Conjugated Macrocycles

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Conjugated Macrocycles: Concepts and Applications

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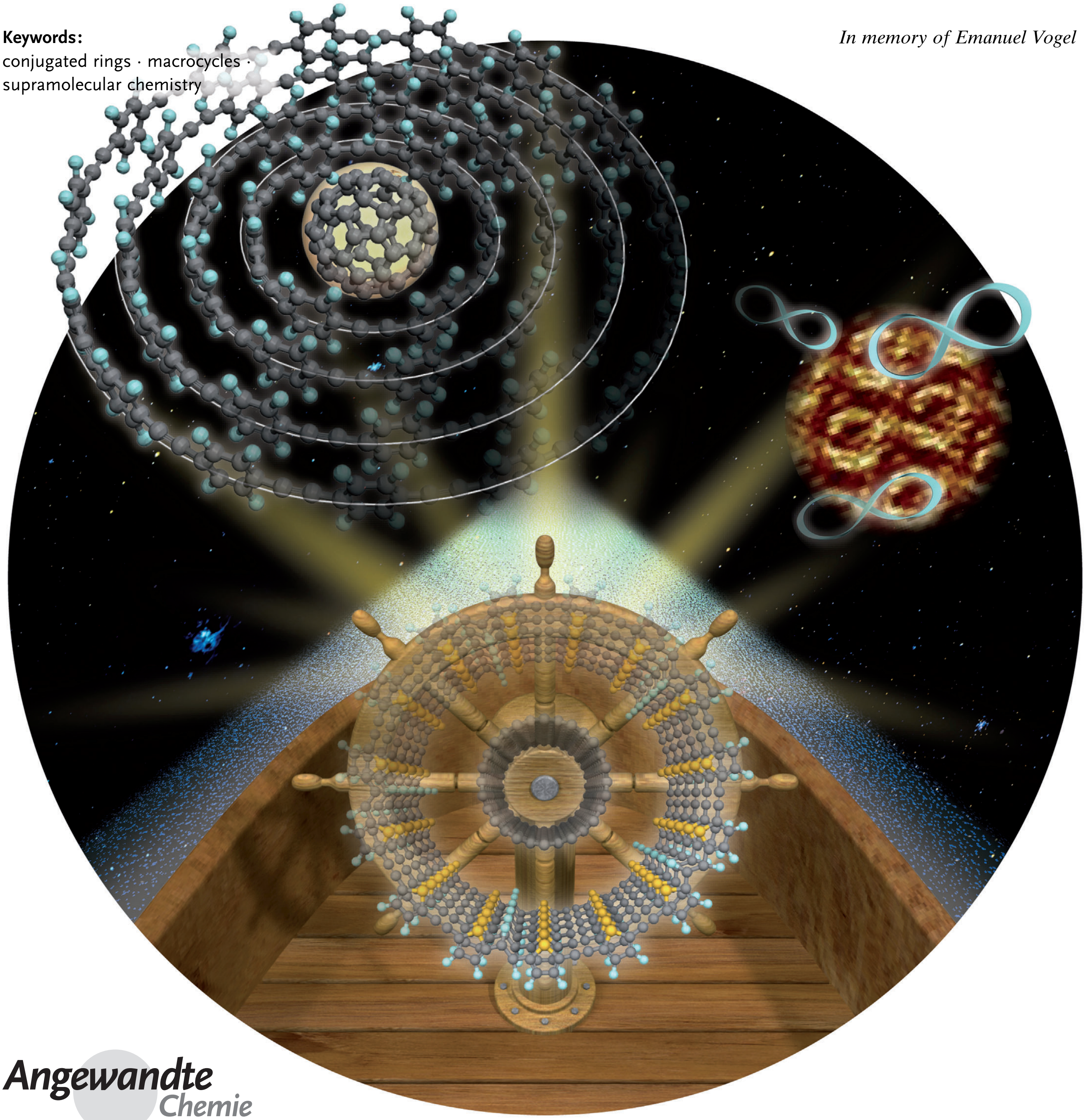
conjugated rings · macrocycles · supramolecular chemistry

In memory of Emanuel Vogel



Angewandte Chemie

One of the most important objectives in materials, chemical, and physical sciences is the creation of large conjugated macrocycles with well-defined shapes, since such molecules are not only theoretically and experimentally interesting but also have potential applications in nanotechnology. Fully unsaturated macrocycles are regarded as models for infinitely conjugated π systems with inner cavities, and exhibit unusual optical and magnetic behavior. Macrocycles have interior and exterior sites, and site-specific substitution at both or either site can afford attractive structures, such as 1D, 2D, and 3D supramolecular nanostructures. These nanostructures could be controlled through the use of π-extended large macrocycles by a bottom-up strategy. Numerous shape-persistent π-conjugated macrocycles have been synthesized, but only a few are on the nanoscale. This Review focuses on nanosized π-conjugated macrocycles (> 1 nm diameter) and giant macrocycles (> 2 nm diameter), and summarizes their syntheses and properties.

From the Contents

1. Introduction

The study of fully conjugated cyclic oligomers with well-defined diameters has become important for gaining specific information concerning structural, electronic, and optical properties, especially in relation to the “inner” and “outer” domains. Macrocyclic structures with shape-persistent, noncollapsible, and fully π-conjugated backbones should be useful for building columnar 1D nanotubes, 2D porous surface networks, and 3D inclusion complexes by self-assembly. Furthermore, macrocycles are considered to be infinite π-conjugated systems which can exhibit unique optical and electronic behaviors with or without substituent groups. Another point of interest concerning π-conjugated redox-active macrocycles is their potential applications in organic electronics, such as devices and switches. Since macrocycles change their charge and shape when they undergo redox processes, the site-specific character of macrocycles can be adjusted at both their interior and exterior sites.

The study of conjugated macrocycles began in the early 1960s, mainly to validate theoretical calculations on annulenes based on the Hückel rule.[1,2] Since the Hückel rule is only valid for systems with a maximum of 34 π electrons,[2b] the first studies focused on the synthesis of large macrocycles up to 1 nm in diameter.[1,2] Over the last two decades, however, shape-persistent conjugated macrocycles composed of benzene, thiophene, pyridine, and acetylene moieties have been synthesized and used to construct 1D, 2D, and 3D supramolecular structures through either π–π stacking or concave–convex interactions.[3–5] Furthermore, Möbius aromaticity, chirality, luminescence and two-photon absorption properties, multimodal coordination abilities, and redox properties of annulenes and expanded porphyrins have been studied as a function of nanosized conjugated macrocycles.[6] Quite recently, large macrocycles have become recognized as ideal molecules for the observation of single molecules, single-molecule manipulation, and single-molecule electronics.[7] However, nanosized conjugated macrocycles are fundamentally important due to their novel structures, properties, and functions.

Although synthetic methods to prepare large conjugated macrocycles are limited in number, new macrocycles with diameters of more than 1 nm have recently been reported, and their unique supramolecular structures, cyclic conjugation behavior, and photophysical and electric properties have been studied.[8] We focus in this Review on nanosized π-conjugated macrocycles (more than 1 nm in diameter) and giant π-conjugated macrocycles (more than 2 nm in diameter). Schiff base macrocycles and cyclic polymers are not summarized here, even though the chemistry of these compounds has received recent attention.[9,10] A few cyclic porphyrin arrays are briefly summarized on the basis of their structure–property correlations. This Review mainly concentrates on the syntheses and versatile properties of nanosized conjugated systems reported in the last decade, since the reviews of shape-persistent macrocycles (Höger 1999,[11a] Grave and Schlüter 2002,[11b] and Yamaguchi and Yoshida 2003)[11c] summarized the syntheses, structures, and some properties of these macrocycles. The most recent developments in nanosized conjugated macrocycles with shape-persistent, noncollapsible, and fully π-conjugated backbones are mentioned, while concentrating on new applications of these unique molecules.

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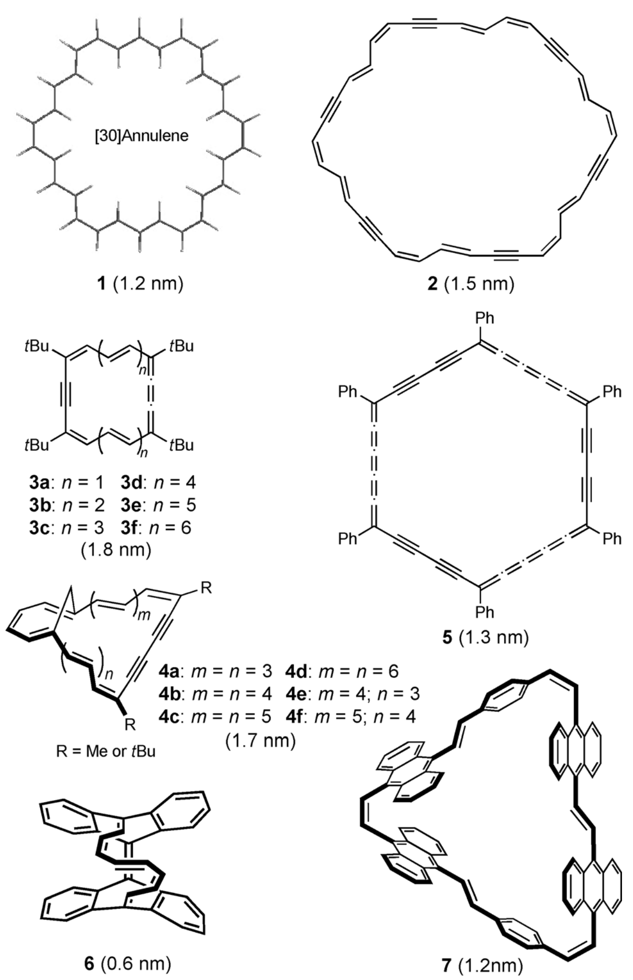
2. Macrocyclic Annulenes

2.1. Annulenes and Dehydroannulenes

The name "annulenes" describes fully conjugated cyclic polyenes with the ring size indicated by a number in brackets. Annulenes and dehydroannulenes are categorized as one group and have been comprehensively reviewed to date.[1,2] The fusion of benzenoid rings with annulene rings forms benzoannulenes. Although incorporation of arene moieties into the cyclic structure enhances bond localization and decreases its tropicity, benzoannulenes and dehydrobenzoannulenes have received considerable recent interest because of their potential applications as optoelectronic, liquid-crystalline, and sensing materials.[3–5] Sondheimer et al. synthesized unstable and the largest unsubstituted annulene and dehydroannulene [30]annulene **1** (Figure 1) and dodecadehydro[36]annulene **2**.[12] The large unsaturated macrocycles **1** and **2** are conformationally flexible, and no ring currents were observed by ^{1}H NMR spectroscopy. There are three reported systems **3a**–**f**, **4a**–**f**, and **5** concerning the ring current effect of macrocyclic annulenes.[13–15] Interestingly, [34]annulene **4c** is aromatic, whereas [38]annulene **4d** does not show any aromatic ring current effects. In contrast, [28]annulene **4e** is paratropic, whereas [32]annulene **4f** is atropic.[14] Furthermore, the D_{6h}-symmetric [30]annulene **5** shows a large diatropic ring current, despite its stability.[15] Quite recently, [36]annulene derivative **7** composed of anthrylene, phenylene, and ethylene units was reported.[16a] Although bianthraquinodimethane-modified [16]annulene **6** shows Möbius aromaticity,[16b] **7** exhibits no tropicity.

Mitchell and co-workers synthesized a large number of dimethyldihydropyrenes (DMDHPs) and investigated the use of these benzoannulenes as aromaticity probes.[2a] Mitchell et al. recently reported photochromic switches based on benzannelated DMDHPs.[18] As shown in Figure 2, **8** converts into **9** upon irradiation with light ($\lambda = 300$ nm) at −90 °C, and **9** thermally reverts back to **8** at −50 °C. Furthermore, **10** is a novel multistate π switch.



1 (1.2 nm)

2 (1.5 nm)

3a: $n = 1$ **3d**: $n = 4$
3b: $n = 2$ **3e**: $n = 5$
3c: $n = 3$ **3f**: $n = 6$
(1.8 nm)

5 (1.3 nm)

4a: $m = n = 3$ **4d**: $m = n = 6$
4b: $m = n = 4$ **4e**: $m = 4$; $n = 3$
4c: $m = n = 5$ **4f**: $m = 5$; $n = 4$
(1.7 nm)
R = Me or tBu

6 (0.6 nm)

7 (1.2nm)

Figure 1. Macrocyclic annulenes and dehydroannulenes **1**–**7**. The maximum distances between ring carbon atoms in **1**–**7** are shown in parentheses.[17]

Iyoda, Kuwatani, and co-workers synthesized several concave benzoannulene systems with alternating arene and alkene functionalities for use as either precursors or prototypes of aromatic belts.[19] The smallest benzo[12]annulene **11** was synthesized independently by the Iyoda and Vollhardt research groups.[20] The synthesis of **11** was improved, and it can now be prepared on a gram scale.[21] Furthermore, the new synthetic route could be used to prepare higher benzoannulenes **12**–**14** (Figure 3).[19,22a] Interestingly, X-ray analysis of benzo[24]annulene **14** showed that it adopts C_3 conformation **14a** with three CH–π interactions, and the triangular arrangement of three benzene rings in **14a** (a: 4.70 Å; b: 4.59 Å; c:

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Jun Yamakawa studied chemistry at Tokyo Metropolitan University (BS 2006, MS 2008). He is currently carrying out PhD research at the same university, focusing on supramolecular nanostructures based on π-conjugated molecules. He was selected as a Research Fellow of the Japan Society for the Promotion of Science (JSPS) in 2009.

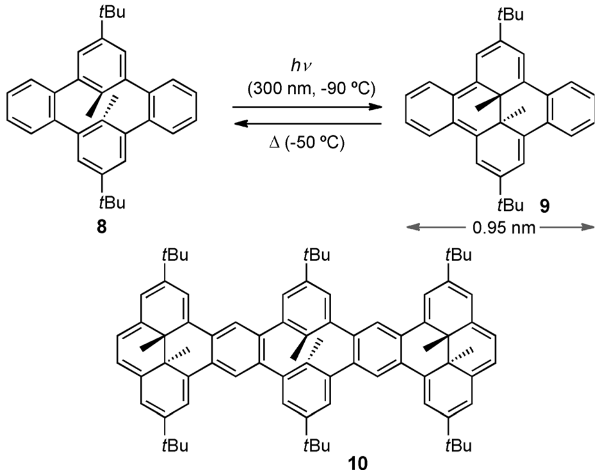


Figure 2. Photochromic switches **8–10**.[17]

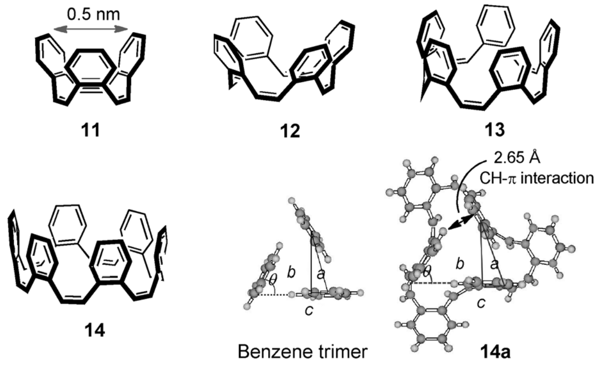


Figure 3. The all-*Z*-configured [*n*]benzo[4*n*]annulenes **11–14** and a model of the benzene trimer in the gas phase. The interatomic distances in **11** and **14a** were determined by X-ray analysis.

0.99 Å; θ: 61.1°) is consistent with the benzene trimer in the gas phase (*a*: 4.70 Å; *b*: 4.55 Å; *c*: 1.16 Å; θ: 61.0°).[22]

2.3. Cyclocarbons and π-Expanded Radialene Macrocycles

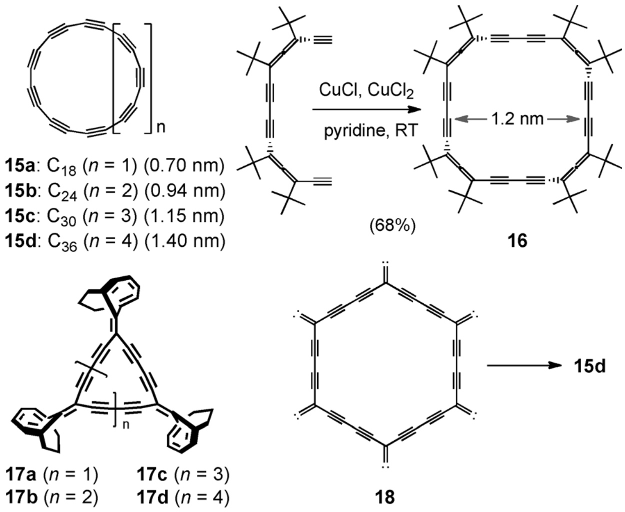


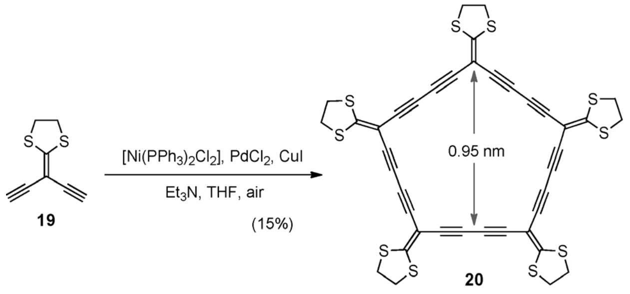
Figure 4. Cyclic hydrocarbons **15a–d** and allenoacetylenic macrocycle **16**. **17a–d** can produce **15a–d** via **18**. The distances between ring carbon atoms in **15a–30d** are shown in brackets.[17]

Monocyclic carbon clusters, known as cyclo[*n*]carbons (**15**; Figure 4), have attracted considerable attention owing to their key role in the formation of carbon cages and completely dehydrogenated annulene frameworks as well as their possible use as interstellar materials.[23] On the other hand, the chiral nanosized macrocycle **16** shows remarkably large Cotton effects.[24] Expanded radialenes are cyclic compounds formed by the insertion of an unsaturated spacer between each pair of *exo*-methylene fragments in the cyclic framework of a radialene.[25] Expanded radialenes **17a–d** containing bicyclo[4.3.1]deca-1,3,5-triene units were designed as new precursors for large-ring cyclo[*n*]carbons.[26] For example, the extrusion of an aromatic fragment (indane) from **17d** should produce the corresponding vinylidene **18**, which would then isomerize to the corresponding cyclocarbon **15d**.

