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Dynamic Covalent Chemistry Approaches Toward Macrocycles, Molecular Cages, and Polymers

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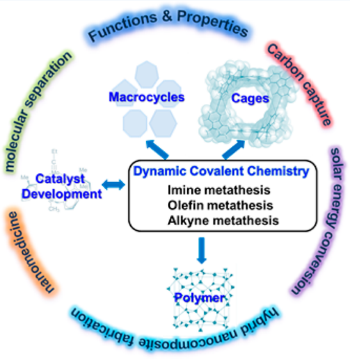
CONSPECTUS: The current research in the field of dynamic covalent chemistry includes the study of dynamic covalent reactions, catalysts, and their applications. Unlike noncovalent interactions utilized in supramolecular chemistry, the formation/breakage of covalent bonding has slower kinetics and usually requires the aid of a catalyst. Catalytic systems that enable efficient thermodynamic equilibrium are thus essential. In this Account, we describe the development of efficient catalysts for alkyne metathesis, and discuss the application of dynamic covalent reactions (mainly imine, olefin, and alkyne metathesis) in the development of organic functional materials.

Alkyne metathesis is an emerging dynamic covalent reaction that offers robust and linear acetylene linkages. By introducing a podand motif into the catalyst ligand design, we have developed a series of highly active and robust alkyne metathesis catalysts, which, for the first time, enabled the one-step covalent assembly of ethynylene-linked functional molecular cages.



Imine chemistry and olefin metathesis are among the most well-established reversible reactions, and have also been our main synthetic tools. Various shape-persistent macrocycles and covalent organic polyhedrons have been efficiently constructed in one-step through dynamic imine chemistry and olefin metathesis. The geometrical features and solubilizing groups of the building blocks as well as the reaction kinetics have significant effect on the outcome of a covalent assembly process. More recently, we explored the orthogonality of imine and olefin metatheses, and successfully synthesized heterosequenced macrocycles and molecular cages through one-pot orthogonal dynamic covalent chemistry.

In addition to discrete molecular architectures, functional polymeric materials can also be accessed through dynamic covalent reactions. Defect-free solution-processable conjugated polyaryleneethynylenes and polydiacetylenes have been prepared through alkyne metathesis polymerization. We prepared imine- or ethynylene-linked porous polymer networks, which exhibit permanent porosity with high specific surface areas. Our most recent contribution is the discovery of a recyclable polyimine material whose self-healing can be activated simply by heating or water treatment.

The facile access to complex functional organic molecules through dynamic covalent chemistry has allowed us to explore their exciting applications in gas adsorption/separation, host–guest chemistry, and nanocomposite fabrication. It is clear that there are significant opportunities for improved dynamic covalent systems and their more widespread applications in materials science.

1. INTRODUCTION

Dynamic covalent chemistry (DC_vC) deals with reversible covalent reactions that allow the free exchange of molecular components to achieve thermodynamic minimum of the system at equilibrium.[1] The fundamental principles of dynamic covalent chemistry come from supramolecular chemistry, which uses weak noncovalent interactions. In the past two decades, supramolecular chemistry has revolutionized the bottom-up development of nanoscale materials and systems. The prospect of combining the error-correction and proof-reading character of supramolecular chemistry with the robustness of covalent bonding has fascinated and challenged researchers in various disciplines. The elegant strategies of supramolecular chemistry, introduced by Lehn, revealed that intricate molecular architectures and responsive materials can be obtained taking advantage of the reversibility of weak interactions.[2] However, through dynamic covalent approach, thus far chemists have mainly focused on the selection of library members as molecular receptors, catalysts, sensors, and so forth.[1b] The potential of DC_vC to form a single clean complex molecular architecture and to prepare responsive materials has been insufficiently explored.

Our research focuses on the design and synthesis of discrete molecular architectures (macrocycles, molecular cages) and polymers as organic functional materials through dynamic covalent chemistry. The most widely practiced reversible covalent reactions in the self-assembly of molecular architectures include imine chemistry, disulfide exchange, and boronic acid condensation. In 1991, the Cram group reported the assembly of hemicarcerand through imine chemistry, and the dynamic nature of such system was first explored by Stoddart and co-workers in 2000.[3] More recently, the assembly of Schiff-base cage compounds has been extensively explored by several groups.[4] In 1999, Tam-Chang et al. reported the molecular self-assembly of macrobicyclic tris(disulfide) through disulfide bond formation under equilibrium conditions.[5] The Sanders and Otto groups have also pioneered the development and

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application of the disulfide exchange reaction.[6] Severin and others have made significant contributions to the development of boronic acid mediated self-assembly.[7] Despite the rapid advances in this field, many important reversible covalent reactions (e.g., olefin metathesis, alkyne metathesis) remain underexplored and exciting facets of even familiar systems have not yet been realized in the majority of their potential applications in material science. In this Account, we summarize our exploration of dynamic metathesis reactions, namely, imine metathesis, olefin metathesis, and alkyne metathesis, covalent assembly of macrocycles and molecular cages, and preparation of functional polymeric materials.

2. DYNAMIC COVALENT REACTIONS

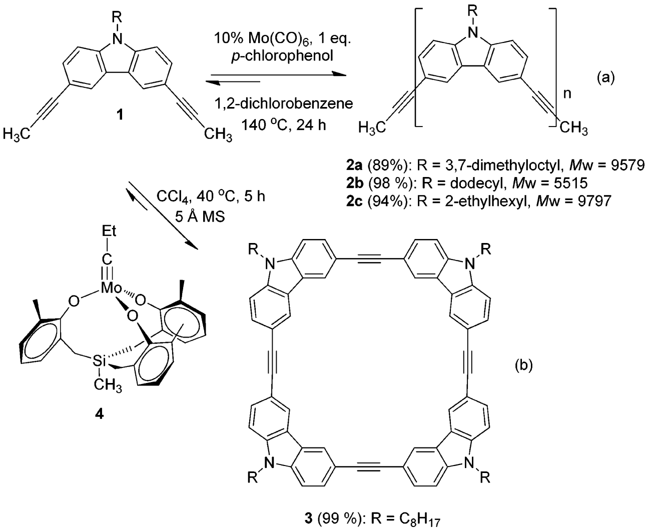
A key feature of DC_vC is the thermodynamically controlled product distribution at equilibrium. Selection of molecular receptors or self-assembly of certain complex molecular architectures is rooted in the investigation of equilibrium states. Therefore, dynamic covalent reactions with fast reaction kinetics under mild conditions are generally preferred to achieve thermodynamic equilibrium within a system in a reasonable time frame. Catalysts are usually required for dynamic covalent reactions to reach the equilibrium quickly.

In addition to the prevalent imine metathesis reaction, our group has been interested in olefin metathesis and alkyne metathesis. In 1997, Grubbs and co-workers reported the template-directed depolymerization of a polymer to form cyclic oligomers, and demonstrated the dynamic nature of olefin metathesis and error-correction character of the dynamic system.[8] The advantages of olefin metathesis are that it has been extensively studied and various catalysts are available. However, the possible complications with olefin metathesis include the uncontrolled double bond configuration (E/Z), and the slower kinetics of bond exchange on diaryl-substituted internal double bonds versus terminal olefins. Compared to olefin metathesis, the development of alkyne metathesis lags far behind. Alkyne metathesis provides a rigid, robust, and linear ethynylene bond, which is an ideal chemical linkage for the covalent assembly of discrete shape-persistent molecular cages and macrocycles. Our group has been developing catalytic systems for alkyne metathesis that are highly active under mild reaction conditions with high functional group compatibility.

