birdwell, P. V. Bonnesen, L. H. Delmau, K.Gloe, (2005). Macrocyclic Chemistry: Current Trends and Future Perspectives. Netherlands: Springer.

[4] B. Wang, E. V. Anslyn, (2011). Chemosensors: principles, strategies, and applications (Vol. 15). John Wiley & Sons.

[5] a) M. Ikeda, Bull. Chem. Soc. Jpn., 86 (2013) 10-24; b) A. Priimagi, G. Cavallo, P. Metrangolo, G. Resnati, Acc. Chem. Res., 46 (2013) 2686- 2695.

[6] S. Erbas-Cakmak, D. A. Leigh, C. T. McTernan, A. L. Nussbaumer, Chem. Rev., 115 (2015) 10081-10206.

[7] Q. Q. Wang, Handbook of Macrocyclic Supramolecular Assembly, (2020) 829-875.

[8] D. Kauerhof, J. Niemeyer, ChemPlusChem, 85 (2020) 889-899.

[9] M. Mastalerz, Acc. Chem. Res., 51(2018) 2411-2422.

[10] E. Alvira, C. Cativiela, J. García, J. Mayoral, Tetrahed. Lett., 36 (1995) 2129-2132.

[11] S. P. Kim, A. G. Leach, K. N. Houk, J. Org. Chem., 67 (2002) 4250-4260.

[12] V. Luzhkov, J. Åqvist, Chem. Phys. Lett., 302 (1999) 267-272.

[13] G. Hattori, T. Hori, Y. Miyake and Y. Nishibayashi, J. Am. Chem. Soc., 129 (2007) 12930-12931.

[14] Y. Li, Y. Feng, Y. M. He, F. Chen, J. Pan, Q. H. Fan, Tetrahedron. Lett., 49 (2008) 2878-2881.

[15] Y. Suzaki, K. Shimada, E. Chihara, T. Saito, Y. Tsuchido, K. Osakada, Org. Lett., 13 (2011) 3774-3777.

[16] Q. Q. Wang, (2020). Handbook of Macrocyclic Supramolecular Assembly, 829-875.

[17] Y. Fang, J. A. Powell, E. Li, Q. Wang, Z. Perry, A. Kirchon, X. Yang, Z. Xiao, C. Zho, L. Zhang, F. Huang, H. C. Zhou, Chem. Soc. Rev., 48 (2019) 4707-4730.

[18] T. Hasell, A. I. Cooper, Nat. Rev. Mater., 1 (2016) 11-14.

[19] A. Pappalardo, R. Puglisi, G. Trusso Sfrazzetto, Catalysts, 9 (2019) 630-651.

[20] Y. Voloshin, I. Belaya, R. Krämer, In The Encapsulation Phenomenon. Springer, Cham (2016) 499-523.

[21] P. Sarkar, S. Sarkar, P. Ghosh, Beilstein J. Org. Chem., 15 (2019) 1505-1514.

[22] M. Yoshizawa, M. Tamura, M. Fujita, Science, 312 (2006) 251-254.

[23] Y. A. Tayade, S. A. Padvi, Y. B. Wagh, D. S. Dalal, Tetrahedron Lett., 56 (2015) 2441-2447.

[24] D. Kauerhof, J. Niemeyer, ChemPlusChem, 85 (2020) 889-899.

[25] J. Simões, Â. de Fátima, A. Sabino, F. Aquino, D. Leite, L. C. Barbosa, S. Fernandes, Org. Biomol. Chem., 29 (2013) 5069-5073.

[26] C. Gaeta, C. Talotta, M. De Rosa, P. La Manna, A. Soriente, P. Neri, Chem. Eur., 25 (2019) 4899-4913.

[27] L. Catti, K. Tiefenbacher, Chem Commun, 51 (2015) 892-894.

[28] Z. Shu, Y. Chen, H. Yu, X. Liao, C. Liu, H. Tang, S. Li, P. Yang, Chem Commun, 55 (2019) 5491-5494.

[29] C. J. Walter, H. L. Anderson, J. K. Sanders, J Chem Soc Chem Comm, 5 (1993) 458-460.

[30] O. Sahin, S. Eymur, A. Uyanik, E. Akceylan, M. Yilmaz, Polycycl. Aromat. Comp., 38 (2018) 168-179.

[31] J. Chen, J. Rebek, Org. Lett., 4 (2002) 327-329.

[32] S. R. Shenoy, F. R. Pinacho Crisóstomo, T. Iwasawa, J. Rebek, J. Am. Chem. Soc., 7 (2008) 0763-0763.