M. Jalilur Rahman studied at Jahangirnagar University, Bangladesh and became a Lecturer at Shahjalal University of Science and Technology in 2001. In 2003 he began PhD research at Tokyo Metropolitan University with Prof. Masahiko Iyoda. After completion of his PhD in 2007, he returned to Shahjalal University of Science and Technology and was promoted to Associate Professor in 2008. His current research interests involve the synthesis and applications of functional π-electron systems.

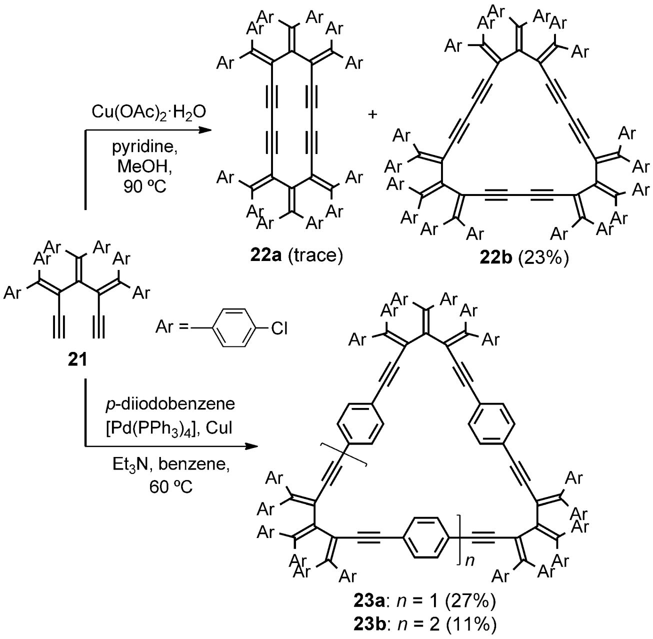
Expanded radialenes were originally prepared by Boldi and Diederich in 1994 by insertion of a diacetylene moiety into the radialene framework.[27a] This class of compounds has been extended by insertion of acetylene and diacetylene linkers[27b–d] as well as aryl moieties[28] into the radialene core. We summarize in the following recent examples of π-expanded radialenes.

The UV/Vis absorption maxima of [3]- and [4]radialenes are at longer wavelength than those of [5]- and [6]radialenes.[29] However, no remarkable functional properties of nanosized expanded radialenes have been reported to date. The expanded 1,3-dithiolan[5]radialene **20**, the first heteroatom-substituted expanded radialene, was reported by Zhang and co-workers.[27d] This radialene was synthesized by means of an oxidative coupling of α-enediyne **19** with [Ni(PPh$_3$)$_2$Cl$_2$]/PdCl$_2$/CuI in a one-pot procedure (Scheme 1). X-ray analysis of a single crystal of **20** obtained from DMSO/acetone showed it to have a nonplanar, envelope-like conformation with a DMSO molecule in its cavity. Moreover, the presence of a strong electron-donating alkylthio group results in **20** showing strong intramolecular push–pull interactions and enhanced macrocyclic cross-conjugation.



Scheme 1. One-step synthesis of alkylthiolated [5]radialene **20**.

Iyoda et al. reported the synthesis of expanded [9]- and [12]radialenes **22** and **23** by homo- or cross-coupling of the acetylene units of bis(ethynyl)[3]dendralene **21** (Scheme 2).[28] The reaction of **21** under Eglinton–Glaser conditions afforded the corresponding trimer **22b** with a trace amount of cyclic dimer **22a**. Expanded radialenes **23a** and **23b** with acetylene–phenylene spacers were obtained from **21** by Sonogashira coupling with *p*-diiodobenzene. Radialene **22b** containing a small inner cavity (2.6 Å) produced a silver complex with $AgOCOCF_3$ or $AgClO_4$, as characterized by ^{1}H NMR spectroscopy and TOF-MS. Macrocycles **23a** and **23b** with large inner cavities (ca. 5.4 and 9.1 Å, respectively) formed no such complexes with silver salts.



Scheme 2. Synthesis of expanded radialenes **22** and **23**.

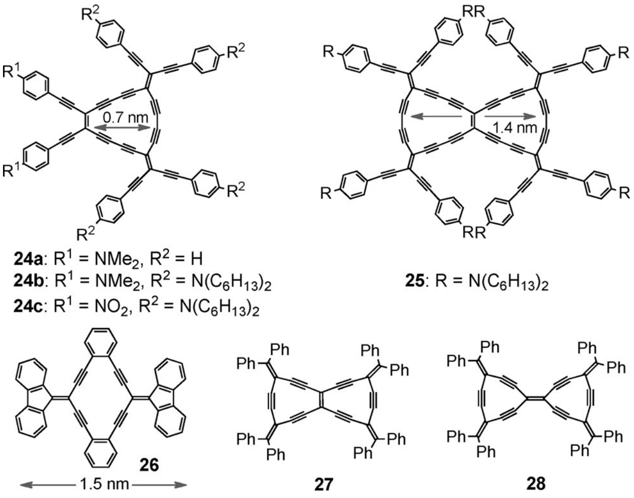


Figure 5. Radiaannulenes **24** and **26**, bisradiaannulenes **25** and **27**, and bisradialene **28**.[17]

Hybrids of dehydroannulenes and expanded radialenes were christened radiaannulenes. Mono- and bicyclic expanded radiaannulenes **24**–**28** were synthesized by homo- and cross-coupling of terminal acetylenic groups (Figure 5).[30] Although limited optical and electronic properties of expanded radialenes were elucidated, radiaannulenes were reported to exhibit novel electronic behavior because of the electron-accepting power of the acetylenic cores. Thus, the peripheral electron-donor groups in **24** result in intense intramolecular charge-transfer (CT) absorptions. Bicyclic radiaannulene **25** exhibits a remarkably low first reduction potential, which means it is a good electron acceptor. The electronic absorption spectrum of **25** showed an unusually strong intramolecular CT absorption with an end absorption at approximately 850 nm (1.46 eV), which is the lowest energy end absorption known for any tetraethynylethylene oligomer.[30a] Radiaanulene **26** and bisradiaanulene **27** show an intermediate state between linearly conjugated dehydroannulenes and cross-conjugated radialenes;[30b,c] both conditions are redox active.

3. Cyclic Phenylene Macrocycles

3.1. Cyclic Oligophenylenes

Cyclic oligophenylenes have attracted considerable attention from theoretical and experimental chemists owing to their thermal, light, and air stability, unique structures, aromaticity, π–π interactions, optoelectronic properties, and ability to act as a host in host–guest chemistry. Furthermore, the self-assembly of oligophenylene macrocycles and formation of nanostructures through the use of π–π interactions as a driving force have been reported. Cyclic phenylenes are classified into *o*-, *m*-, and *p*-phenylenes (Figure 6). *o*-Tetraphenylene **29a** and its derivatives have been investigated extensively as a consequence of their applications in molecular devices, as supramolecular scaffolds, chiral sources, and liquid crystals.[31] [*n*]Cycloparaphenylenes (CPPs) **31** have received much attention because of their belt-shaped structure, concave–convex π–π interactions, and 3D conjugation, similar to fullerenes and carbon nanotubes.[32a] Quite recently, the research groups of Bertozzi,[33] Itami,[34] and Yamago[35] independently synthesized **31a**–**g**.

Bertozzi and co-workers reported the first synthesis of [9]-, [12]-, and [18]CPPs **31b,c,g** (Scheme 3).[33] The key to

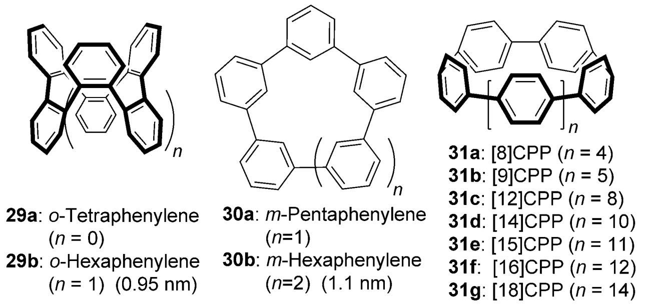
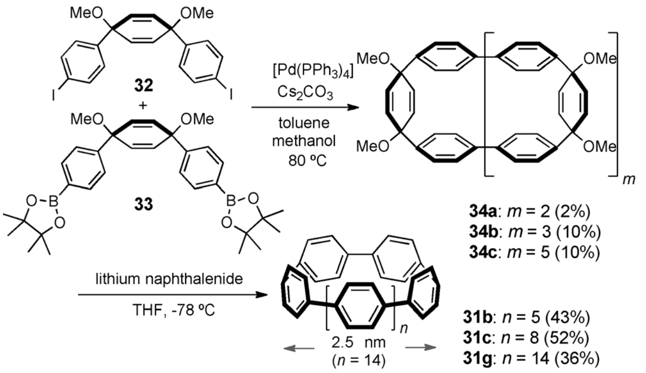
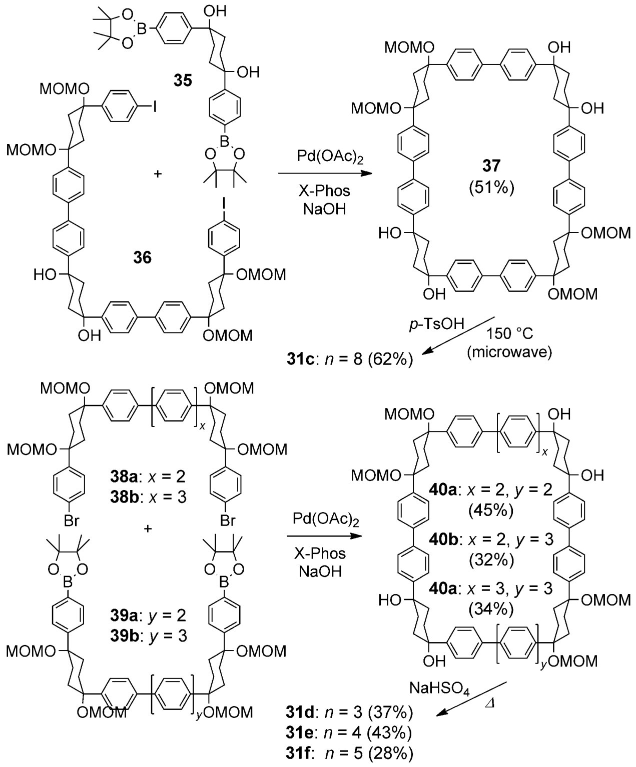


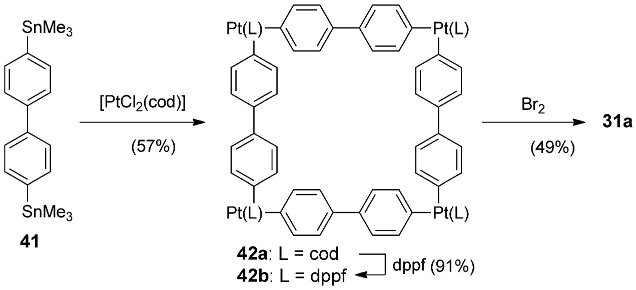
Figure 6. Cyclic oligophenylenes **29**–**31**. The maximum distances between phenylene carbon atoms in **29b** and **30b** are shown in brackets.[17]



Scheme 3. Synthesis of [9]-, [12]-, and [18]CPPs **31b**,**c**,**g**.[17]



Scheme 4. Synthesis of [12]-, [14]-, [15]-, and [16]CPPs **31c**–**f**. MOM = methoxymethyl.



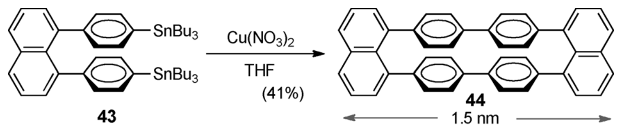
Scheme 5. Synthesis of [8]CPP **31a**. cod = cyclooctadiene, dppf = 1,1′-bis(diphenylphosphanyl)ferrocene.

constructing strained paraphenylene molecules lies in the use of a 3,6-*syn*-dimethoxycyclohexa-1,4-diene moiety as a masked aromatic ring in the macrocyclic intermediate. Macrocyclization was carried out by a Suzuki cross-coupling of **32** with **33** to afford **34a**–**c**. Subsequent aromatization with lithium napthalenide produced CPPs **31b**,**c**,**g**. The strain energies of **31b**,**c**,**g** were estimated theoretically to be 47, 28, and 5 kcal mol^{-1}, respectively. In general, the absorption maxima of linear paraphenylenes are red-shifted when the conjugation is extended by increasing the number of phenylene units.[32b] However, when the fluorescence spectra of **31b**,**c**,**g** are compared with each other, the emission maximum of the smallest macrocycle **31b** has the longest wavelength. Furthermore, **31b** exhibits the most significant Stokes shift.

Itami and co-workers reported a modular and size-selective synthesis of [12]-, [14]-, [15]-, and [16]CPPs **31c**–**f** (Scheme 4).[34] The synthesis of **31c**–**f** capitalizes on the ability of the *cis*-1,4-dihydroxycyclohexane-1,4-diyl unit to attenuate the build-up of strain energy during macrocyclization and exploits its ability to be converted into benzene. Suzuki cross-coupling of dihalides with diboronic acids gave the precursors **37** and **40** of target molecules **31c**–**f**. The conversion of **37** and **40** into [12]-, [14]-, [15]-, and [16]CPPs **31c**–**f** was carried out in moderate yields by treatment with acid.

Yamago et al. synthesized [8]CPP **31a** (Scheme 5) in 25% overall yield from 4,4′-bis(trimethylstannyl)biphenyl **41** via formation of the square platinum complexes **42a** and **42b**.[35] Reductive elimination of platinum complex **42b**, which induces no marked strain, afforded **31a**. Interestingly, **31a** has an absorption maximum at 340 nm, which is similar to that of [9]CPP **31b**, and a fluorescence emission at approximately 540 nm. This Stokes shift is larger than that of [9]CPP **31b**.

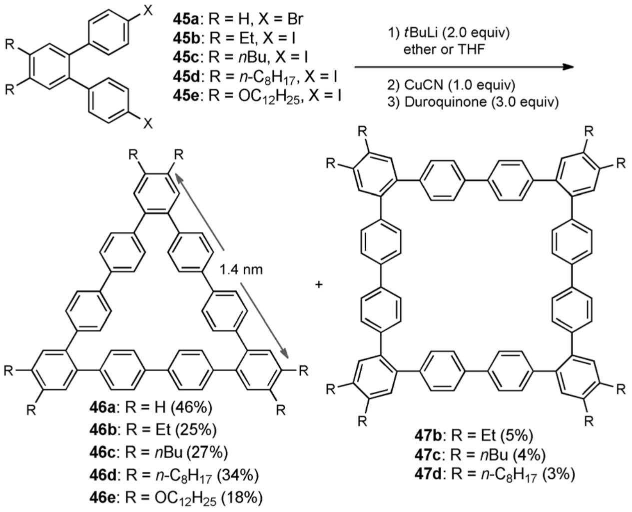
Cyclic oligophenylenes with stacked benzene rings are called cyclophanes.[36] The strong π–π interactions in cyclophane **44** results in it being thermally, light, and air stable despite its high HOMO and low LUMO levels (Scheme 6).[37] The synthesis of **44** was carried out in moderate yields by a simple copper-mediated coupling of tributyltin(IV) derivative **43** under mild conditions.[38] Although strained cyclophanes are π acids and can be reduced chemically and electrochemically to produce the corresponding radical anions and dianions,[36c] **44** behaves as a π base and forms a CT complex with TCNE ($\lambda_{max} = 638$ nm) and DDQ ($\lambda_{max} = 790$ nm) in



Scheme 6. Synthesis of cyclic oligophenylene **44** composed of two 1,8-naphthalene units bridged by biphenyl linkages.[17]

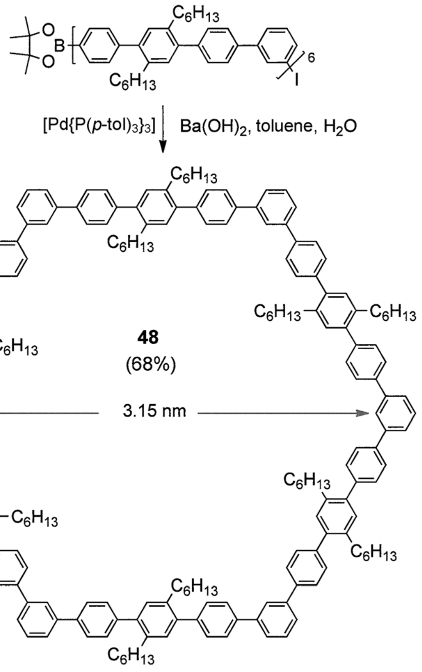
CH_2Cl_2. In other words, the oxidation potential of **44**, determined by cyclic voltammetry, is fairly low ($E^{ox1}_{1/2}$ = 0.85 V versus Fc/Fc$^+$; Fc = ferrocene), whereas open-chain oligomers show no oxidation peak under similar conditions.