2.1. Equilibrium of a Dynamic System

When a dynamic system reaches equilibrium, the product distribution solely depends on the relative stabilities of all possible products, and the species that is most thermodynamically stable predominates. Completely different outcomes can be expected from a system that has reached the equilibrium and one that has not. As shown in Scheme 1, the alkyne metathesis of monomer **1** can produce either polymer **2** or macrocycle **3** predominantly. When a catalyst system generated in situ from molybdenum hexacarbonyl and *p*-chlorophenol was used to catalyze the reaction, polymers **2** were predominant after 24 h at 140 °C.[9] In contrast, macrocycle **3** was obtained as a major species using a catalyst with higher activity, such as **4**.[10] The formation of macrocycle **3** is thermodynamically favored, and thus longer polymers **2** are expected to transform into **3** when the system reaches the equilibrium. Moore and co-workers experimentally demonstrated the formation of macrocycle **3** (R = $C_{10}H_{21}$) through the depolymerization of polymer **2** (R = $C_{10}H_{21}$, obtained from Sonogashira coupling).[11] These results clearly indicate the system in Scheme 1a had not reached the equilibrium, though the reaction was run for extended time at elevated temperature. It is conceivable that, provided enough time and a long-lived catalyst, the reaction (Scheme 1a) could reach the equilibrium, yielding macrocycle **3** as the major species. However, the key concern is the time scale for equilibration. In this regard, the development of highly active catalysts to achieve fast equilibrium is of paramount importance.

Scheme 1. Alkyne Metathesis of Monomer 1



2.2. Exploration of Dynamic Covalent Reaction: Alkyne Metathesis

Our initial motivation for developing alkyne metathesis catalysts was to construct well-defined ethynylene-linked 3-D molecular cages from simple tetrayne building blocks through thermodynamically controlled assembly process. The predominant formation of oligomers and polymers instead of target cages using available catalysts prompted us to develop a new catalytic system with high catalytic activity, good functional group tolerance, and suppressing polymerization of small alkyne byproduct. In the past two decades, a series of well-defined catalytic systems based on Schrock's prototype neopentylidyne complex (**5**) have been developed, consisting of various monodentate ligands, such as alkoxide, aryloxide, amido, imidazolin-2-iminato, phosphoraneiminato, or silanolate ligands.[12] The most common problems with these catalysts include the high sensitivity to air and moisture, low/no reactivity toward heterocyclic substrates, and the undesired polymerization of small alkyne substrates. Alkyne metathesis catalysts with monodentate ligands (e.g., **6**) usually have two substrate binding sites available at the metal center, which allow the undesired alkyne polymerization to occur through the "ring expansion" mechanism. In order to block the extra substrate-binding site, we introduced the podand motif to the catalyst design. Using monodentate catalyst **6** developed by Moore as a starting point,[13] we synthesized a series of multidentate molybdenum catalysts (Figure 1, **4** and **7**−**11**).[10,14] The first generation of multidentate ligands we developed are triphenolamines, which indeed effectively coordinate to molybdenum forming a cage-shaped metal center and block the extra substrate-binding site and suppress the small alkyne polymerization.[14] However, later we found the central nitrogen of triphenolamine coordinates to the molybdenum metal center, which lowers its Lewis acidity, thus the catalyst activity (no

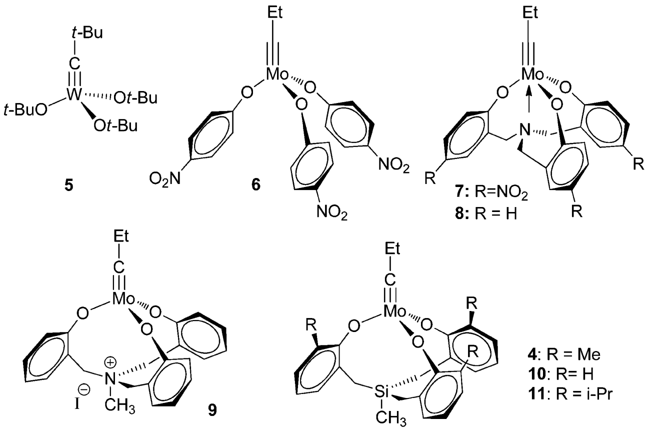
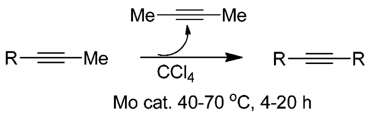
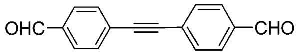
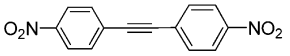
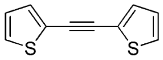
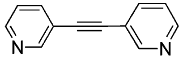
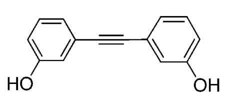
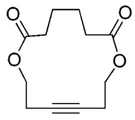


Figure 1. Structures of tungsten(VI) or molybdenum(VI) carbyne complexes.

activity observed without the nitro substituents, i.e., **8**).[14b] Although methylation of the nitrogen atom in the ligand prevents its metal coordination and restores the catalyst activity (**9**), the synthetic difficulty and poor solubility of the charged triphenolammonium ligand are big disadvantages.[14b] Triphenolsilane-based catalysts (**4**, **10**, and **11**) are therefore developed, which can be easily synthesized and purified.[10] They are completely resistant to the small alkyne polymerization, and exhibit high catalytic activity, broad substrate scope, and long lifetime (remain active in solution for months at −30 °C). In particular, they can catalyze cross-metathesis of a variety of challenging substrates (e.g., pyridine, phenol, benzaldehyde, nitrobenzene, Table 1). They are also compatible with 5 Å molecular sieves, which scavenge the 2-butyne byproduct.[15] These factors (high activity, functional group tolerance, and stability) all serve to significantly enhance the ability of multidentate molybdenum complexes to function as efficient catalysts for $\mathrm{DC_vC}$.

Table 1. Homodimerization and Ring Closing Alkyne Metathesis of Propynyl Substrates



 **12**: 71% (Cat. **7**, 7 h)[a,c] 80% (Cat. **9**, 9 h)[a,c] 94% (Cat. **4**, 16 h)[a,d]	 **13**: 55% (Cat. **7**, 12 h)[a,c] 43% (Cat. **9**, 13 h)[a,c] 86% (Cat. **4**, 20 h)[a,d]
 **14**: 74% (Cat. **7**, 4 h)[a,c] 80% (Cat. **9**, 4 h)[a,c] 92% (Cat. **4**, 5 h)[a,d]	 **15**: 61% (Cat. **7**, 3 h)[b,c] 79% (Cat. **9**, 4 h)[b,c] 84% (Cat. **4**, 4 h)[b,d]
 **16**: 76% (Cat. **4**, 20 h)[b,d]	 **17**: 63% (Cat. **7**, 4 h)[a,c] 95% (Cat. **9**, 4 h)[a,c] 95% (Cat. **4**, 4 h)[a,c]

[a] 3 mol % catalyst loading, 40 °C. [b] 10 mol % catalyst loading, 70 °C. [c] 2-Butyne was removed by occasional exposure to vacumn. [d] 5 Å molecular sieves were added to remove 2-butyne.