Transition-metal-mediated coupling of aryl halides is frequently employed for the synthesis of cyclic oligophenylenes. In many cases, however, the target macrocycles can be prepared only in low yields because of the formation of linear oligomers as side products, which require additional separation. Iyoda and co-workers have developed a new method for preparing cyclic oligophenylenes by using electron-transfer (ET) oxidation of Lipshutz cuprates (Scheme 7).[38,39] Nonaphenylene **46a** was first synthesized by Meyer and Staab (1969) in very low yield (0.97 %) by the $CuCl_2$-mediated coupling of a Grignard derivative of 4,4″-dibromo-*o*-terphenyl.[40] Fujioka also obtained **46a** in 4.5 % yield as a by-product in the synthesis of hexaphenylene (16 %) by a $CuCl_2$-mediated cross-coupling of the Grignard derivatives of 4,4″-dibromo-*o*-terphenyl and 2,2″-dibromo-*p*-terphenyl.[41] The ET oxidation of the corresponding Lipshutz cuprate, however, resulted in **46a** being obtained in 46 % yield.[42] Furthermore, hexaalkylnonaphenylenes **46b–d** and hexadodecyloxynonaphenylene **46e** were synthesized in moderate yields with small amounts of octaalkyldodecaphenylenes **47b–d**. Since only small amounts of linear oligomeric by-products are produced by the ET oxidation of Lipshutz cuprates, the isolation of **46a–e** and **47b–d** is rather simple.



Scheme 7. Synthesis of **46** and **47** by ET oxidation of Lipshutz cuprates.[17]

Grave and Schlüter used Suzuki cross-coupling reactions in the synthesis of large macrocyclic oligophenylenes.[11b] The synthesis of 90-membered macrocycle **48** composed of 24 phenylene units was also achieved by using an intramolecular Suzuki cross-coupling reaction (Scheme 8).[43] High-dilution conditions were applied to produce **48** in good yield (68 %).



Scheme 8. Synthesis of giant macrocycle **48**.[17]

One of the most interesting properties of macrocyclic oligophenylenes is the polymorphism of nonaphenylene **46e**, which has long alkoxy chains and forms different nanostructured films on surfaces as well as fibrous materials from solution.[42b,44] A film of **46e** had a lamellar structure rising at 50° diagonally from the surface and could be employed to detect explosives, such as 1,3-dinitrobenzene (DNB) and 2,4-dinitrotoluene (DNT) by fluorescence quenching. On the other hand, fibers of **46e** obtained from diisopropyl ether/methanol exhibit strong anisotropic fluorescence ($\Phi_F = 53\,\%$) as a consequence of its "Lego-like" interlocking structure (Figure 7). The stacking direction of **46e** is parallel to the direction of the fiber.[42b]

3.2. Cyclacenes, Cyclophenacenes, and Related Compounds

The synthesis of belt-shaped π-conjugated molecules, such as cyclacenes **49**, cyclophenacenes **50**, and related compounds, have attracted attention, although **49** and **50** have not yet been synthesized.[45] Recently, fully conjugated rigid belt-shaped molecules **52** and **54** were synthesized by Gleiter and co-workers (Scheme 9).[46,47] Cyclotrimerization of **51** with $[CpCo(CO)_2]$ under photoirradiation afforded **52** in 14 % yield,[46b] whereas an intramolecular McMurry coupling of **53** afforded **54** in 8 % yield.[46c] X-ray analysis of **52** and **54**

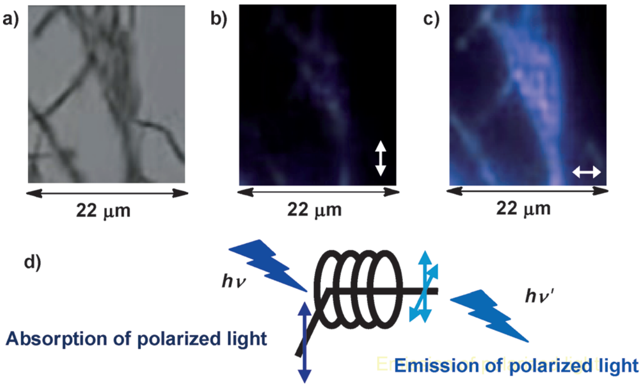
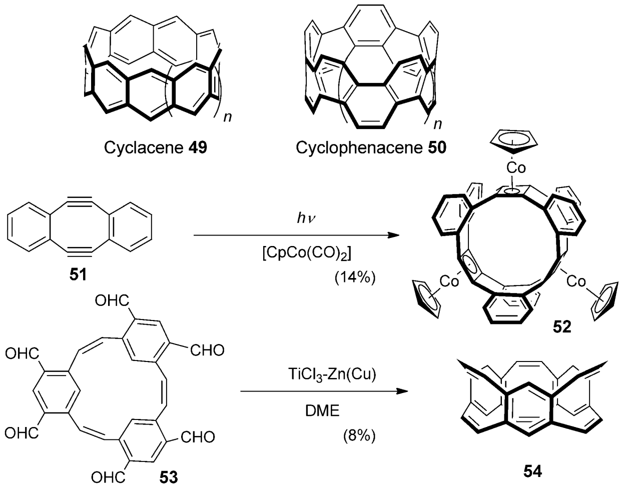


Figure 7. a) Transmission microscopy image of fibers of **46e** on a glass plate. b,c) Fluorescence images of the sample irradiated with linearly polarized UV light ($\lambda = 355$ nm). The double-headed arrows show the directions of polarization. d) Excitation with polarized light (dark blue arrow) and corresponding spontaneous emission (light blue arrow).



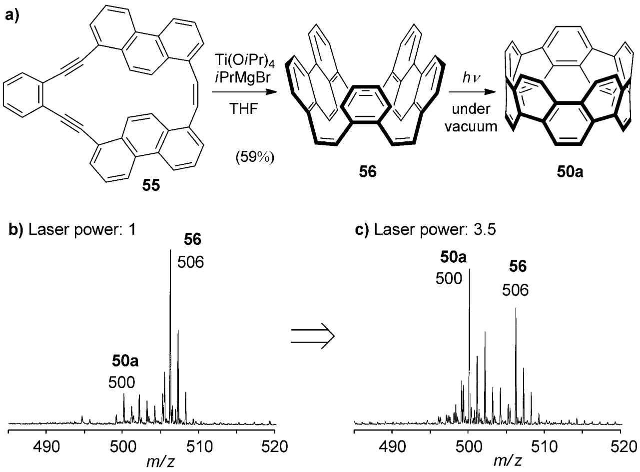
Scheme 9. Belt-shaped molecules **49**, **50**, **52**, and **54**. Cp = cyclopentadienyl, DME = dimethoxyethane.

showed unique cyclic structures, although the cavities of these molecules are too small to include any guest molecules.

In the case of cyclophenacenes, the all-*Z*-configured cyclophanetriene **56** was synthesized as a precursor for cyclo[10]phenacene **50a**. X-ray analysis shows **56** has a rigid cage structure, and the interatomic distances between the phenanthrene carbon atoms are in the range 3.28–7.28 Å, whereas the closest interatomic distances between phenanthrene and benzene carbon atoms are 3.45 and 3.51 Å. Although photochemical cyclization of **56** was unsuccessful, signals corresponding to **50a** were observed in the LD-TOF mass spectrum of **56** (Scheme 10).[19b]

4. Phenylene-Ethynylene Macrocycles

Phenylene-ethynylene macrocycles usually adopt shape-persistent, noncollapsible structures because of their rigid π frames comprised of acetylene and benzene. Recent developments in the methods to access phenylene-ethynylene macrocycles have enabled synthetic chemists and materials scientists to design and construct complex molecules with unique functions and novel properties. Therefore, these macrocycles have been used to prepare various supramolecular aggregates, including 3D nanostructures, discotic liquid crystals, extended tubular channels, host–guest complexes, and porous organic solids, and have found use in molecular machines. The fusion of benzenoid rings to conjugated macrocycle frames produces three types of cyclic phenylene-ethynylenes: *ortho*-cycle **57**, *meta*-cycle **58**, and *para*-cycle **59** (Figure 8). The *ortho*-cycle **57** and *para*-cycle **59** form a fully conjugated system, whereas *meta*-cycle **58** consists of cross-conjugated benzene units.



Scheme 10. Synthesis of *all-Z*-configured cyclophanetriene **56** and its conversion into cyclo[10]phenacene **50a** through LD-TOF-MS. a) Synthetic route to **50a**. b) LD-TOF-MS of **56** at a laser power of 1. c) LD-TOF-MS of **56** at a laser power of 3.5.

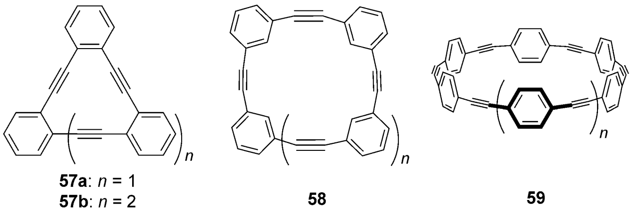


Figure 8. *ortho*-Cycle **57**, *meta*-cycle **58**, and *para*-cycle **59**.

4.1. ortho-Phenylene-Ethynylene Macrocycles

Fully conjugated *ortho*-phenylene-ethynylene macrocycles are known as dehydrobenzoannulenes (DBAs).[48] Macrocycles composed of [12]-, [14]-, and [18]annulene rings have been vigorously investigated because of their optoelectronic properties and aromaticity, and also because of their potential as substructures of the 2D carbon networks graphyne and graphdiyne.[49] Quite recently, semiconducting graphdiyne films have been reported.[49b] Larger DBAs are nonplanar due to ring strain, and they have been investigated from the viewpoints of their structure–property relationship, chirality for twisted π systems, and molecular dynamics.

Various transition-metal-mediated coupling reactions (such as the Sonogashira reaction and Glaser, Hay, and Eglington coupling reactions, the Heck reaction, Negishi, Stille, and Suzuki coupling reactions, McMurry coupling, and metathesis) have been utilized to produce *ortho*-fused conjugated macrocycles such as **57**.[2e] C_3-Symmetric [12]DBA **57a** is a versatile building block, and many research groups have employed it to create new materials.[50–52] The amphiphilic compound **60a** with polar ethylene oxide side chains spontaneously self-assembled into vesicles upon exposure of a $CHCl_3$ solution to water (Figure 9).[50] The self-assembly of disklike **60b**, with three carboxy groups at the periphery, into spherical vesicles represents a new molecular architecture for the formation of vesicles.[51] Interestingly, flash photolysis time-resolved microwave conductivity (FP-TRMC) experiments on a single crystal of **60b**·3DMSO showed it had significant anisotropic charge mobility ($\Sigma_{\mu} = 1.5 \times 10^{-1}\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$) along the columnar axis.[52]

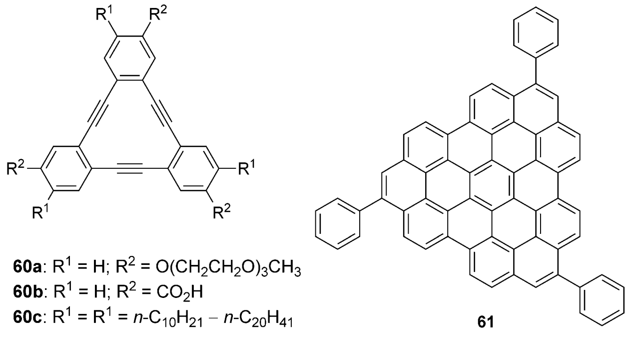
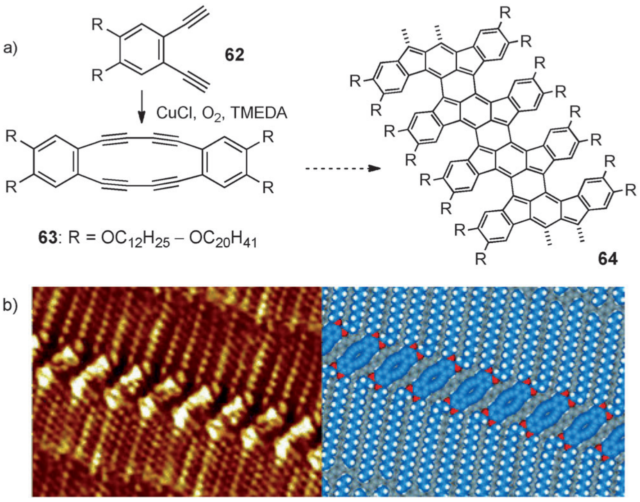


Figure 9. Hexasubstituted [12]DBA derivatives **60** and nanographene **61**.

Tahara, Lei, De Feyter, and Tobe have reported 2D surface-confined nanoporous molecular networks.[53] The self-assembly of **60** with long alkoxy chains was analyzed by STM at the liquid–solid interface. The 2D porous molecular networks of **60** formed by interdigitation of the alkoxy chains.[53a] Furthermore, in the presence of nanographene guest **61**, **60** converted from guest-free, densely packed linear-type patterns into guest-containing 2D porous honeycomb-type patterns.[53b]

Octadehydrodibenzo[12]annulenes **63** were synthesized by copper-mediated coupling of **62** (Scheme 11a).[54] Tahara, Tobe et al. recently reported that **63** formed self-assembled monolayers (Scheme 11b).[54] The structure of the 2D networks of **63** depended on the length of the alkyl chain, and incorporation of a C_{18} alkyl chain length led to the chains aligning in a parallel fashion to form a lamellar structure. Although the closest interatomic distance between the diacetylenic units of **63** ($R = OC_{18}H_{37}$) is only slightly greater than the typical distances necessary for topochemical polymerization to produce **64**, no evidence for polymerization on the surface was observed.



Scheme 11. a) Preparation of **63** by Hay coupling of **62**. b) STM image of a 2D molecular network of **63** ($R = OC_{18}H_{37}$) and a tentative network model of the lamellar structure (adapted from Ref. [54]). TMEDA = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine.

In the case of bicyclic DBAs (Figure 10), bow-tie-shaped **65a** composed of two 12-membered macrocycles fused to a central arene core was first isolated by Haley and co-workers in a low overall yield (4%).[55] In 2003, Vollhardt and co-workers reported the synthesis of **65a** in 6% yield by using a sixfold intermolecular methathesis reaction with only three steps.[56] However, as a consequence of solubility problems, the properties of **65a** were not determined. Iyoda et al. synthesized octabutyl-substituted **65b** by copper-mediated cross-coupling in the presence of PPh_3 (1%).[57] Compound **65b** exhibited a strong emission with $\Phi_F = 0.21$ and an associated Stokes shift of 190 nm. Diamond-shaped **66** and trefoil **67** also have a graphyne network (Figure 10).[55,58] Although some of the photophysical properties of **66a–c** have been predicted theoretically,[59] the most interesting is the two-photon absorption (TPA) properties of **67**.[60] Trefoil **67** showed the most intense TPA of the hexaarylethynylben-

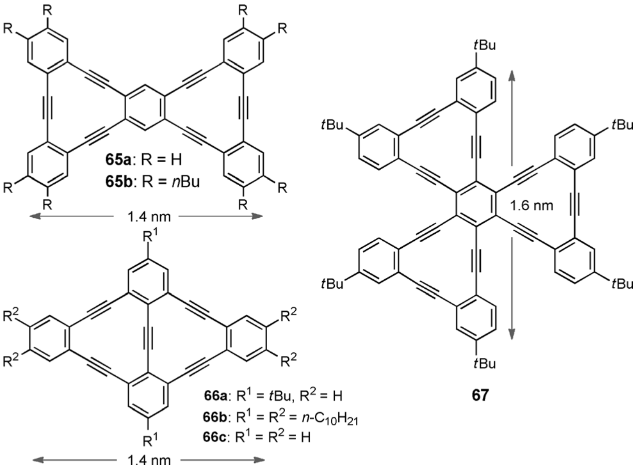


Figure 10. Fused dehydrobenzo[12]annulenes **65**, **66**, and **67**.[17]

zenes and related annulenes, with a maximum TPA cross-section of 1300 GM at 572 nm.

A large number of dehydrobenzo[14]annulenes, such as **68**–**71** (Figure 11), and dehydrobenzo[16]annulenes **72** and **73** were prepared to study the aromaticity (diatropicity and paratropicity), CT absorptions of donor-acceptor systems, structure–property correlations of organometallic aggregates, and new topologies in relation to new properties. Since previous reviews summarized these topics in detail,[1f,2e] we only present a few of their structures.

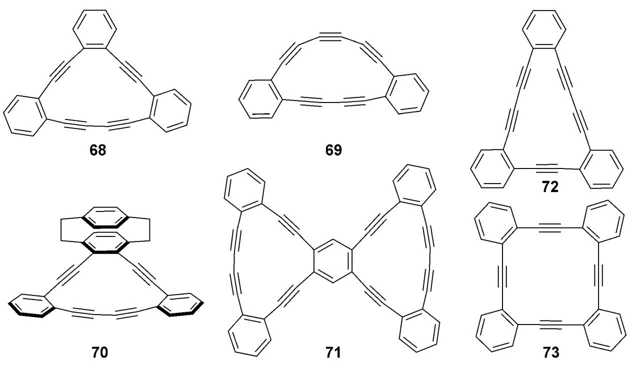


Figure 11. Examples of dehydrobenzo[12]annulenes **68**–**71** and dehydrobenzo[16]annulenes **72** and **73**.

The synthesis and TPA cross-sections of expanded graphdiyne substructures **74**–**78** were investigated by Haley, Goodson, and co-workers (Figure 12).[61,62] These multiannulene systems were synthesized by a stepwise route involving a final intramolecular cyclization of suitable α,ω-polyyenes in the presence of copper reagents. The electronic absorptions of **74**–**78** suggested a strong dependence on the effective conjugation length of the subunits. Interestingly, measurements of the TPA cross-sections showed unprecedented enhancement as a result of delocalized excitons for tri- and tetraannulene systems.[62] Furthermore, entangled photons generated by spontaneous parametric down-conversion (SPDC) have been used to investigate entangled two-photon absorption (ETPA) in multiannulene systems. Recently, Haley and co-workers also reported the synthesis of annulenoannulene trefoils.[63]

4.2. meta-Fused Phenylene-Ethynylene Macrocycles

Macrocycles **79** (Figure 13) are representative structures of the general class of *m*-phenylene-ethynylene macrocycles. Since they have a shape-persistent flat structure and can be functionalized at both the interior and/or exterior of the macrocyclic framework, they have been studied extensively from many viewpoints over the past two decades, including the guest-binding ability of the internal binding site, construction of supramolecular structures through the peripheral functionalities, self-aggregation in solution, liquid-crystalline properties, and organization at various interfaces.[3b,64] For example, *m*-phenylene-ethynylene macrocycle **79b** formed a discotic nematic phase as well as a hexagonal phase with liquid-like fluctuations along the column direction. High-resolution X-ray diffraction studies revealed that **79b** formed tubular liquid crystals with a distortion and doubling of the underlying hexagonal lattice.[65] Doping of **79b** with a small amount of silver triflate resulted in the silver ions intercalating within the tubes, thereby providing a route to channel-conducting liquid crystals.

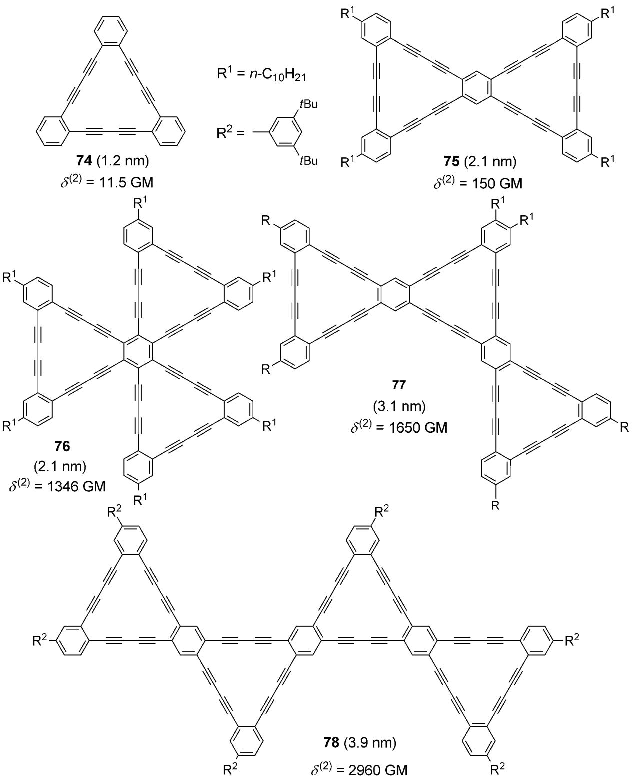
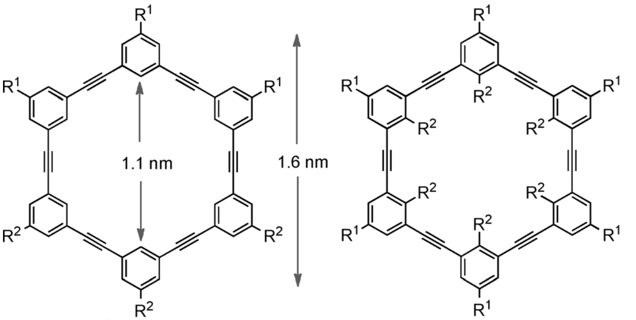


Figure 12. TPA cross-section ($\delta^{(2)}$) values of [18]DBA **74** and [18]DBA systems **75**–**78**. The maximum distances between the benzene carbon atoms in **74**–**78** are shown in parentheses.[17]



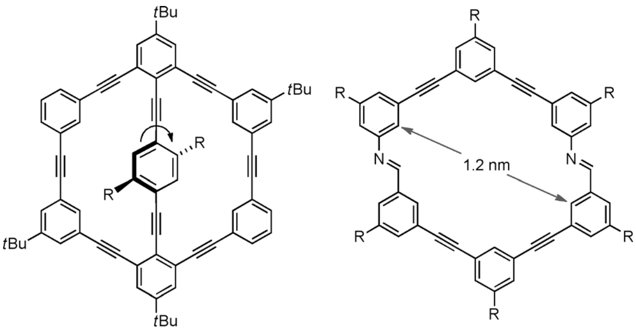
79a: $R^1 = R^2 = H$
79b: $R^1 = CO_2C_6H_{13}$, $R^2 = OC_6H_{13}$

80a: $R^1 = t$Bu, $R^2 = $ OMe
80b: $R^1 = $ N-nBu$_2$, $R^2 = $ O-nBu

Figure 13. *m*-Phenylene-ethynylene macrocycles **79** and **80** with interior binding sites.[17]

Kawase and co-workers reported the synthesis and ionophoric properties of **80a**, which has an interior binding site (Figure 13).[66] Macrocycle **80a** has a sizeable inner cavity of about 5 Å in diameter that is surrounded by six oxygen atoms and selectively coordinates to ammonium ions (2.86 Å). A similar functionalized macrocycle, **80b**, was synthesized by Cho and co-workers through a Sonogashira coupling reaction.[67a] The large Stokes shift observed in polar solvents indicates significant charge transfer in the excited state. The maximum value of the two-photon absorption cross-section at 800 nm was 125 GM.[67b]

An artificial "molecular machine" was designed and synthesized by Bedard and Moore (Figure 14). The central benzene ring of this "molecular turnstile" **81** underwent conformational motion in solution.[68a] In addition, Zhao and Moore synthesized imine-containing *m*-phenylene-ethynylene macrocycle **82** (Figure 14)[68c] by reversible imine metathesis, and it was found to self-aggregate in solution.[69]



81

82: R = $CO_2(CH_2CH_2O)_3CH_3$

Figure 14. Molecular turnstile **81** and diazamacrocycle **82**.

Yamaguchi and co-workers reported the synthesis and self-aggregation behavior of nonplanar chiral macrocycles **83** ($n = 1$–6) (Figure 15).[70] The smaller cycloalkynes **83** with $n =$ 1–5 have rigid structures, whereas the $n = 6$ cycloalkyne **83** has a flexible structure.[70a] Furthermore, chiral cycloalkyne **83a** self-aggregated in chloroform and benzene to afford dimers: When the concentration was greater than 2 mm, (*M*,*M*,*M*)-**83a** formed a dimer in solution, whereas (*M*,*P*,*M*)-**83a** only formed a dimer when the concentration was greater than 15 mm.[70b]

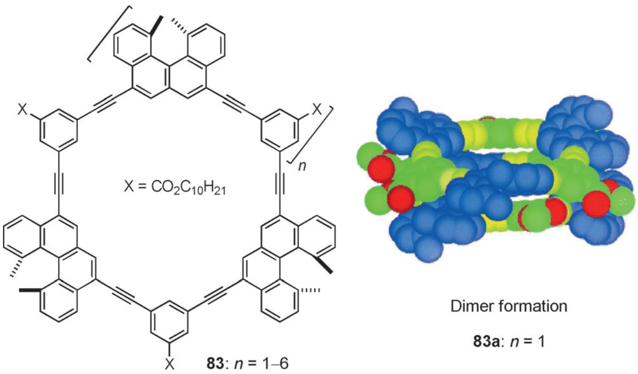
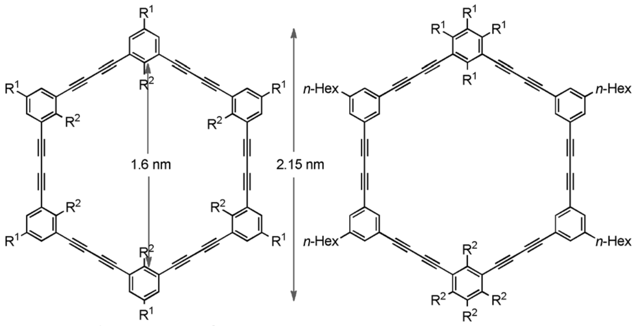


Figure 15. Macrocyclic ethynylhelicene oligomers **83** ($n = 1$–6; adapted from Ref. [70b]).

Various shape-persistent *m*-phenylene-diethynylene macrocycles were synthesized by Tobe and co-workers by intermolecular oxidative coupling of dimer units or intramolecular cyclization of the corresponding open-chain oligomers under Eglinton conditions.[64] Interestingly, **84b** with interior cyano substituents did not self-aggregate, as a result of electrostatic repulsion between the nitrogen atoms of the cyano groups and the nonplanarity of the macrocyclic framework (Figure 16).[71] However, **84b** formed heteroaggregates with **84a** in $CDCl_3$ and afforded 2:1 host–guest complexes with tropylium and guanidinium cations in $CDCl_3/CD_3CN$.



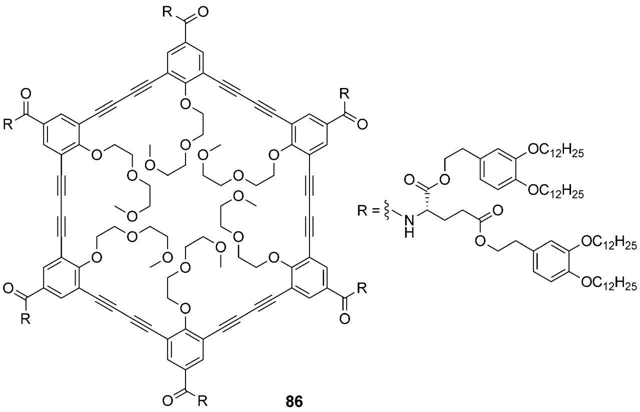
84a: $R^1 = CO_2C_8H_{17}$, $R^2 = H$
84b: $R^1 = CO_2C_8H_{17}$, $R^2 = CN$

85a: $R^1 = H$, $R^2 = F$
85b: $R^1 = R^2 = F$

Figure 16. Macrocycles **84** and **85** with interior substituents.[17]

Mayor and co-workers recently reported the synthesis, self-aggregation behavior, and formation of microrods of shape-persistent macrocycles containing perfluorinated benzene subunits (Figure 16).[72] Macrocycles **85** self-aggregated in solution to afford dimers as the major aggregates. Interestingly, macrocycle **85b** formed microscale hexagonal rods upon heating in toluene.

Recently, Kato and co-workers reported the columnar liquid-crystalline (LC) macrocycle **86**, which has a nanosegregated structure (Figure 17).[73] Macrocycle **86** formed a hexagonal columnar liquid-crystalline (LC) phase at ambient temperature through nanosegregation and formation of intermolecular hydrogen bonds. A 1D LC assembly of **86**



86

Figure 17. Macrocycles **86** with glutamic acid and oligooxyethylene moieties.

should be able to incorporate ions, and hence, it has the potential to act as an ion-conducting channel.

4.3. para-Fused Phenylene-Ethynylene Macrocycles

Cyclic [*n*]para-phenyleneacetylenes ([*n*]CPPAs) containing alternating 1,4-phenyleneacetylene units have attracted particular interest because of their belt-shaped rigid structures and well-defined cavities (Figure 18).[5a,74] The synthesis and complexation behavior of [*n*]CPPAs **87a–e** and their 2,6- and 1,4-naphthalene analogues **88–90** were reported by Kawase and Oda. These macrocycles, which are in essence carbon nanorings, were synthesized by intermolecular McMurry coupling of diformylstilbene or related formyl-substituted arylene-ethylene precursors, followed by bromination/dehydrobromination reactions. Recrystallization of [6]CPPA **87b** from dichloromethane/hexane containing excess amounts of hexamethylbenzene (HMB) afforded the 1:1 inclusion complex **87b**·HMB as distorted hexagonal prisms.[75] In the crystals, the molecules aligned in a fairly smooth cylindrical structure with curved triple bonds and benzene rings bent in a boat conformation.

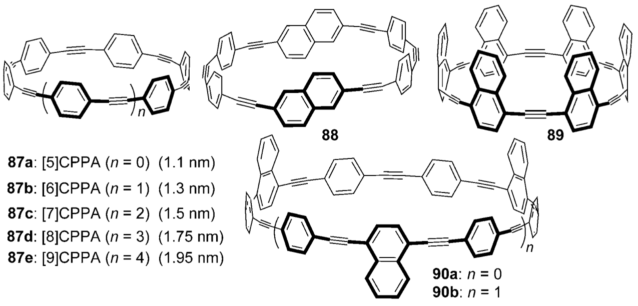


Figure 18. The [*n*]*para*-phenyleneacetylenes ([*n*]CPPAs) **87–90**. The distances between phenylene carbon atoms in **87a–e** are shown in brackets.[17]

Carbon nanorings with appropriate cavity sizes (1.3–1.4 nm) can form stable 1:1 inclusion complexes with the fullerenes C_{60}, C_{70}, and $C_{61}(COOEt)_2$ in solution as well as in the solid state.[76] The molecular structure of **87b**·$C_{61}(COOEt)_2$ indicated that concave–convex π–π interactions were operating between the host and guest molecules (Figure 19a). The intense fluorescence ($\Phi_f = 0.2$–0.5) of the CPPAs was quenched effectively by the guest fullerenes. An energy-transfer process from the host to the guest molecule can cause this fluorescence quenching. The Stern–Volmer constants (K_{sv} values) determined by fluorescence spectroscopy provided a reliable measure of the stability of the complexes. The K_{sv} values of fullerene (both C_{60} and C_{70}) complexes of **89** were much larger than other fullerene complexes, thus indicating a correlation between the stability of the complexes and the van der Waals contact between the host and the guest molecule.

The onion-type complexation behavior based on these carbon nanorings and C_{60} was also investigated. [9]CPPA **87e** and its tribenzo derivative **90b**, which have large diameters, formed inclusion complexes with [6]CPPA **87b** and its dibenzo derivative **90a**, respectively, in chloroform. Furthermore, each of these complexes formed double inclusion complexes with onion-type supramolecular structures in the presence of excess amounts of C_{60} (Figure 19b).

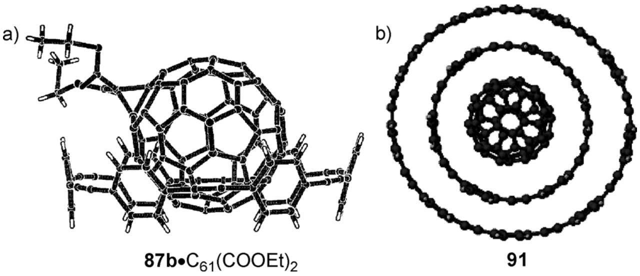
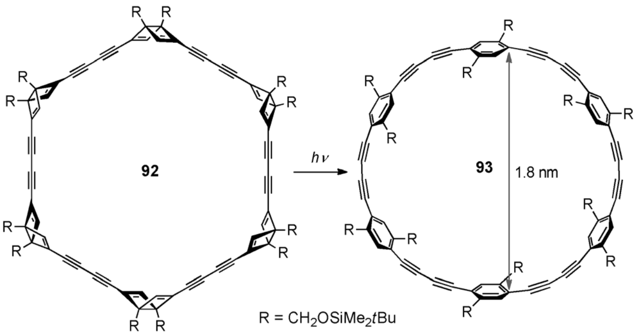


Figure 19. a) Crystal structure of **87b**·$C_{61}(COOEt)_2$. b) Onion-type complex **91** formed from **87e**·**87b**·C_{60} (adapted from Ref. [76a,b]).

Tsuji and co-workers reported the photochemical generation of belt-shaped [4_6]paracyclophanedodecayne **93** from the corresponding Dewar benzene precursor **92** (Scheme 12).[77] Macrocycle **93**, isolated as an air-sensitive pale-yellow solid, decomposed gradually within several days in solution or in the solid state at room temperature in air.

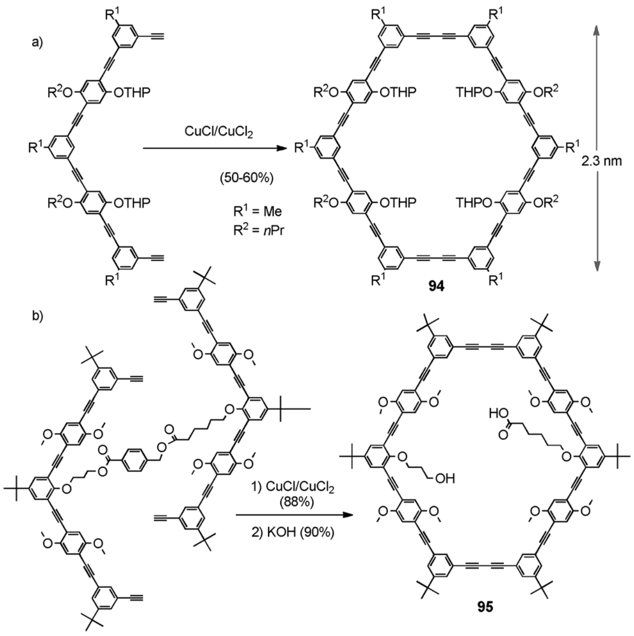


Scheme 12. Synthesis of **93** via a Dewar benzene intermediate.[17]

4.4. Mixed-Fused Phenylene-Ethynylene Macrocycles

Höger and co-workers reported a series of shape-persistent macrocycles with arylene-ethynylene backbones.[4b,11e] The macrocycles **94** and **95** were synthesized either by statistical or by template-supported oxidative Glaser coupling of rigid phenylene-ethynylene oligomers (“half-rings”) under pseudo-high-dilution conditions (Scheme 13). The use of a covalent template should make it possible to prepare nonsymmetrical macrocycles simply by using a nonsymmetrical template.