3. COVALENT ASSEMBLY OF MOLECULAR ARCHITECTURES

The concept of self-assembly is found throughout nature. For example, the 30S subunit of bacterial ribosome is formed through assembly of rRNA with 21 unique proteins.[16] Mimicking nature's elegant biomolecular self-assembly, chemists have prepared an extensive array of dauntingly complex molecular architectures, such as helicates, catenanes, and Borromean rings, employing noncovalent bonding interactions, and more recently through covalent bonding.[17] The energy landscape principle accounts for the predominant formation of target structures over other possible products. Building blocks of molecular architecture can be specifically designed such that the target species is the most thermodynamically stable one. The geometrical features, rigidity, and solubility of building blocks are critical factors for successful assembly of molecular architectures.[4c]

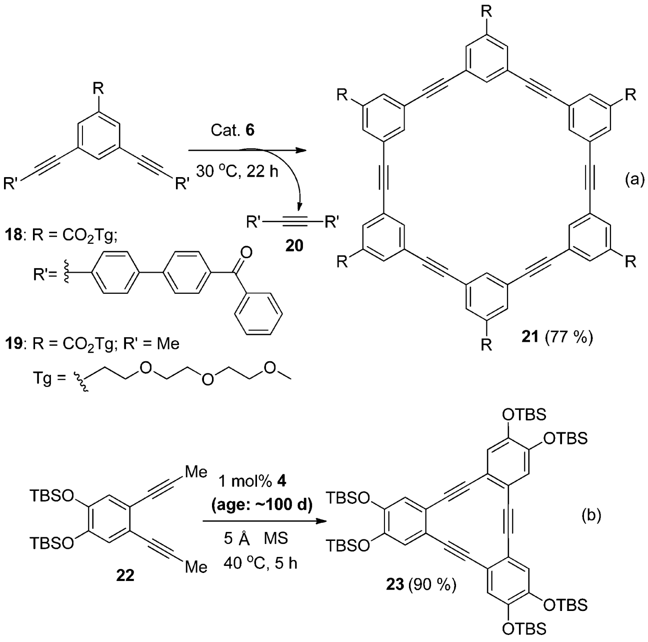
3.1. Assembly of Shape-Persistent Macrocycles

Shape-persistent macrocycles with conjugated backbones and nanometer-sized interiors are among the most sought-after structures in chemistry.[18] Macrocycles have been used as building blocks for 1-D tubular superstructures, 2-D ordered monolayers, and 3-D host−guest complexes through self-assembly.[18] The rigid backbones give rise to large molecular surfaces that organize into higher order structures, and allow engineering of both interior and exterior functionalities.

Aryleneethynylene macrocycles (AEMs) represent an important and well-studied class of cyclic compounds.[18b] Recent advances in alkyne metathesis catalysts have made it possible to prepare homosequenced AEMs (e.g., **21**) in one step from simple building blocks. The first example of cyclooligomerization to form AEMs through alkyne metathesis was reported by Moore.[19] The reaction was driven to completion by precipitation of the diarylacetylene byproduct, or by applying continuous dynamic vacuum (Scheme 2a). However, these methods suffer from either poor-atom economy or strict requirement of moisture and air free vacuum system. The Fürstner group and our group have demonstrated that 5 Å molecular sieves can be used as an efficient small alkyne scavenger.[15] In the presence of molecular sieves, various macrocycles (e.g., cyclic tetramer **3** and cyclic trimer **23**) are obtained from simple propynyl-substituted monomers through alkyne metathesis in a closed system. In the case of cyclotrimer **23**, 1 mol % of aged (stored in solution for 100 days) catalyst **4** was sufficient to catalyze the formation of macrocycle **23** (90%, Scheme 2b) on multigram scale, highlighting the efficiency and long lifetime of multidentate catalysts.[10]

In contrast to the intensive research efforts devoted to AEMs, arylenevinylene macrocycles (AVMs), the structure analogues of AEMs, have rarely been studied. Olefin metathesis has become a powerful tool in organic synthesis and has been widely used in synthesis of flexible large cyclic compounds through ring closing metathesis (RCM),[8] or polymers through acyclic diene metathesis (ADMET).[20] Our group explored the synthesis of AVMs through rapid and reversible olefin metathesis. Various AVMs (**25a−c**, **27**) of different sizes and substitutions can be prepared via one-step acyclic diene metathesis macrocyclization (ADMAC) (Scheme 3).[21] Inter-

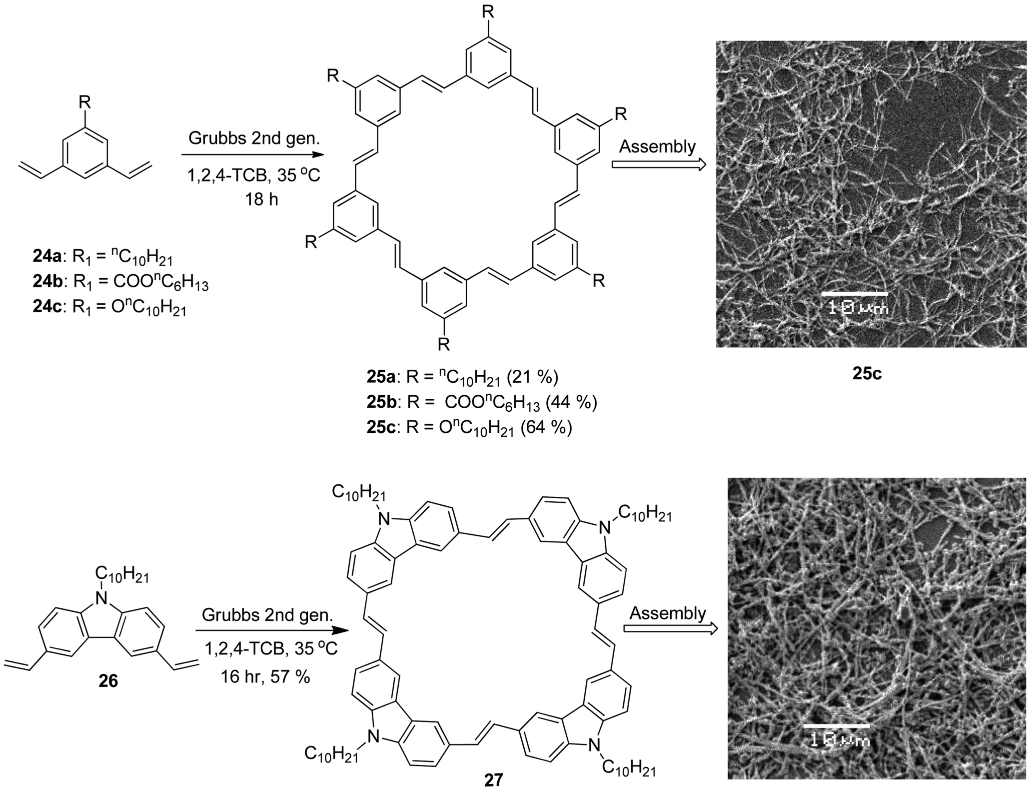
Scheme 2. Synthesis of Aryleneethynylene Macrocycles through Alkyne Metathesis



estingly, although AVMs seem to have more conformational freedom and less rigidity due to the possible conformational isomerism of vinylene moieties, they generally exhibit much stronger self-association compared to the AEMs bearing similar substituents. For example, in contrast to the nonaggregating character of alkoxy substituted AEM **21** (R = OC_4H_9, $K_{\text{assoc}} \sim 0$),[22] the AVM **25c** showed strong self-aggregation ($K_{\text{assoc}} = 60$ M^{-1}) in the same solvent ($CDCl_3$), which indicates the strong dependence of macrocycle's aggregation behavior on its backbone structure. These AVMs can form 1-D nanofibrils when concentrated solutions of AVMs (e.g., **25c** or **27**) in $CHCl_3$ are rapidly dispersed into CH_3CN (SEM, Scheme 3). Most of the fibers are tens of μm in length, with diameters on the order of a few hundred nanometers.