Höger’s shape-persistent macrocycles showed multifunctional properties, such as self-aggregation, incorporation of small molecules, liquid-crystalline behavior, and formation of ordered monolayers on highly oriented pyrolytic graphite (HOPG).[78] For example, macrocycle **96** with long flexible side arms adsorbed on HOPG to form 2D ordered self-assembled monolayers. In addition, it should be possible to



Scheme 13. Synthesis of macrocycles **94** and **95**. a) Statistical cyclization. b) Template-supported cyclization.[17]

incorporate functional groups in the interior of **96** to afford functionalized nanopatterned surfaces. In contrast, cationic shape-persistent macrocycle **97** was reported to form nanosized supramolecular dimers (Figure 20).[79,80]

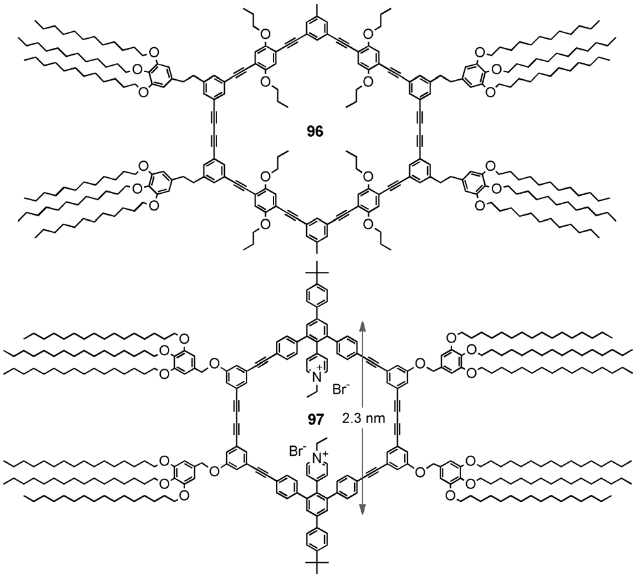


Figure 20. Shape-persistent **96** and **97** with flexible arms.[17]

The synthesis and complexation ability of optically active 1,1′-binaphthalene-derived macrocycles **98** and **99** with rectangular cavities linked by convergent phosphate and carboxy residues were reported by Diederich and co-workers (Figure 21).[81] Oxidative acetylenic homocoupling and palladium-catalyzed aryl–alkyne cross-coupling protocols were used to synthesize the cyclophanes. Macrocycles **98** and **99** can be used to recognize mono- and disaccharides through complexation.

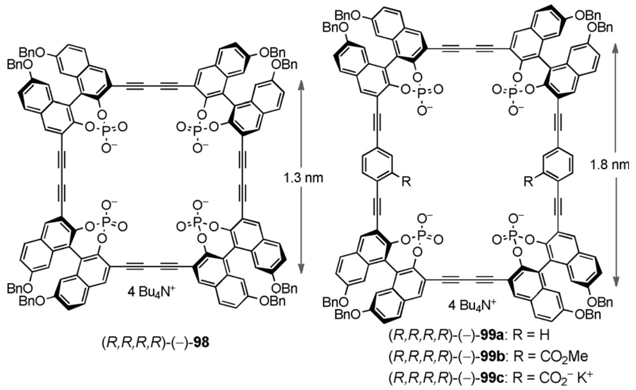


Figure 21. Optically active 1,1′-binaphthalene-fused macrocycles **98** and **99**.[17] Bn = benzyl.

Toyota and co-workers synthesized 3D π-conjugated cyclic 1,8-anthrylene-ethynylene oligomers **100a**,**b** by Sonogashira coupling (Figure 22).[82a] The same research group also reported the synthesis and enantiomeric separation of cyclic arylene-ethynylene tetramers **101** and **102**.[82b] The enantiomers of **101** and **102** were resolved by chiral HPLC, and their rotational barriers were determined to be 114 and greater than 146 kJ mol^{-1}, respectively.

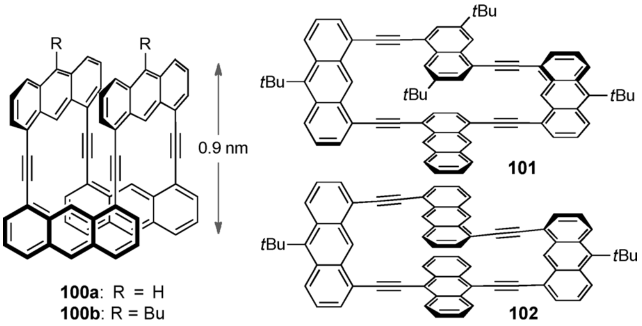
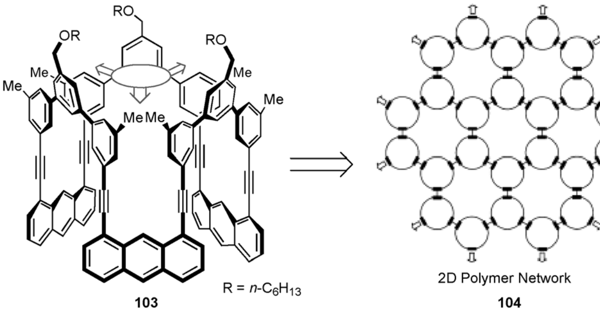


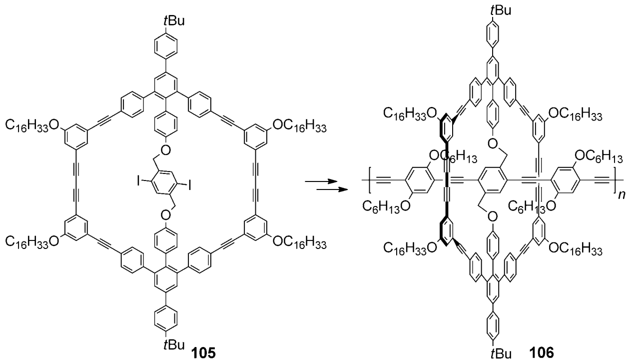
Figure 22. Cyclic 1,8-anthracene-ethynylene oligomers **100**–**102**.[17]

Macrocycle **103** with three C_{3v}-symmetrical 1,8-anthrylene units was designed as a monomer for the synthesis of 2D polymer **104** (Scheme 14).[83] Photochemical studies suggested that the macrocycle **103** had the potential to undergo UV-induced [4+4] cycloaddition at the anthracene unit without any undesired side reaction, thereby leading to the 2D polymer **104**.

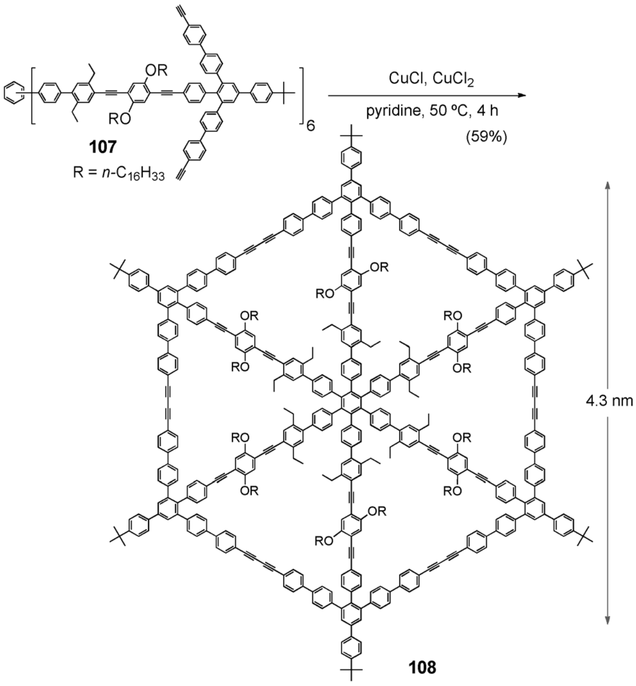
Höger and co-workers reported the accumulation of excitons with the macrocycle-encapsulated conjugated polymer **106** (Scheme 15).[84] Gel permeation chromatography (GPC) led to the number average molecular weight (M_n) being estimated as 33 000 g mol^{-1}, and the weight average molecular weight (M_w) as 75 000 g mol^{-1}. The combination of the light harvesting and the multichromophoric nature of the conjugated polymer made it possible to accumulate excitation energy within an individual molecule rather than merely



Scheme 14. Formation of laterally periodic 2D network **104** from monomer **103**.



Scheme 15. Synthesis of macrocycle-encapsulated conjugated polymer **106** from **105**.



Scheme 16. Synthesis of giant spoked wheel **108** from **107**.[17]

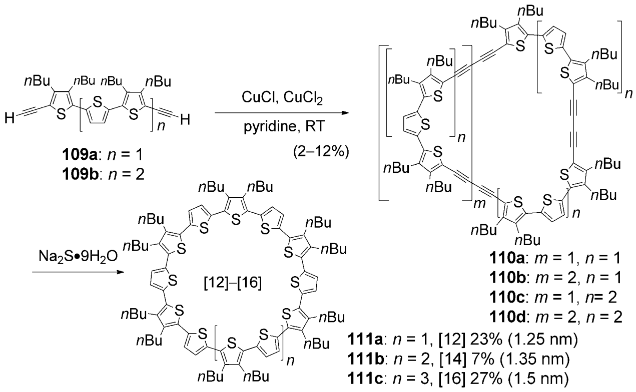
directing it. The accumulation of excitation energy could be applicable to photovoltaics, lasing, and novel photochemical sensors.

Large 2D carbon-rich giant macrocycles with defined sizes, shapes, and compositions show interesting properties, such as 2D crystallinity on surfaces, liquid crystallinity, and optical properties. For example, shape-persistent macrocycles with interior spokes can be regarded as large, planar, reinforced discs. Höger and co-workers recently reported the synthesis of shape-persistent molecular spoked wheel **108** (Scheme 16)[85] by intramolecular coupling of the acetylene units in the precursor dendrimer **107** with CuCl/$CuCl_2$. The ^1H NMR spectrum of **108** showed broad signals at ambient temperature, thus indicating hindered rotation of the *p*-phenylene units close to the hub and the corner of the wheel. The supramolecular assembly of **108** was investigated both at the solid/liquid interface and in thin films by using STM and AFM. The STM investigations revealed that **108** adsorbed with its molecular plane parallel to the surface and aggregated into hexagonal crystalline domains at both octanoic acid/graphite and air/graphite interfaces.

5. Cyclic Oligothiophenes

Oligothiophenes have attracted considerable attention because of their potential applications in organic electronics.[86] They exhibit unique optical and electrochemical properties. Moreover, they are effectively electronically conjugated as a result of contributions from the sulfur atoms in the thiophene rings. Macrocyclic oligothiophenes and their π-extended derivatives are considered to be infinite π-conjugated systems with inner cavities, and nanosized macrocycles are expected to exhibit unusual electronic properties, such as nonlinear optical effects. Several kinds of macrocyclic oligothiophenes and their π-extended derivatives have been reported.[87–99]

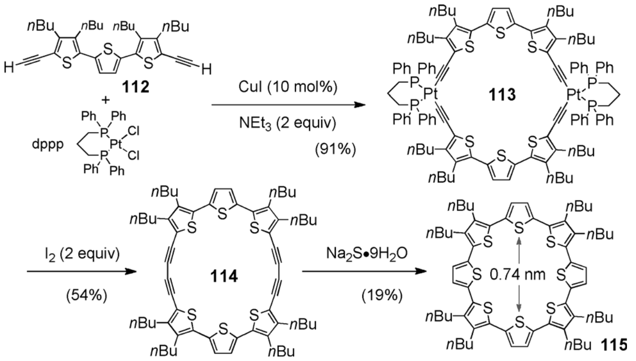
The first synthesis of fully α-conjugated macrocyclic oligothiophenes by the macrocyclization of thiophenediynes **109** as the building blocks was reported in 2000 by Bäuerle and co-workers (Scheme 17).[87a] Copper-mediated coupling of **109** yielded oligo(thienylbutadiynes) **110**, which reacted with sulfur nucleophiles to give the corresponding α-conju-



Scheme 17. Synthesis of fully α-conjugated macrocyclic oligothiophenes **111 1 a–c**. The distances between sulfur atoms are shown in parentheses.[17]

gated macrocyclic oligothiophenes **111a–c**. These macrocycles are stable orange to red microcrystalline solids and are soluble in most common organic solvents. Although **111a–c** could be considered to be antiaromatic (48π, 64π, and 72π frames), they have benzenoid rather than annulenoid character. Compound **111a** was found to form well-ordered 2D monolayers at the solution/HOPG interface.[87a] Moreover, a 2D porous network of hexagonally ordered **111a** formed a two-component system with C_{60}.[87d] The STM images showed 1:1 donor/acceptor complexes and a 3D supramolecular assembly.

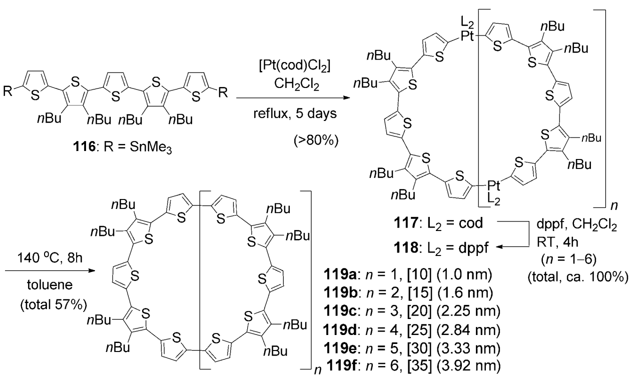
Bäuerle and co-workers developed a new method for the formation of a stable metallamacrocycle **113** from thienyl-diyne building block **112** and *cis*-[Pt(dppp)Cl_2] (Scheme 18).



Scheme 18. Synthesis of macrocyclic oligothiophene **115** via platinum complex **113**.[17]

Subsequent C–C bond formations through reductive elimination led to the strained cyclodimeric terthiophene-diyne **114**, which was converted into cyclo[8]thiophene **115**.[87b,88a]

Recently, the same research group reported a new approach to synthesize highly symmetric macrocyclic oligothiophenes **119a–f**, which have interesting optoelectronic and supramolecular properties (Scheme 19).[88a] They were prepared via multinuclear macrocyclic Pt^{II} complexes **117** and **118**. The high symmetry of the cyclic structures of **119a–f** influences their photophysical properties: the absorption maxima corresponding to an $S_0 \rightarrow S_2$ electronic transition were red-shifted and showed a hyperchromic effect as the ring size increased. Although the emission maxima of **119c–f** were similar, the fluorescence of the smaller macrocycles **119a** and **119b** was much less intense and was red-shifted as result of significant ring strain. The cyclic oligothiophenes exhibited a particularly low first oxidation potential, which increased as the ring size increased. The very low oxidation potential (0.03 V vs. Fc/Fc^+) of the smallest cycle **119a** was attributed to a high HOMO level arising from the *syn* conformation of the thiophene units. Interestingly, the oxidation of **119a** formed the polaron pair **119a**$^{2(\bullet+)}$.[88b]



Scheme 19. Synthesis of macrocyclic oligothiophenes **119a–f**. The maximum distances between thiophene carbon atoms in **119a–f** are shown in parentheses.[17]

Marsella et al. reported the synthesis of rigid, tubular sexithiophene **120** by copper-mediated cyclization of its linear precursor (Figure 23).[89] The crystal structure of **120** showed four Cl···Cl interactions between the sexithiophenes, thereby causing a zigzag motif. Octathio[8]circulene **121a** (which is also called a sulflower) was synthesized by Nenajdenko and co-workers by sulfurization of tetrathiophene, followed by vacuum pyrolysis.[90a] X-ray analysis showed that **121a** had a flat structure with a columnar stacking and that the bonds alternated in the inner eight-membered ring.[91] STM studies on **121a** and "selenosulflower" **121b** in a hydrogen-bonded matrix of trimesic acid at the solid/liquid interface revealed that they formed 2D and 3D supramolecular aggregates.[90b] Although **121a,b** exhibited very weak inner and peripheral cyclic conjugation, **122a–c** showed fairly large antiaromatic ring currents involving the cyclooctatetraene (COT) core.[92] In addition, the colors of solutions of **122a–c** in CH_2Cl_2 were purple, red, and orange, respectively, thus indicating narrow HOMO–LUMO separations.

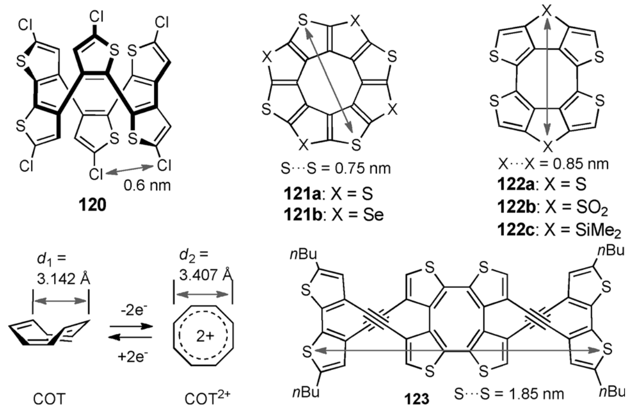


Figure 23. Cyclic oligothiophenes **120–122** and the helical cyclic oligothiophene **123**.[17]

Marsella et al. reported molecules **123** containing two rings with potential use as single-molecule electromechanical actuators (Figure 23).[2c,93] COT could be oxidized to give the unstable planar COT^{2+}, and distance d_1 (3.142 Å) in the tub form increased to distance d_2 (3.407 Å) when it was oxidized to COT^{2+}. A large redox-induced conformational change between twisted and planar topologies, associated with an 18% change in distance, was predicted for the two-electron oxidation of **123** on the basis of DFT calculations.

Recently, π-expanded cyclic oligothiophenes have been reported by several research groups. Although dehydrothienoannulenes **124**–**127** were synthesized to investigate their cyclic conjugation, novel topologies, and organometallic assembly,[94] oligothiophenes with large macrocyclic systems have attracted considerable attention as a result of their multifunctional properties. Kawase, Oda et al. reported the synthesis and X-ray structure of dehydrothieno[24]annulene **128a** (Figure 24).[95a] Although the X-ray structure of **128a** was planar, the tetrabutyl derivative **128b** had a highly twisted structure.[95b] Interestingly, the solid structure of dehydrothieno[24]annulene **128c** exhibited polymorphism, and **128c** aligned layer-by-layer on the surface and showed organic field-effect transistor (OFET) behavior. The maximum hole mobility was $2.8\times10^{-3}\,\mathrm{cm^2V^{-1}s^{-1}}$.[95c] Similarly, Aso and coworkers reported the synthesis and OFET performance of rectangular oligothiophene **129** with benzothiophene units at the corner positions (Figure 24).[96] A film fabricated by spin-coating exhibited a hole mobility with a maximum value of $7.3\times10^{-3}\,\mathrm{cm^2V^{-1}s^{-1}}$.

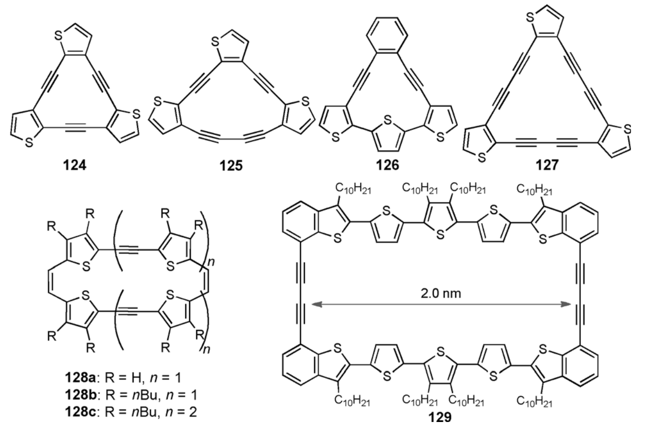


Figure 24. Dehydrothienoannulenes **124**–**127** and rectangular cyclic oligothiophenes **128a**–**c** and **129**.[17]

Two-dimensional supramolecular structures comprised of shape-persistent macrocycle **130** and its co-deposition with C_{60} on HOPG were investigated by Höger and co-workers (Figure 25).[97a] High-resolution STM investigation revealed that monolayers with a perfect ordering of the molecules formed over a relatively large area. The presence of two individual bithiophene units as well as the size of the macrocycle led to the formation of a superstructure with a 1:2 stoichiometry. The fullerene units were located around the periphery of the bithiophene units, thus indicating the donor–acceptor interaction between C_{60} and the electron-rich bithiophene units of the ring.

Very recently, Pan, Höger, Wan, and co-workers reported STM investigations on the co-deposition of shape-persistent arylene-ethynylene-butadiynylene macrocycles **131a** and **131b** and metallacycles **132a** and **132b** (Figure 25).[97b] Under ambient conditions, 2D ordered arrays of the macrocycles and macrocycle/metallacycle architectures (1:1) formed on HOPG through self-assembly. The ordered macrocycle array was found to act as a template for the deposition of adlayer molecules. One metallacycle was detected for each underlying macrocycle, and the structural information of the macrocycle layer was nicely transferred to the guest metallacycle. Unexpectedly, **131a** and **131b** were not coadsorbed with C_{60}, thus indicating a dramatic effect from a minor change in the structure of the macrocycle on the ability of the monolayer to bind additional guest molecules.

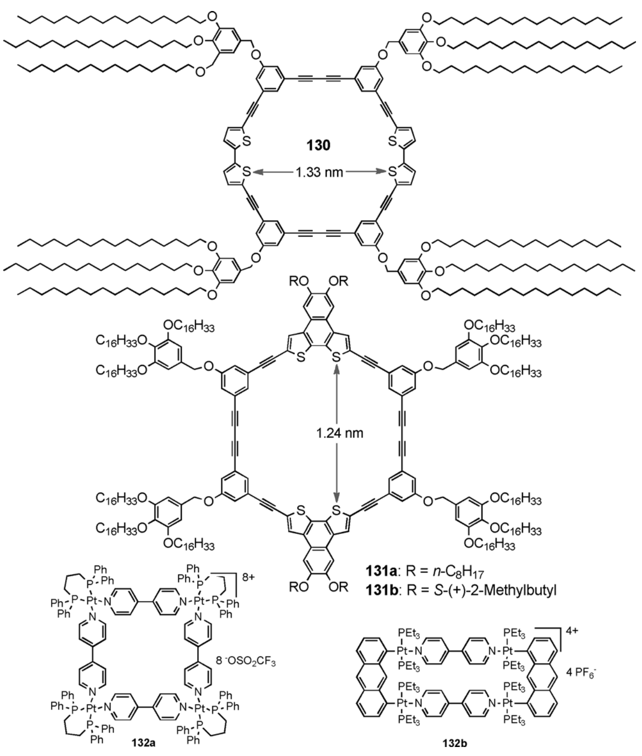
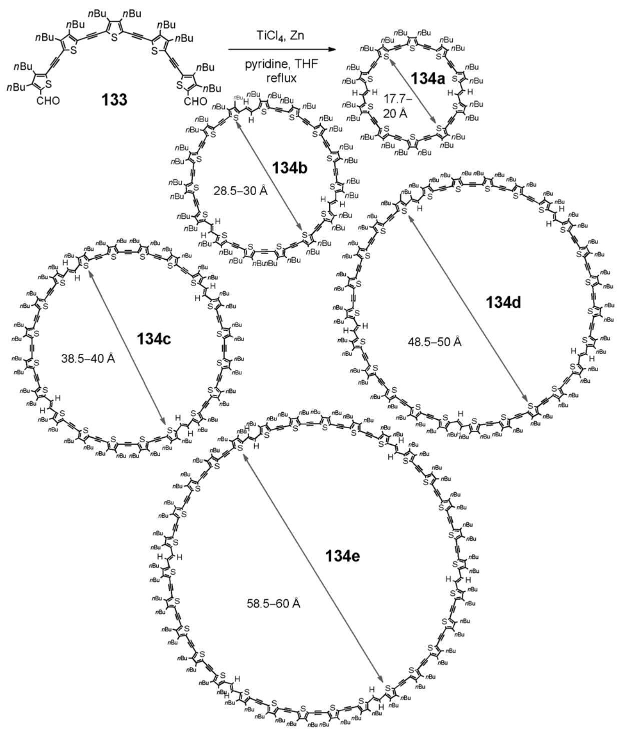


Figure 25. Shape-persistent macrocycle **130** with bithiophene units, and macrocycles **131a,b** with host metallacycles **132a,b**.[17]

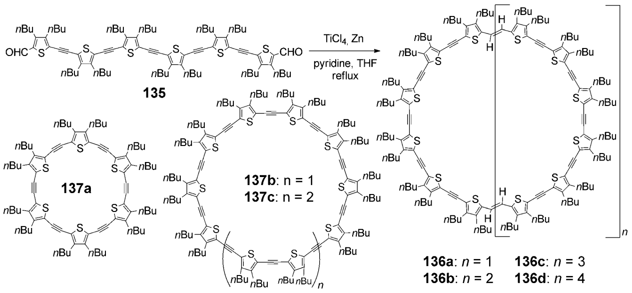
π-Expanded cyclic oligothiophenes composed of thienylene, ethynylene, and vinylene units have been investigated by Iyoda and co-workers.[98a] Giant macrocycles **134a**–**e** were synthesized by using McMurry coupling as the key reaction (Scheme 20). Intermolecular cyclization of dialdehyde **133** under moderately dilute conditions produced the 60π dimer **134a**, 90π trimer **134b**, 120π tetramer **134c**, 150π pentamer **134d**, and 180π hexamer **134e** in 32%, 9.4%, 6.2%, 3.9%, and 2.3% yields, respectively.

Similar to the synthesis of **134a**–**e**, a McMurry coupling of **135** yielded 72π dimer **136a**, 108π trimer **136b**, 144π tetramer **136c**, and 180π pentamer **136d** in 39%, 8.3%, 2.5%, and 1.2% yields, respectively (Scheme 21).[98c] Although the isomeric macrocycle **128c** with six thiophene units was synthesized by McMurry coupling, **135** did not afford the intramolecularly cyclized 36π macrocycle. In addition, cyclo[*n*](3,4-dibutyl-2,5-thienylene-ethynylenes) **137a**–**c** (*n* = 6, 10, and 12) were synthesized by using a bromination/dehydrobromination procedure.

The molecular structure of **134a** was determined by X-ray analysis (Figure 26).[98a] A single crystal of **134a** suitable for X-ray analysis was obtained from a chloroform/heptane solution and contained heptane in a 1.5 molar ratio to **134a**.



Scheme 20. Synthesis of giant macrocycles **134a**–**e**.



Scheme 21. Giant macrocycles **136a**–**d** and **137a**–**c**.

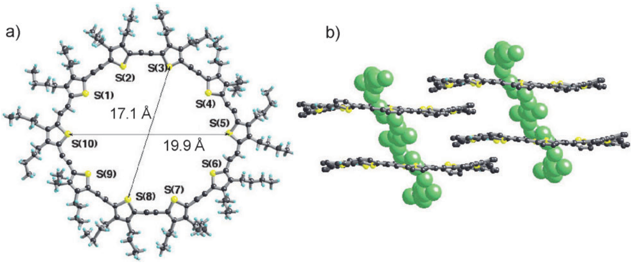


Figure 26. X-ray crystal structure of **134a**: a) Top view; heptane residues are omitted for clarity. b) Side view of the packing structure with heptane chains (green). Butyl groups are omitted for clarity (adapted from Ref. [98a]).

The macrocyclic rings were partially stacked at a distance of 3.6 Å to form channels, and the large cavity filled with heptane molecules and butyl groups of neighboring molecules caused its frame to have a slight chairlike conformation.

Although **134a**–**e** had the same molecular compositions, they showed different morphologies depending on the ring size: **134a** forms single crystals, **134b** forms either microcrystals or nanowires, and **134c** forms nanowires (Figure 27). Aggregates of **134b** and **134c** had well-defined fibrous structures with thicknesses of 100–200 nm. On the other hand, **134d** and **134e** formed nanoparticles with sizes in the range 300–800 nm.

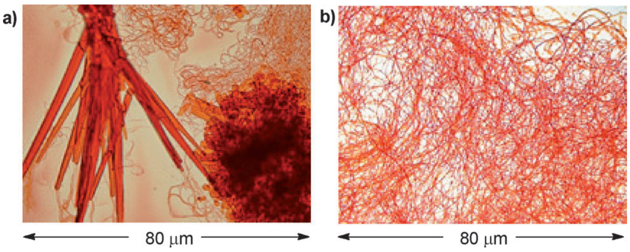


Figure 27. Optical micrographs of a) **135b** and b) **135c**.

The search for new organic materials with enhanced nonlinear optical effects has recently been driven by the formation of novel building block motifs. Redox-active macrocycles have attracted considerable attention for their potential applications in single-molecule electronics and in nanofabrication as well as for their unusual electronic and optical properties. Thus, giant macrocycles composed of thiophene, acetylene, and ethylene building blocks are considered to be infinite π-conjugated systems with a large inner cavity, and hence their physical properties should be strongly affected by their structures in solution and in the solid state. In fact, the longest wavelength absorption maxima in the absorption and emission spectra of the giant macrocycles **134a**–**e** and **136a**–**d** were red-shifted as the ring size increased, thus reflecting that the rings were almost fully conjugated. In the case of the emission spectra, the giant macrocycles showed two major emissions at almost the same wavelengths (559–562 and 600–606 nm) with a large Stokes shift in the range 3600–5820 cm^{-1}. The large increases in the TPA cross-sections of **136a**–**d** arose from intramolecular interactions.[98c] The TPA cross-sections of **136a**–**d** were: **136a** 15100 GM, **136b** 66700 GM, **136c** 82600 GM, and **136d** 107800 GM (Figure 28). The maximum TPA cross-sections

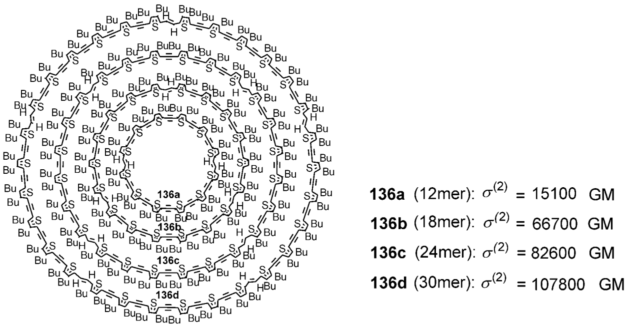
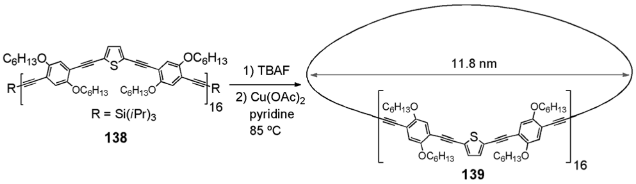


Figure 28. TPA cross-section ($\sigma^{(2)}$) values of **136a**–**d**.

increased 4.4-, 5.5-, and 7.1-fold from **136a** (72π) to **136b** (108π), **136c** (144π), and **136d** (180π), respectively. Furthermore, the thienylene-ethynylene units in **136a–d** show a delocalized state upon excitation, and this delocalized state decays on an ultrafast timescale and can be followed by the presence of incoherent hopping. It is noteworthy that the initial delocalized state increases with ring size to distances (and number of chromophores) comparable to those in the natural light harvesting system.[98e]

Mayor and Didschies reported one of the largest macrocycles, **139**, with a diameter of 11.8 nm (Scheme 22).[99] It has a fully conjugated periphery composed of ethynylene, butadiynylene, 2,5-thienylene, and 1,4-phenylene units. The absorption maximum of **139** was observed at 461 nm, which is very close to the theoretical value of 462 nm.



Scheme 22. Synthesis of giant macrocycle **139**. TBAF = tetrabutylammonium fluoride.

6. Pyrrole-Containing Macrocycles

Pyrrole-containing macrocycles have attracted much attention as a consequence of their interesting structural, optical, electrochemical, and coordination properties.[100] Although a large amount of research has been devoted to the chemistry, biology, and physics of porphyrins and related systems with four pyrrole rings, we focus here on macrocycles containing more than five pyrrole or related heteroaromatic units. Furthermore, since many reviews of expanded porphyrins have been published recently,[101,102] we also briefly discuss their structure–property correlations.

6.1. Expanded Porphyrins

Expanded porphyrins, such as pentaphyrins, hexaphyrins, heptaphyrins, octaphyrins, nonaphyrins, and decaphyrins, are well documented.[101] Their diverse applications in near-infrared (NIR) dyes,[102a] anion sensors,[102b] nonlinear optical (NLO) materials,[103a] photosensitizers,[103b] and photodynamic therapy[103c] have resulted in numerous expanded porphyrin families having been developed. One of the most distinct features of expanded porphyrins is that their absorption spectra are red-shifted as the ring size increases because the π electrons delocalize over the ring. Although the delocalization brings about the interesting features of expanded porphyrins, expanded porphyrins having more than six pyrrole rings have distorted nonplanar structures (Figure 29). Thus, larger expanded porphyrins with distorted topologies show broad and ill-defined absorption spectra. Therefore, the overall molecular structure is an important factor controlling the electronic structures of expanded porphyrins.

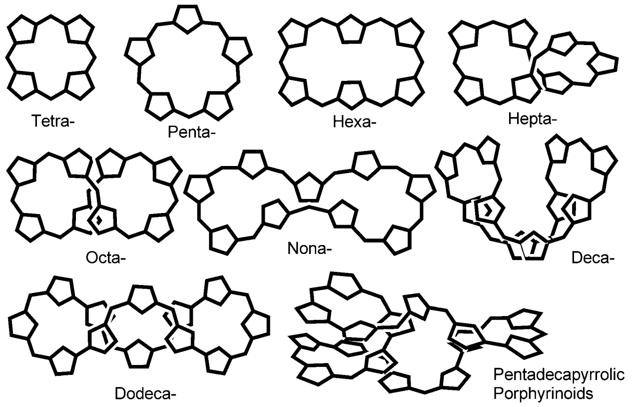


Figure 29. Structures of various porphyrinoids.