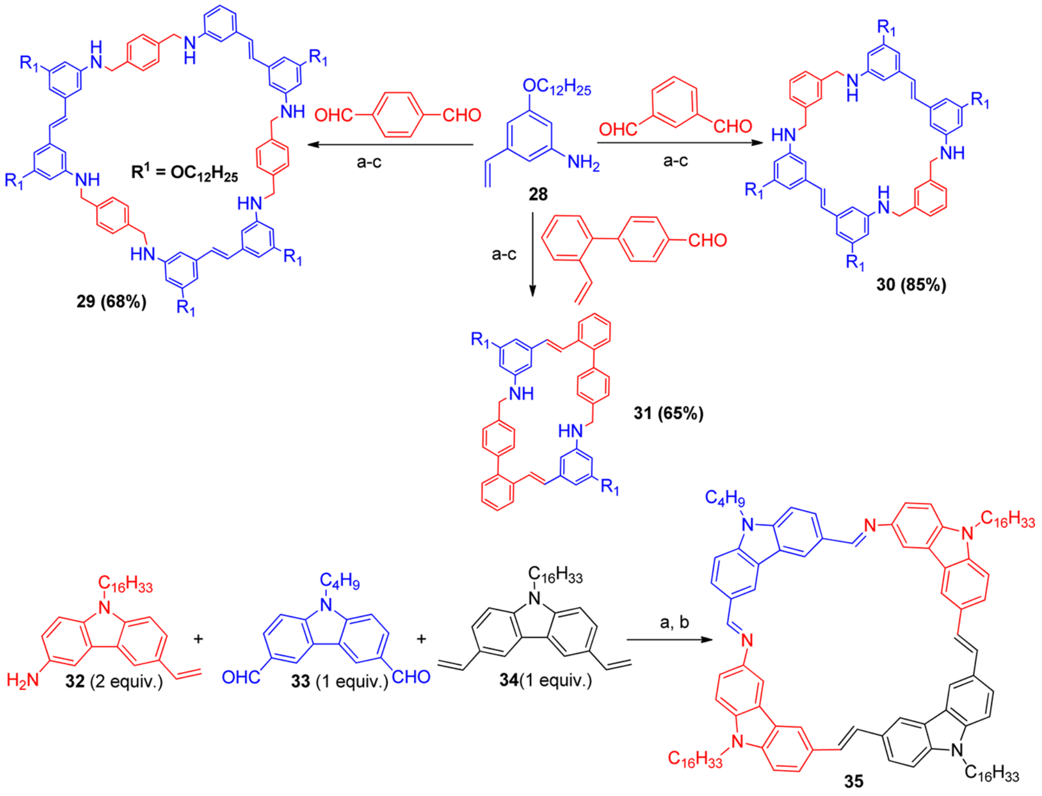
In spite of significant progress in macrocycle synthesis via DC_vC, this method is usually limited to homosequenced macrocycles. Heterosequenced and/or multifunctional macrocycles with interior and/or exterior site-specific substitution would be interesting building blocks for complex interlocked molecular architectures and novel functional molecular devices (e.g., molecular machines). To overcome the "homosequence" limitation of conventional DC_vC, we explored a multicomponent orthogonal dynamic covalent chemistry (ODCC) method, in which two or more different dynamic covalent reactions are conducted in one pot. We found that imine metathesis and olefin metathesis are orthogonal and can be used in one-pot cyclooligomerizations. A series of multicomponent macrocycles (**29**–**31**) of different size and shape were prepared in good yields (64–85%) in a modular fashion by employing various combinations of a small set of building blocks: *ortho*-, *meta*-, and *para*-phenylenes (Scheme 4).[23] Although imine condensation/metathesis and olefin metathesis are orthogonal, these two reactions were operated sequentially in one pot by adding trifluoroacetic acid (TFA) first, followed by Grubbs second generation catalyst. We observed sluggish cyclooligomerization (3 d vs 18 h) when imine condensation and olefin metathesis were conducted simultaneously from the

Scheme 3. ADMAC Approach to AVMs and Their Self-Assembly into Nanofibrils[a]



[a]Scale bars in SEM images are 10μm.

Scheme 4. ODCC Approach to Heterosequenced Macrocycles[a]



[a] One-pot conditions: (a) TFA (4 mol %), rt, 30 min, then vacuum; (b) Hoveyda−Grubbs catalyst 2nd generation (10 mol %, 50 °C, 16 h); (c) DIBAL-H (rt, 20 min).

beginning of the reaction. This sequential ODCC methodology was successfully applied to the synthesis of heterosequenced carbazole-containing macrocycles (e.g., **35**). Up to three different building blocks have been incorporated into a single macrocycle.[24] This result demonstrates the versatility and modularity of the ODCC approach in heterosequenced macrocycle design and synthesis.

3.2. Assembly of Covalent Organic Polyhedrons (COPs)

Molecular cages have been the subject of intense research for both their unique structural features and numerous applications in the areas of molecular recognition,[4b,25] chemical sensing,[26] catalysis,[27] and gas separation and storage.[28] Compared to supramolecular cages, purely organic covalent molecular cages are relatively rare mainly due to synthetic inefficiencies. DC$_v$C is arguably the most efficient strategy to access covalently linked cage molecules. The most widely used rapid and reversible reaction for the synthesis of covalent organic polyhedrons (COPs) has been imine chemistry.[4]

We prepared a series of [3 + 2] COPs (**38**−**46**, Figure 2) with different shapes (trigonal prisms, or elongated triangular bipyramids) and sizes through dynamic imine chemistry, and investigated the design principle of the building blocks. We found that the orientation of complementary functional groups is critical to the formation of strain-free COP structures (Scheme 5).[4c] Planar triamine **36** reacts with dialdehyde connectors, which have an angle between the two aldehyde groups close to 0°, to form a trigonal prismatic COP^{I}. However, the reaction of **36** with dialdehydes bearing a 60° angle between the two formyl groups resulted in partially closed intermediates without any noticeable amount of the desired COP structures, presumably due to the “misalignment” of amine and aldehyde functional groups. Compared to the planar triamine **36**, pyramidal triamine **37** appears to be slightly more conformationally flexible and more tolerant of geometrical mismatch with the dialdehyde counterparts, reacting with dialdehydes with 0° or 60° angle to form the elongated triangular bipyramids COP^{II}. The alkyl substituents on the building blocks are also important as they ensure good solubility of intermediate species. When building blocks without solubilizing groups were used, significant precipitation occurred, kinetically trapping intermediates and preventing their subsequent participation in the dynamic exchange process (e.g., **38a**, **39a**).

Some cage compounds (**39b**, **40**, **41**, and **43**) exhibit exceptionally high ideal selectivities (up to 138/1) in adsorption of CO_2 over N_2 under standard temperature and pressure (STP, 20 °C, 1 bar).[29] Gas adsorption studies on as-synthesized amorphous samples indicate that the high selectivity is dependent on both the amino group density (mol/g) and the intrinsic pore size of the cage. The amino group density largely determines the CO_2 uptake,[30] while N_2 adsorption capacity correlates to the dimensions of molecular prisms.[29a] These COPs can also be covalently cross-linked to form cage frameworks (the “cage-to-framework” strategy).[31] Covalently linked frameworks **40** were obtained through Sonogashira coupling of COP **39b** with various linker molecules (**L1**-**L3**) (Scheme 6). These framework materials exhibited high ideal selectivities (up to 213/1) in adsorption of CO_2 over N_2 under ambient conditions. Both the functionality and length of linkers determine the gas adsorption capacity and selectivity of these frameworks. Given a rich diversity of linkers

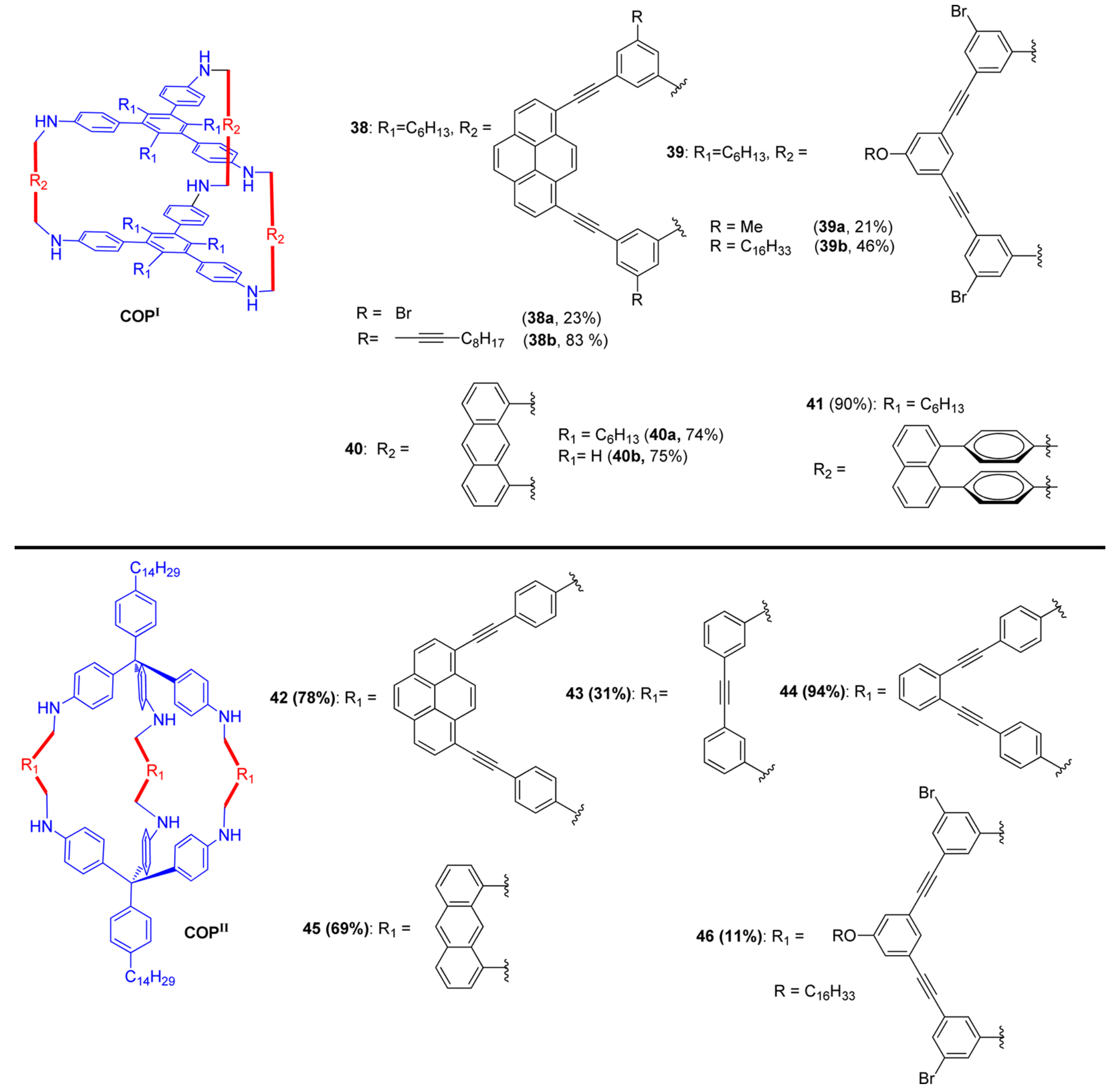


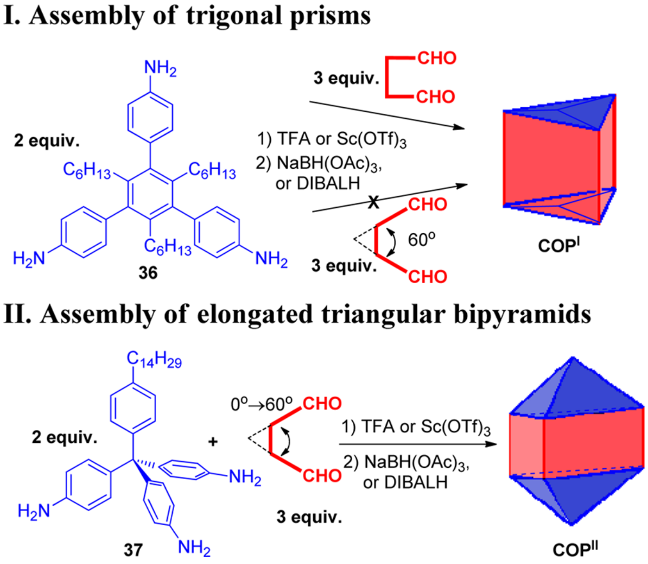
Figure 2. Structures of imine-linked COPs.

and individual cage molecules, facile tuning of framework properties can be achieved by integration of dimensional and functional parameters of porous 3-D building blocks and linkers into the final frameworks.

Cage structures have also been obtained through the ODCC approach by combining imine metathesis and olefin metathesis. Providing a 90° angle, 3,6-disubstituted carbazole moieties serve as corner pieces of trigonal prismatic cages. Under the sequential one-pot conditions described above, six carbazole building blocks **32** and two planar top and bottom panels **41** were assembled into COP **42** in good yield (Scheme 7).[24]

Although imine chemistry provides facile access to various molecular cages, the potential drawback of imine-linked cages is the structural distortion due to rotational freedom in imine bonds, which leads to the loss of shape-persistency. Moreover, imine groups are sensitive to acidic conditions and water, and prone to decomposition. Compared to imine, the acetylene linker is linear, more rigid, and chemically robust. Our group successfully synthesized the first ethynylene-linked cage compound **44**, via alkyne metathesis using our multidentate molybdenum catalyst (Scheme 8).[25b] Our initial attempt of using monodentate Mo(VI) carbyne **6** only yielded a large amount of oligomeric intermediates with a trace amount of the target cage. In contrast, cage **44** was successfully obtained in decent yield (56% isolated) using multidentate catalyst **7** with higher activity, which enables efficient "error-correction" and converts large oligomers to the most thermodynamically stable **44**. The unique combination of the conjugated system and the rigidity of cage **44** render its high binding affinity for fullerenes. Rapid binding of C_{70} and C_{60} in toluene was observed with the unprecedented high binding selectivity (>1000/1) for C_{70} over C_{60} ($K_{assoc} = 2 \times 10^6$ for C_{60} and $K_{assoc} = 2 \times 10^8$ for C_{70}). We found C_{60}@**44** complex efficiently binds to single-walled carbon nanotube (SWCNT) surface to form a novel donor–acceptor nanohybrid for light-harvesting.[32] The cage-fullerene binding is fully reversible under acid–base stimuli. The pH-

Scheme 5. Covalent Assembly of COPs through Dynamic Imine Chemistry



driven reversible association and dissociation of fullerene-cage complexes enables the isolation of valuable C_{70} as the major species from a C_{60}-enriched (C_{60}/C_{70}, 10/1 mol/mol) fullerene mixture through the "selective complexation−decomplexation" strategy.