One of the most interesting properties of expanded porphyrins is their large TPA cross-sections ($\sigma^{(2)}$). Although normal porphyrin monomers only exhibit $\sigma^{(2)}$ values of less than 100 GM,[104] the $\sigma^{(2)}$ values of pentapyrrolic expanded porphyrins are one order of magnitude higher. The absorption maxima of the lowest Q-like bands of pentapyrrolic porphyrins **140–142** (Figure 30) appeared at 801, 700, and 552 nm, respectively. Compared to aromatic **140** and **141**, the absorption spectrum of antiaromatic **142** was extremely broad. In addition, **140** and **141** fluoresced, whereas **142** did not. The calculated nuclear independent chemical shift (NICS(0)) values for **140–142** were −16.1, −14.1, and +42.9 ppm, respectively. Compounds **140** and **141** had similar $\sigma^{(2)}$ values (3300 GM for **140** and 2700 GM for **141**), whereas **141** had a much lower $\sigma^{(2)}$ value (1200 GM).[101d,f]

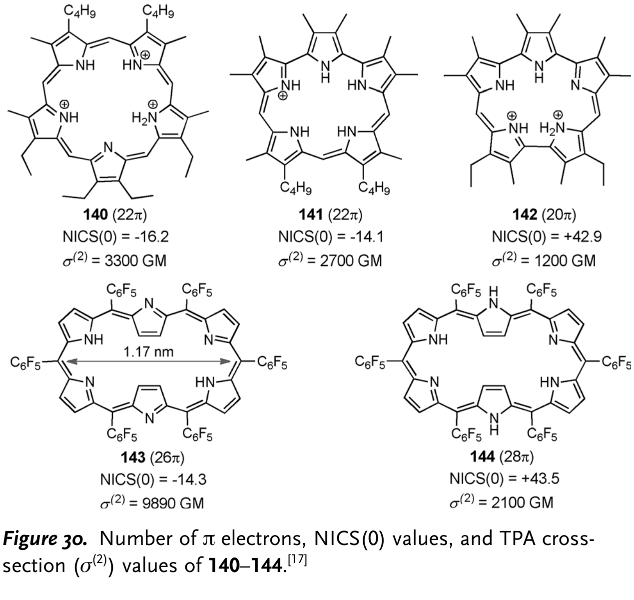
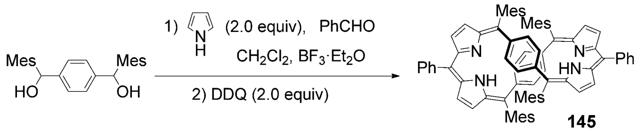


Figure 30. Number of π electrons, NICS(0) values, and TPA cross-section ($\sigma^{(2)}$) values of **140–144**.[17]

Hexapyrrolic expanded porphyrins **143** and **144** are [4n+2]/[4n] heteroannulene systems and interconvert between each other (Figure 30). Compound **144** undergoes dehydrogenation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to produce **143** with a color change from blue to violet; **143** is easily converted back into **144** by treatment with $NaBH_4$. Although **143** and **144** showed similar absorption and emission spectra, the calculated NICS(0) values were -14.3 ppm for aromatic **143** and $+43.5$ ppm for antiaromatic **144**. Interestingly, the measured $\sigma^{(2)}$ value for **143** was 9890 GM at 1200 nm, whereas that for **144** was 2600 GM at 1200 nm. Thus, the $\sigma^{(2)}$ values can be used to discriminate between systems with $[4n]$ and $[4n+2]\pi$ electrons.[101f]

As described in an earlier section, the stable neutral Möbius [16]annulene **6** reported by Herges and co-workers exhibited relatively weak aromaticity.[16a] Recently, expanded porphyrins have emerged as a new promising class of molecules for preparing Möbius aromatic systems. Their conformational flexibility, ability to flip out the constituent pyrrolic subunits, capacity to respond to two-electron redox reactions, and the possibility of "locking in" the conformations through metalation have made them attractive for constructing Möbius aromatic systems.

Latos-Grażyński and co-workers reported the expanded porphyrin analogue di-*p*-benzi[28]hexaphyrin **145**, which adopted a Möbius structure in the solid state but exhibited temperature- and solvent-dependent dynamic switching between Hückel and Möbius topologies in solution (Scheme 23).[105] In this system, the *p*-phenylene ring was used for the first time to control the topology. When it was rotated by 90°, a 180° decrease or increase in the overall twist of the molecule occurred, thus leading to a change in the topology of the π system.



Scheme 23. Synthesis of di-*p*-benzi[28]hexaphyrin **145**. DDQ = 2,3-dichloro-5,6-dicyanbenzoquinone. Mes = 2,4,6-trimethylphenyl.

Soon after the discovery of dynamic switching between Hückel and Möbius topologies, Osuka, Kim, and co-workers explored several methods to realize Möbius aromatic expanded porphyrins. They used metalation,[106] temperature,[107a] solvent polarity,[107b] intramolecular fusion of peripheral positions,[108] and protonation[107b] of meso-aryl-substituted expanded porphyrins to prepare Möbius aromatic systems.

[36]Octaphyrin **146**, a 36 π-electron system, was considered to be non-aromatic on the basis of UV/Vis and ^{1}H NMR spectroscopic studies and NICS calculations (Figure 31). Metalation with palladium acetate resulted in the formation of the two bispalladium complexes **147a** and **147b**, which possess a twisted double-sided Hückel topology and a singly twisted Möbius topology, respectively.[106] Complex **147a** with a 36π-electron circuit exhibited a paratropic ring current, which was supported by a large calculated NICS value ($\delta = +38.4$ ppm). On the other hand, ^{1}H NMR spectroscopy showed that complex **147b**, which has the same π-electron circuit, exhibited a diatropic ring current. The diatropicity of **147b** was supported by UV/Vis spectroscopy. An intense Soret-like band at 735 nm and Q-like bands at 822, 1020, and 1143 nm were observed. In addition, NICS calculations gave $\delta = -14.6$ ppm.

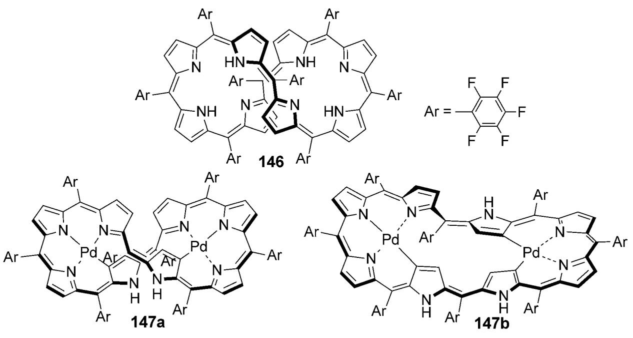
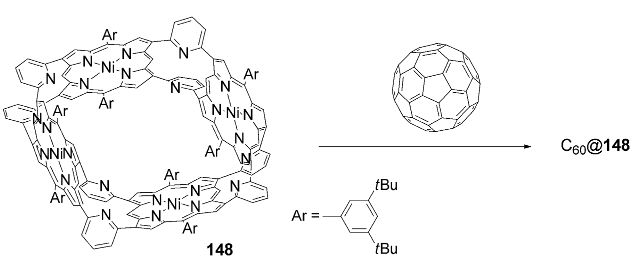


Figure 31. Expanded porphyrin **146** and its metal complexes **147a** and **147b**.

Osuka and Kim studied various Möbius porphyrins and reported their aromaticity, π delocalization, and photophysical properties, particularly focusing on topology-controlling effects. They found that the structure greatly affected the aromaticity and photophysical properties. Their topology-controlling method has the following two advantages: 1) easy control of the molecular topology in the desired direction, and 2) it can affect the molecular properties without side effects. If this innovative method can be used to its fullest potential, it will only be a matter of time before topology control and photophysical properties find applications in widely used devices.

Quite recently, a cyclic porphyrin tetramer **148** was reported by Aratani and co-workers (Scheme 24).[109] Tetramer **148** has a nanobarrel structure with a diameter of 1.4 nm (Ni···Ni distance). Interestingly, **148** forms the 1:1 complex C_{60}@**148** in $CDCl_3$ (association constant $= 5.3\times10^5\,\text{M}^{-1}$), and the X-ray analysis of C_{60}@**148** showed that a C_{60} molecule is nicely captured within the void space with an average distance of about 3.6 Å.



Scheme 24. Porphyrin nanobarrel **148** and its complex C_{60}@**148**.

Giant macrocycles containing porphyrin arrays have attracted considerable current interest not only because of their light-harvesting properties but also because of their extraordinary electrooptical and NLO properties.[110] Sugiura and co-workers reported the construction of the square π-conjugated porphyrins **149** by linking two meso positions with acetylene bridges (Figure 32).[111] Ultrahigh-vacuum scanning tunnelling microscopy (UHV-STM) on a Cu(111) surface showed that **149** had a square structure with side lengths of approximately 5 nm.

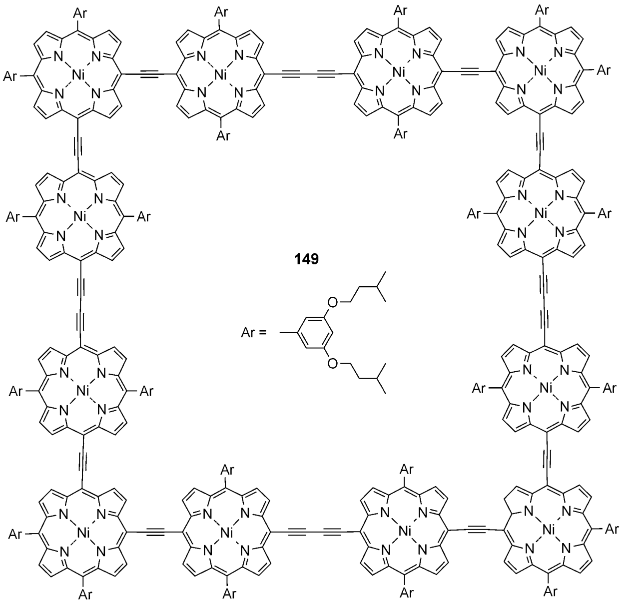
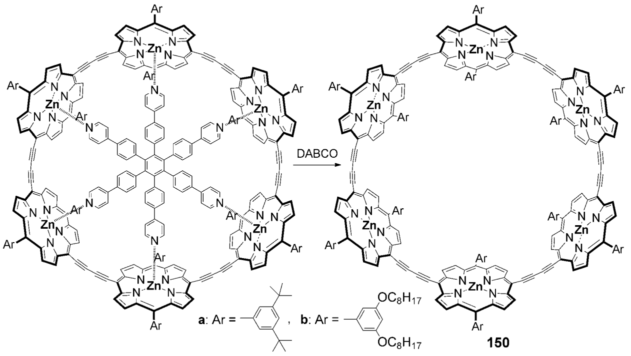


Figure 32. The square π-conjugated porphyrin oligomer **149**.

The template-directed synthesis of fully conjugated butadiyne-linked cyclic porphyrins, such as hexamer **150** with a large interior site (Zn···Zn: 3.4 nm), was reported by Anderson and co-workers (Scheme 25).[112] The remarkable features of the strained macrocycle **150** are its D_{6h} symmetry and very high affinity for templates (association constant $= 1.4 \times 10^{28}\,\text{M}^{-1}$). The absorption and emission maxima of **150** were red-shifted compared to those of the linear hexamer, thus indicating greater π conjugation in the nanoring than that in the linear analogue.



Scheme 25. Synthesis of the nanoring **150**. DABCO = 1,4-diazabicyclo-[2.2.2]octane.

6.2. Core-Modified Expanded Porphyrins

Core-modified expanded porphyrins are porphyrin analogues where one or more pyrrolic nitrogen atoms have been replaced by other heteroatoms. They retain the basic porphyrin framework but possess altered electronic, photochemical, and optical properties. The first syntheses of furan- and thiophene-containing sapphyrins were reported by Johnson and co-workers.[113] Later, Sessler et al. reported a series of β-substituted sapphyrins containing one or more heteroatoms, and the monooxasapphyrin was found to form stable in-plane aromatic uranyl complexes (**151**; Figure 33).[114] The sulfur analogue of 22π-pentaphyrin **152** was reported by Vogel et al.[115] As the synthetic methods and remarkable properties have already been reported in other reviews,[100,101,116] here we only summarize recent topics involving core-modified expanded porphyrins.

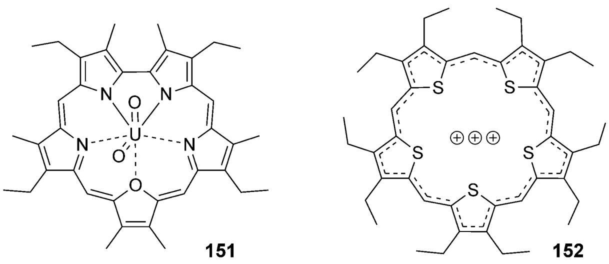


Figure 33. The uranyl complex of monooxasapphyrin **151** and the sulfur analogue of pentaphyrin **152**.

Three core-modified pentaphyrins **153–155** were synthesized by three independent research groups to create new metal-sensing systems, catalytic systems, and well-organized π spaces (Figure 34). Compound **153** has a twisted structure and is conformationally mobile.[117a] The N-fused pentaphyrins **154a,b** are 24π systems that exhibit a paratropic ring current and ill-defined absorption spectra,[117b] whereas **155** is a 22π system that exhibits a diamagnetic ring current and an intense Soret band with weak Q bands in the absorption spectrum.[117c] Recently, trithiapentabenzosapphyrin was synthesized in good yield by a thermal retro-Diels–Alder reaction.[117d]

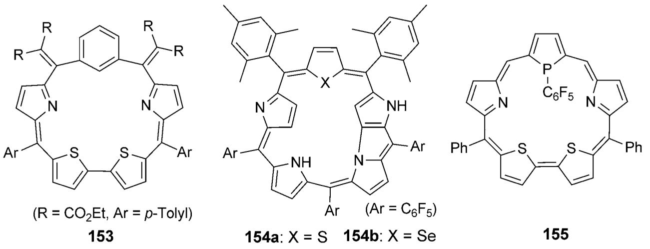


Figure 34. Core-modified pentaphyrin derivatives **153–155**.

The synthesis of core-modified rubyrin **156** with fused polycyclic aromatic phenanthrene units was reported by You and co-workers (Figure 35).[118] An expanded porphyrin in which four pyrrolic nitrogen atoms were replaced by sulfur atoms was embedded into a polyurethane membrane to produce simple test strips for the rapid screening of Hg^{2+} ions. The response of **156** to Hg^{2+} ions was shown by a shift in the Soret band from 597 nm to 638 nm, with a clear isosbestic point at 617 nm. Although **156** can formally be represented as [26]hexaphyrin, its lower energy absorptions and redox properties suggest that the ring fusion in **156** leads to a dye with cross-conjugated [26]hexaphrin and [52]hexaphyrin chromophores **156a** and **156b**, respectively.

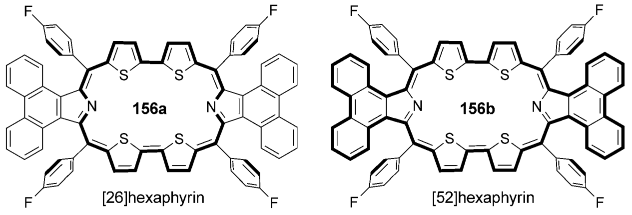
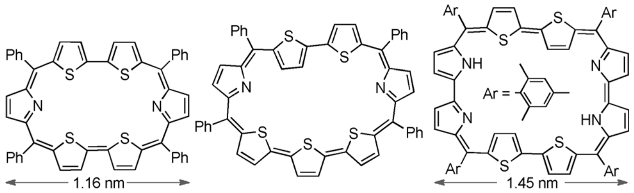


Figure 35. Core-modified rubyrin **156**.

As the number of pyrrole rings increases, the expanded porphyrins typically do not maintain their flat structure. However, some core-modified expanded porphyrins show higher planarity than the corresponding porphyrins. Chandrashekar and co-workers reported tetrathiaoctaphyrin **159**, which showed a fairly strong aromatic ring current.[100d,119] As shown in Figure 36, **157**–**159** have 26, 30, and 34π-electron systems, respectively, and the NICS(0) values indicate strong diatropicity. As expected from the large negative NICS(0) values, and hence relatively flat structures, **158** and **159** had $\sigma^{(2)}$ values (> 10000 GM) larger than that of **157** (2460 GM). Interestingly, the $\sigma^{(2)}$ values of **158** and **159** are much larger than those of [30]octaphyrin (3030 GM) and [36]octaphyrin (870 GM).[101f]



157 (26π)
NICS(0) = -15.0
$\sigma^{(2)}$ = 2460 GM

158 (30π)
NICS(0) = -14.6
$\sigma^{(2)}$ = 15100 GM

159 (34π)
NICS(0) = -13.3
$\sigma^{(2)}$ = 11200 GM

Figure 36. Number of π electrons, NICS(0) values, and TPA cross-section values ($\sigma^{(2)}$) of **157**–**159**.

7. Pyridine-Containing Macrocycles

Macrocycles composed of heteroarylene units, such as pyridine, have recently been investigated. To date, there have been only a few reports on the construction of macrocycles composed of pyridine, pyridine-phenylene, pyridine-ethynylene, and pyridine-ethynylene-phenylene units.

Newkome and Lee first synthesized cyclosexipyridine **160** by an initial macrocyclization, followed by insertion of nitrogen (Figure 37).[120] Cyclosexipyridines are insoluble solids in common organic solvents, and their Na^+ and K^+ complexes can be employed for their characterization. Lehmann and Schlüter reported the synthesis of shape-persistent macrocycle **161** with two opposing terpyridine units.[121] The macrocycle appeared to self-aggregate in solution, and the chemical shifts in the ^1H NMR spectrum were dependent on the concentration.