Further structure−property relationship study showed that a slight structural variation leads to the selective binding of C_{84} over C_{70}. Macrocycle **45** was synthesized as a two-arm analogue of cage **44** through one-step alkyne metathesis.[33] Interestingly, **45** shows greater binding affinity for C_{84} ($2.2 \times 10^7\ M^{-1}$) than C_{60} ($1.3 \times 10^4\ M^{-1}$) and C_{70} ($2.0 \times 10^6\ M^{-1}$). This study suggests that structure-tunable cage molecules can target different fullerene separations.

4. SYNTHESIS OF POLYMERS

Reversible reactions are vital for the synthesis of various functional materials, including: porous covalent organic frameworks,[34] stimuli-responsive materials,[2b,35] self-healing polymers,[36] and many others. Reversible covalent reactions provide previously unobtainable robust materials with the benefit of self-correction. In addition, reversibility confers adaptability to the materials, which can be made responsive to external stimuli, such as the pH of the medium, the solvent, or other physical factors (temperature, light, electric, mechanical stress, etc.). Our group has been actively involved in the application of alkyne metathesis and imine chemistry to the synthesis of conjugated polymers, porous frameworks, and malleable covalent network polymers.

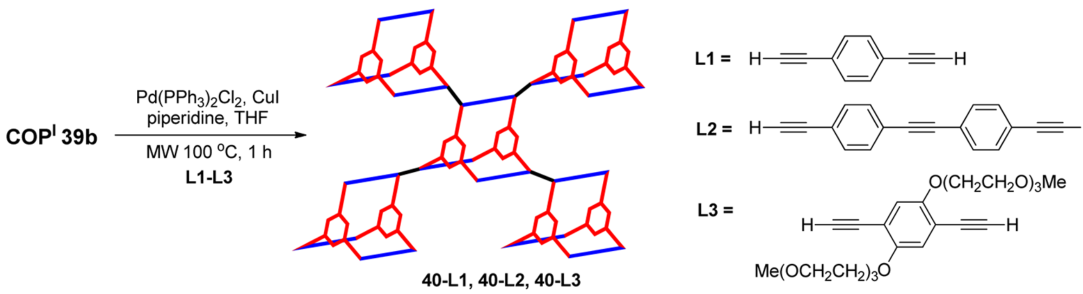
4.1. Conjugated Polymers

Conjugated polymers have been used extensively in electronics and optoelectronics as chemical sensors,[37] organic field effect transistors,[38] organic light emitting diodes,[39] and organic solar cells.[40] Aryleneethynylene polymers are among the most widely studied conjugated polymers. Palladium catalyzed cross-coupling is typically used to synthesize ethynylene-linked polymers, and butadiyne defects often occur in the growing polymer chain when two terminal acetylenes are coupled. Given the high activity, broad functional group tolerance, and long lifetime of the multidentate molybdenum catalysts, we utilized alkyne metathesis as an efficient alternative synthetic route to defect-free ethynylene bridged polymers.

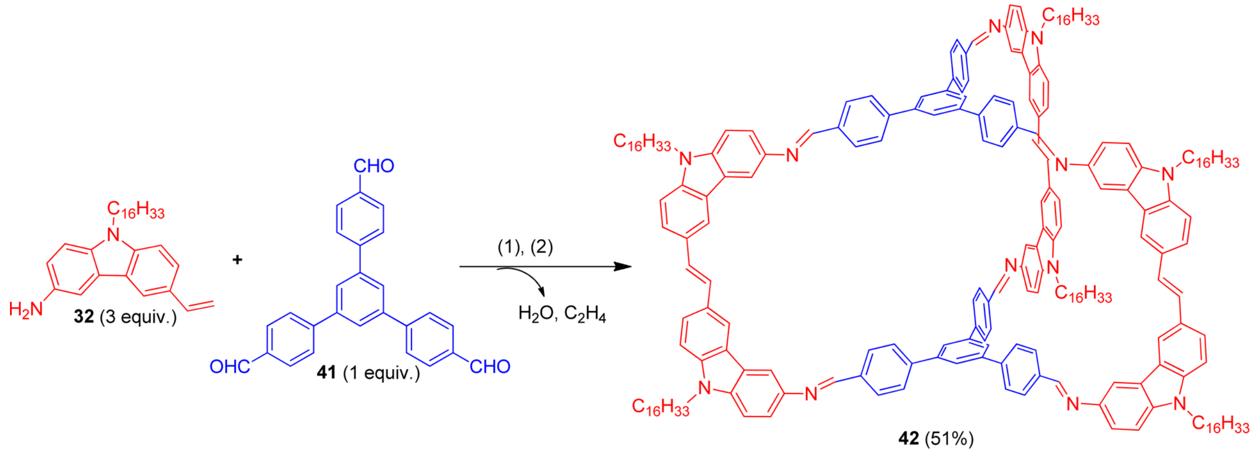
Since conjugated porphyrin polymers linked by ethynylenes are good candidates for molecular electronics due to their capacity for efficient long distance charge transfer,[41] we studied the polymerization of porphyrin-containing monomer **47** (Scheme 9).[14b] With the aid of solubilizing chains, the alkyne metathesis polymerization remained homogeneous throughout the reaction and yielded porphyrin polymer **48** with high molecular weight (M_n = 12 100, PDI = 1.50). The defect-free backbone structure of the porphyrin polymer was confirmed by the ^{13}C NMR spectrum, which showed a single alkyne signal corresponding to the carbons in the ethynylene repeating units.

Another type of extensively researched conjugated polymers is polydiacetylenes (PDAs). PDAs have found application in nonlinear optics, organic semiconductors, and sensory materials.[42] PDAs are typically prepared by solid-state polymerization of diacetylene (DA) monomers in crystals, films, gels, and micellar structures.[43] However, this approach is limited by (1) the narrow scope of monomers and limited structure tunability: only DA monomers with alkyl spacers between DA cores and functional side groups have been successfully polymerized; (2) low solubility of the resulting PDA products, making integration of these materials into solution-fabricated electronic devices challenging. In this context, alkyne metathesis polymerization provides an exciting alternative to prepare PDAs with tunable steric and electronic properties. Solution processable PDAs (**50a**, **b**) bearing alkyl and phenyl substituents have been obtained through acyclic enediyne metathesis polymerization (AEDMET) of methyl terminated *trans*-enediyne monomers (**49a**, **b**) using multidentate catalyst **4** (Scheme 10).[44] The good solubility of **50a**, and **50b** in common organic solvents enabled easy fabrication of these polymers into electronic devices, such as organic solar cells.[44]

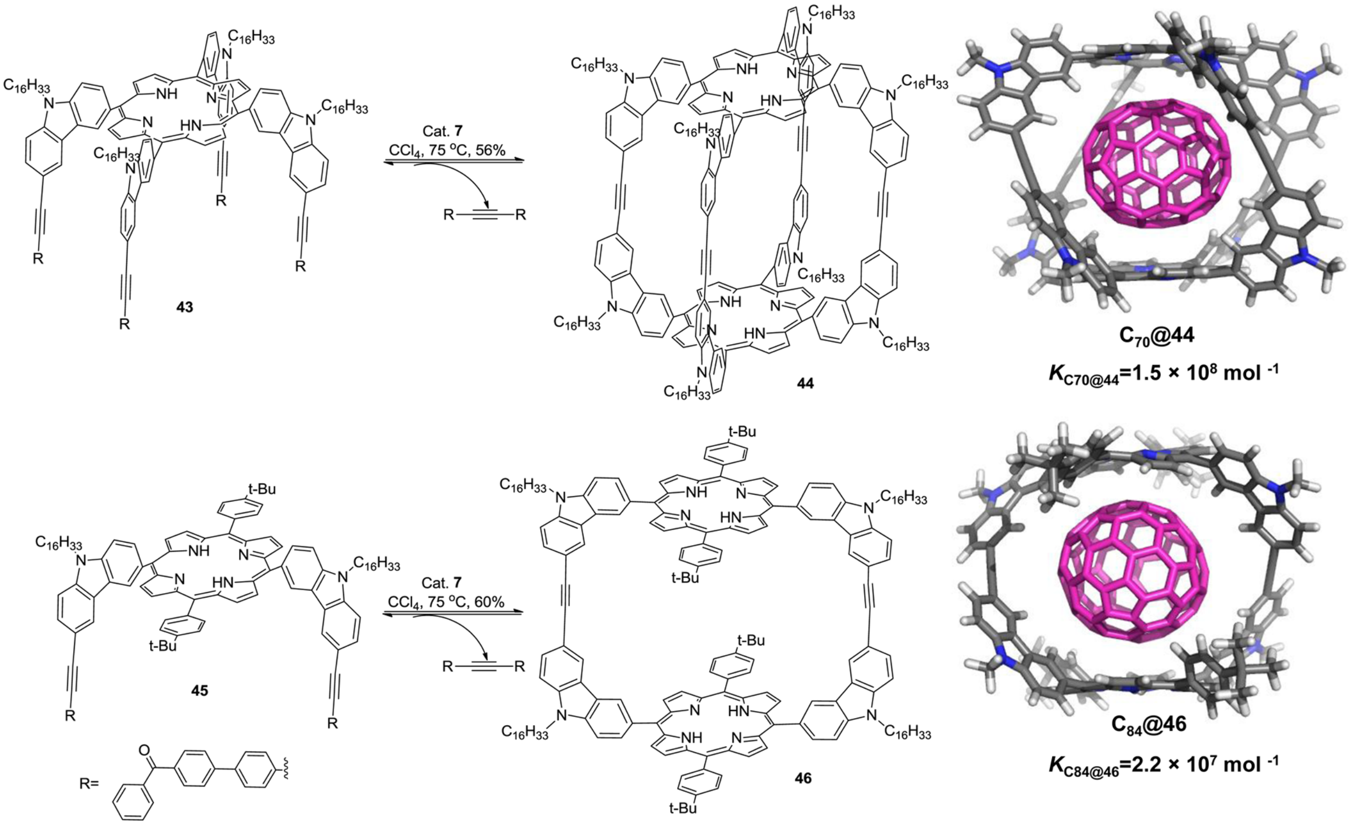
Scheme 6. Cage-to-Framework Strategy to Form Porous Polymer 40



Scheme 7. Synthesis of COP 42 through ODCC



Scheme 8. Synthesis of COP 44 and Macrocycle 46 through Alkyne Metathesis[a]



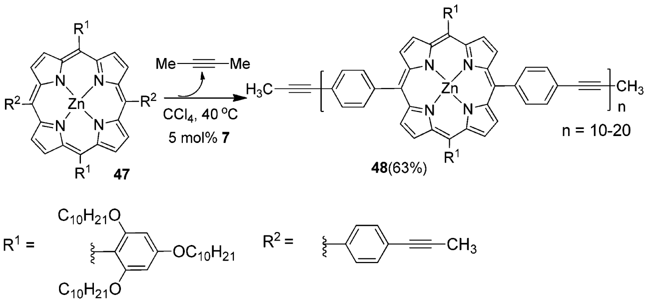
[a]Energy minimized structures of complexes C_{70}@**44** and C_{84}@**46** are shown.

4.2. Porous Organic Polymers

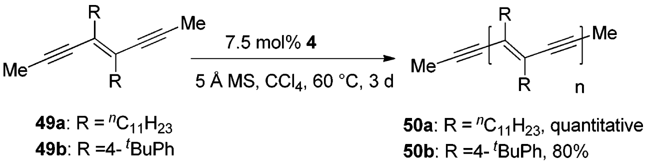
Organic porous materials are emerging as promising next-generation highly porous materials. Light weight, stability, and structural tunability represent their advantages. Reversible reactions play a critical role in the preparation of ordered covalent organic frameworks (COFs).[34] Although the mechanism of formation of crystalline COFs through reversible covalent chemistry is unclear, it is generally held that the reversibility provides some error-correction mechanism which positively affects a material's crystallinity and porosity. Our group is exploring the preparation of porous materials through imine chemistry and alkyne metathesis. Although reversible imine condensation and alkyne metathesis have the potential to prepare highly ordered frameworks, we have not yet obtained highly crystalline materials.

Imine-linked porous organic polymer **53** with a [3 + 4] structural motif was synthesized via imine condensation (Scheme 11).[45] The framework shows encouraging gas adsorption properties with a Brunauer−Emmett−Teller (BET) specific surface area of 1740 $m^2\ g^{-1}$ and a Langmuir surface area of 2157 $m^2\ g^{-1}$. More importantly, the porous network exhibits outstanding H_2 (up to 2.75 wt %, 77 K, 1 bar), CO_2 (up to 26.7 wt %, 273 K, 1 bar), CH_4 (up to 2.43 wt %, 273 K, 1 bar), and C_2H_2 (up to 9.4 wt %, 273 K, 1 bar) uptakes, all of which are among the highest reported for organic porous

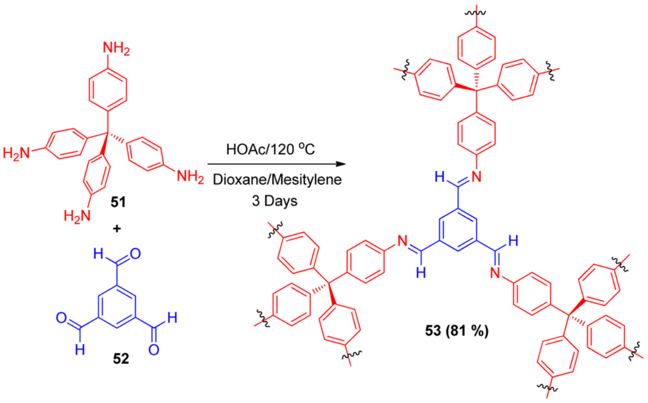
Scheme 9. Synthesis of Porphyrin Polymer 48 through Alkyne Metathesis



Scheme 10. Synthesis of PDAs through Alkyne Metathesis



Scheme 11. Synthesis of Imine-Linked Porous Organic Polymer 53



materials. It also shows excellent thermal stability, and no decomposition is observed until 500 °C. Thus, this material has great potential for gas storage and separation applications.

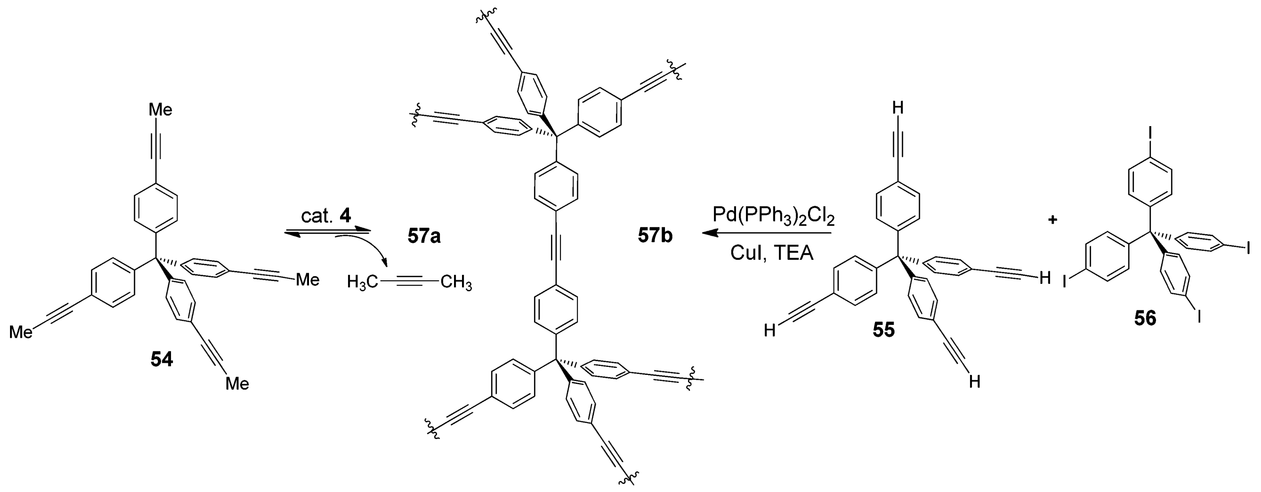
Boronic acid condensation and imine formation have been the most widely used reversible reactions in the preparation of COFs. However, the drawback of imine or boronate-containing materials is their sensitivity to water. Dynamic alkyne metathesis offers both more robust alkyne linkages and the potential to provide fully conjugated and well-ordered porous crystalline frameworks. As the key step toward this goal, we have reported the first example of alkyne metathesis polymerization to prepare the all-hydrocarbon porous network **57a** with high permanent porosity (BET specific surface area [P/P_0 = 0.01−0.1] of 2312 m^2·g^{-1}) (Scheme 12).[46] A framework with the same chemical connectivity (**57b**) was also prepared through Sonogashira cross-coupling of **55** and **56**. Interestingly, the framework (**57a**) prepared through alkyne metathesis at three different temperatures (40, 55, and 75 °C) under otherwise similar reaction conditions consistently exhibits higher specific surface area and higher thermal stability than **57b**. This suggests that dynamic alkyne metathesis is advantageous in the preparation of highly porous organic materials over the irreversible cross-coupling reaction.

4.3. Malleable Covalent Network Polymers

Covalent network polymers, which offer robust mechanical properties, generally lack the ability to be recycled. There has been a great deal of research effort to incorporate reversible covalent cross-links into covalent network polymers in order to obtain mechanically tough materials that can be recycled and reprocessed.[35,36] This new class of polymers, which are called covalent adaptable networks (CANs),[36b,c] or vitrimers,[36e] has the potential to replace thermoset polymers for many applications. With dynamic covalent bonds incorporated into the polymer backbone and cross-links, the resulting polymers can be reprocessed at high temperatures or with the aid of catalysts while retaining thermoset-like mechanical properties under ambient conditions. Cross-link exchange allows the cross-linking density of the polymer to remain constant even under extreme processing conditions. Essentially all of the dynamic covalent reactions discussed above fulfill the requirements for malleable cross-link exchange: reversibility by bond exchange with simultaneous bond forming/breaking reactions.

Our group is investigating the malleability of polyimines, as there are many commercially available amine and aldehyde monomers, and the reaction does not require incorporation of

Scheme 12. Synthesis of Polyaryleneethynylene 57 through Alkyne Metathesis and Cross Coupling Reaction



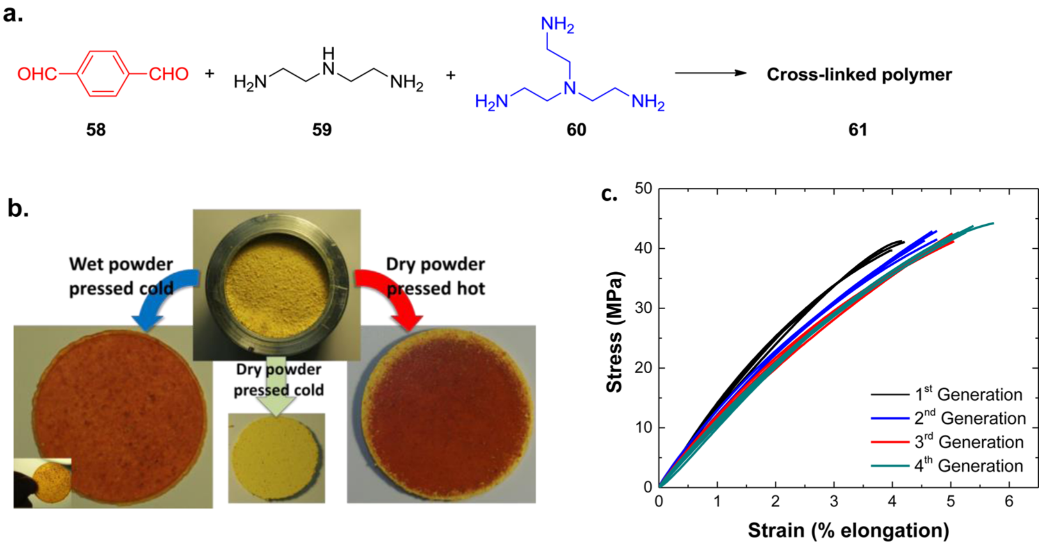


Figure 3. (a) Synthesis of polyimine **61**. (b) Reprocessing of polyimine powder to a disc with heat or water. (c) Stress–strain curves for the polyimine disc through four generations of recycling from powder to a disc under heat.

expensive or sensitive catalysts. In addition, polyimines provide unique access to functionalities such as stimuli responsiveness (pH, moisture, temperature), and conductivity. We prepared inexpensive, catalyst-free polyimine network **61** through imine condensation of **58** with **59** and **60** (Figure 3a). Polyimine **61** is able to relax 90% of an applied mechanical stress within 30 min at 80 °C without the incorporation of a catalyst, while the same process would take ∼480 days at room temperature.[47] The polyimine can be completely reprocessed from powder to solid with no degradation in mechanical strength through four generations of recycling. Remarkably, we found water can also activate the stress relaxation, recyclability, and reshaping of polyimine **61**. The polyimine powder can be reprocessed into a translucent polymer disc by simply molding it under water. Soaking hard polyimine films in water softens the material and allows reshaping. The new shape is maintained upon drying, and the hard, glassy strength of the dry film returns. Importantly, the polyimine material retains its mechanical integrity in water even at high temperatures (96 °C, 1 week). This represents the first malleable thermoset that can be reprocessed using only water, enabling green room-temperature healing and processing of the material. Our work demonstrates the unique recyclability, and robustness of polyimines, and sheds new light on their potential as structural and functional materials.

■ CONCLUSION

In this Account, we summarize our research on the development of organic functional materials through dynamic covalent chemistry. Dynamic reactions of our particular interest include imine condensation/exchange, olefin metathesis, and alkyne metathesis. Efficient catalyst systems are usually required in order to achieve fast equilibrium of a dynamic system. We have developed multidentate alkyne metathesis catalysts that are highly active, tolerant of various functional groups, and resistant to small alkyne polymerization side reaction. The newly developed catalysts enabled the construction of 3-D molecular cages through one-step assembly process. In addition to alkyne metathesis, we also employed dynamic imine chemistry, and olefin metathesis to construct discrete shape-persistent macrocycles and covalent organic polyhedrons from simple building blocks. We found that the critical factors for the successful formation of the target species are geometrical features of building blocks, solubility, and fast equilibration of the dynamic system. Macrocycles and covalent organic polyhedrons have shown interesting applications, such as nanofibril formation, gas adsorption/separation, host–guest chemistry, and solar energy conversion. Imine metathesis and alkyne metathesis are also applied to the syntheses of defect-free polyaryleneethynylenes, polydiacetylenes, porous networks, and heat and water responsive malleable polymers. The results presented here have shown the power of the dynamic covalent approach, and further exciting development in this research field is anticipated.

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