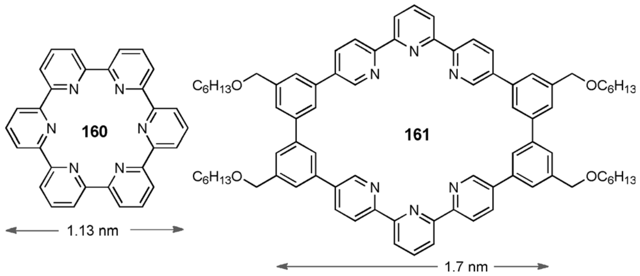


Figure 37. Cyclosexipyridine **160** and pyridine-phenylene macrocycle **161**.[17]

The shape-persistent macrocycles **162a** and **162b** composed of pyridine-butadiyne units were first reported by Tobe et al. (Figure 38).[122] Although **162a** and **162b** did not self-aggregate in solution, **162b** formed heteroaggregates with **84a**,**c**, which has a similar ring size. Moreover, **162a** and **162b** could bind a tropylium ion to form both 1:1 and 2:1 complexes.

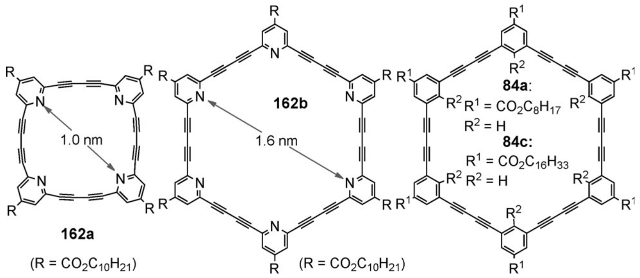
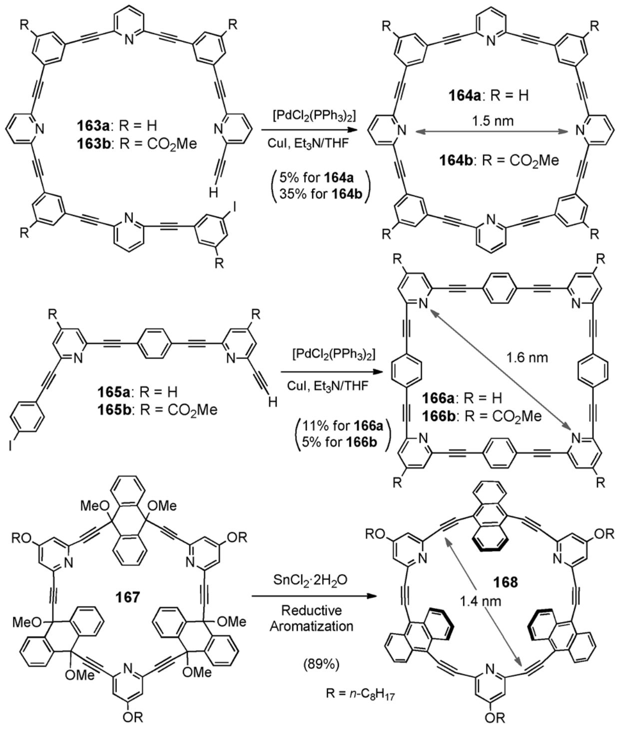


Figure 38. Pyridinophanes **162a**,**b** and **84a**,**b**.[17]

Yamaguchi, Yoshida, and co-workers reported the synthesis and light-emitting properties of octakis-*m*-cyclynes **164a**,**b** and square octakis-*p*-cyclynes **166a**,**b** (Scheme 26).[123a,b] Compounds **164a**,**b** were obtained by intramolecular cyclization of linear arylene-ethynylene octamers **163a**,**b** under highly dilute conditions, and octakis-*p*-cyclynes **166a**,**b** were obtained by intermolecular dimerization of **165a**,**b**. Both cyclynes are unusually fluorescent, in contrast to their acyclic counterparts. Interestingly, **164b** formed a greenish blue pentacoordinate complex with $[Cu^{II}(hfac)_2]$ (hfac = hexafluoroacetylacetonato) to afford **164b**·$[Cu^{II}(hfac)_2]_2$. Surprisingly, the Cu^{II} complex is remarkably fluorescent, even though Cu^{II} ions typically quench fluorescence.



Scheme 26. Synthesis of **166** and **168**.[17]

The high quantum yield of the complex seems to be a consequence of the inhibition of internal conversion as a result of the increased rigidity of the cyclyne ring. Quite recently, strained pyridine-containing cyclyne **168** was synthesized in a high yield by Ohe and co-workers through reductive aromatization of **167**.[123c] Compound **168** showed strong fluorescence around 500 nm with a high fluorescence quantum yield ($\Phi_F = 0.47$).

Baxter reported the synthesis and metal complexation of arene-azaarenecyclyne **169** having a dehydroannulene framework with two 2,2′-bipyridine units in its structure (Figure 39).[124] This cyclyne functions as a multiple readout sensor, giving different outputs depending on the type of metal ion, and thus, it can be used to detect biologically important metal ions, such as Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. Cyclyne **169** emitted bright turquoise fluorescence in the presence of Zn^{2+} ions. The synthesis of the similar shape-persistent arene-azaarenecyclynes **170a**,**b** with two 2,2′-bipyrdine units were reported by Schlüter and co-workers.[125a–c] Single-crystal X-ray analysis of **170b** revealed a layered structure with channels partly filled with the flexible chains and solvent molecules.

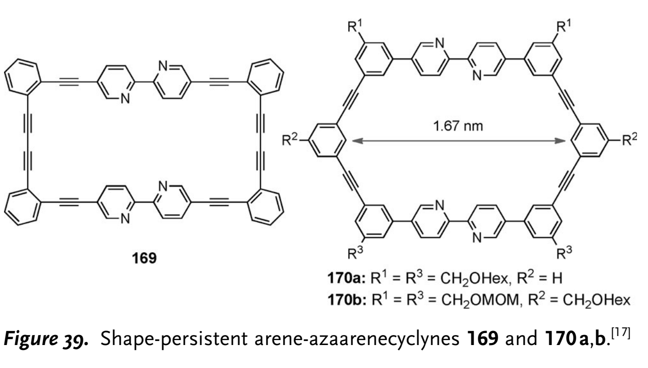


Figure 39. Shape-persistent arene-azaarenecyclynes **169** and **170a**,**b**.[17]

Schlüter and co-workers reported the construction of large terpyridine-containing shape-persistent macrocycles **171** and **172** (Figure 40).[125d] Single-crystal X-ray analyses of **171a** and **171b** showed the macrocycles to form layer structures, with consecutive layers forming columnar stacks that were filled with solvent molecules and the flexible side chains. STM investigations on **172c** and **172d** revealed that only **172c** physisorbed into highly ordered nanostructures at the solution/HOPG interface.

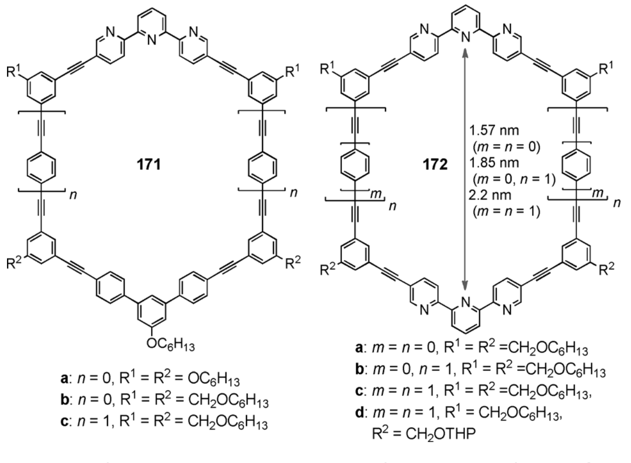


Figure 40. Shape-persistent giant macrocycles **171a–c** and **172a–d** with terpyridine units.[17]

Haley and co-workers reported an isomeric pair of donor-functionalized 15-membered dehydrobenzopyridannulenes (**173a**,**b**; Figure 41), which visibly fluoresced and showed weak intramolecular CT behavior.[126] The macrocycles exhibited unusually large Stokes shifts compared to the corresponding open-chain precursors. There were remarkable changes in both the absorption and emission spectra upon stepwise protonation. The UV/Vis spectrum of **173a** in the presence of CF_3CO_2H (TFA) showed two new bands at 494 and 619 nm, and the bright blue-green fluorescence was quenched.

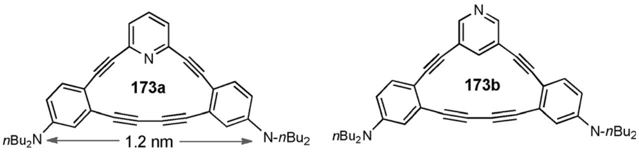


Figure 41. Dehydrobenzopyridannulenes **173**.[17]

Pyridine-containing phenylacetylenic macrocyclic ligands **174a**,**b** and their dinuclear rhenium(I)tricarbonyl complexes **175a**,**b** were reported by Sun and Lees (Figure 42).[127a] Both the shape-persistent ligands and their dinuclear rhenium(I) complexes showed strong luminescence in solution at room temperature. ^{1}H NMR spectroscopy indicated that no self-

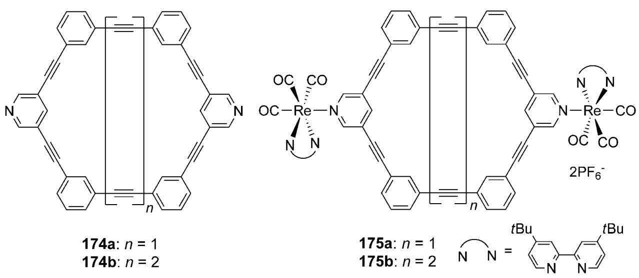


Figure 42. Marocyclic ligands **174a**,**b** and their dinuclear Re complexes **175a**,**b**.

aggregation occurred. However, **174a**,**b** exhibited concentration-dependent fluorescence. The fluorescence maxima of the ligands red-shifted as the concentration increased, which was ascribed to the formation of excimers in the excited states. In contrast, the luminescence of the rhenium(I) complexes **175a**,**b** was not dependent on the concentration.

Pyridine-containing cross-conjugated system **176a** was reported by Tykwinski and co-workers (Figure 43).[127b,c] They behaved as 4,4′-bipyridine mimics and aggregated through axial coordination with metalloporphyrins into nanoscale structures (**176b**). Analysis of the solid-state structure of **176b** revealed that this cross-conjugated cyclyne could form a highly ordered, channel-like material. Cyclyne **176a** aggregated with *cis*-[Pt(TfO)$_2$(PEt$_3$)$_2$] in solution to form a discrete supramolecular species, which subsequently crystallized to give a solid with bidirectional porosity. The regioselective synthesis and complex formation of chiral (2,5)-pyrido[7$_4$]allenoacetylenic cyclophane **177** was reported by Cid and co-workers.[128] The reaction of C_1-symmetric twisted cyclophane (*M*,*P*,*P*,*P*)/(*P*,*M*,*M*,*M*)-**177** with [Re(CO)$_5$Br] led to an uncommon tetracarbonylrhenium complex.

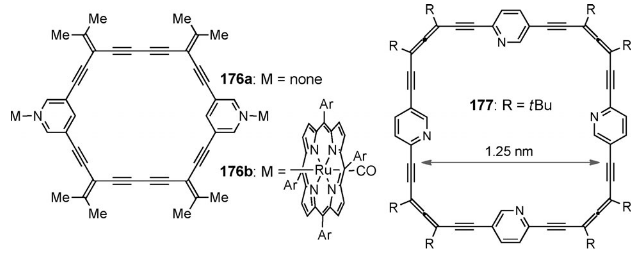


Figure 43. Cross-conjugated cyclyne **176a**, its dinuclear complex **176b**, and pyrido[7$_4$]allenoacetylenic cyclophane **177**.[17]

8. Other Functional Macrocycles

In the previous sections, we summarized the syntheses and functional properties of carbocyclic macromolecules along with their structural elements. Two functional macrocyclic systems containing tetrathiafulvalenes (TTFs) and carbazoles will be discussed in this section.

8.1. TTF-Containing Macrocycles

Tetrathiafulvalene (TTF) and its derivatives are strong π-electron donors capable of forming stable cation radicals and dicationic species upon oxidation. Therefore, TTFs have been widely applied as building blocks for organic conductors and superconductors.[129] TTF derivatives are frequently used as donor units in donor–acceptor systems, which have potential applications in sensors, molecular electronics, and optoelectronics.[130] Furthermore, there is considerable current interest in TTF-based supramolecular chemistry, and redox-active TTF-containing oligomers, polymers, and dendrimers have been synthesized.[131]

There have been only a few reports of TTF-fused macrocycles. Mono-, bis-, and tris(tetrathiafulvaleno)hexadehydro[12]annulenes **178**–**181** were reported by Iyoda and co-workers (Figure 44).[132] Single-crystal X-ray analysis of **178a** revealed that the planar [12]annulene ring with a boat-shaped TTF moiety formed a slipped-stack dimer with a staggered cofacial arrangement. Cyclic voltammetry showed that annulenes **178**–**180** had π-amphoteric properties. Compounds **178** and **179** formed sandwich complexes with AgOCOCF$_3$ in CDCl$_3$. The ^{1}H NMR chemical shifts of the aromatic protons of **178b** and **179** shifted upfield by 0.04–0.06 ppm for **178b** and 0.14–0.21 ppm for **179** upon addition of a half equivalent of AgOCOCF$_3$. Compound **180b**, which is unstable at ambient temperature in air, self-aggregated in benzene and toluene ($K_2 = 176 \pm 8.0\,\text{M}^{-1}$).

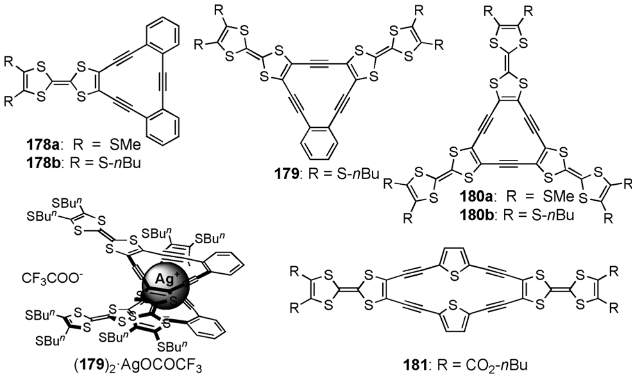


Figure 44. TTF-fused dehydroannulenes **178**–**181** and silver sandwich complex (**179**)$_2$·AgOCOCF$_3$.

Zhao and co-workers synthesized highly expanded TTFs **182a,b** (Figure 45).[133] The solid-state structure of **182a**, as determined by X-ray analysis, showed a bent, S-shaped molecular backbone. On the other hand, the X-ray structure of **182b** showed the central enyne macrocycle to be coplanar with adjacent phenyl and dithiol rings, with the electron-rich dithiol rings directly overlapping with the relatively electron-deficient macrocyclic enyne moiety.

The research groups of Iyoda and Diederich independently reported the synthesis of tris(tetrathiafulvaleno)-dodecadehydro[18]annulenes **184a**–**d** (Scheme 27).[134,135] Although hexyl-substituted **184a** did not self-aggregate in solution or the solid state,[134] butylthio-substituted **184b** self-

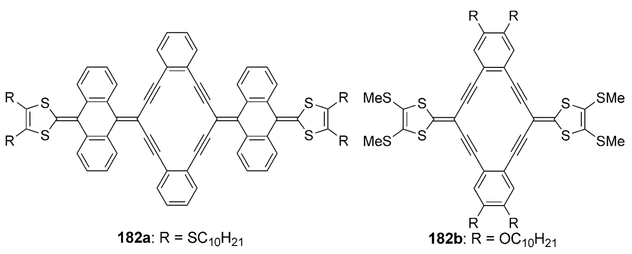
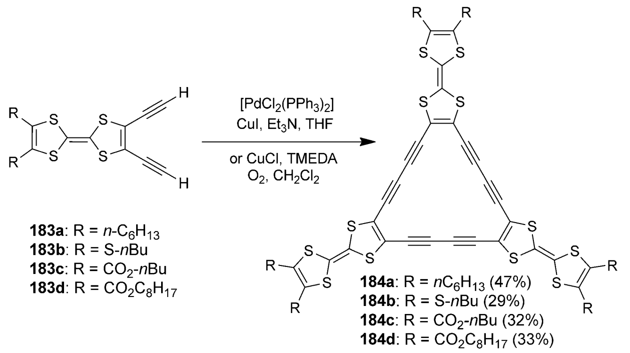


Figure 45. The π-expanded TTFs **182a**,**b**.



Scheme 27. Synthesis of tris(tetrathiafulvaleno)dodecadehydro[18]-annulenes **184a–d**.

aggregated in diethyl ether, benzene, and toluene as a result of its enhanced amphiphilic properties, and formed a fibrous material in a THF/H_2O solution.[135c] In addition, ester-substituted **184c** and **184d** showed multifunctional properties as a consequence of their strong ability to self-associate.[135a,b]

^{1}H NMR spectroscopy and vapor pressure osmometric (VPO) measurements were consistent with **184c**,**d** strongly self-aggregating in benzene and toluene. Compounds **184c**,**d** exhibited thermochromism, which is indicative of the formation of a dimer or higher aggregates at low temperatures.[135a] In addition, **184c** formed fibrous violet materials with thicknesses of 50–500 nm in a 1:1 THF/H_2O mixture. The induced ring-current effect of the central [18]annulene ring resulted in **184c** showing a large diamagnetic response in a magnetic field. The molecules oriented parallel to the direction of the external magnetic field, thereby resulting in the alignment of the nanofibers perpendicular to the direction of the external magnetic field (Figure 46).[135c] In contrast, **184d** did not form fibers, but a solution of **184d** did show a significant temperature hysteresis of the color near room temperature (Figure 47). NMR and UV/Vis absorption spectroscopy suggested that the temperature hysteresis of **184d** in a THF/H_2O mixture could be attributed to the microscopic structure of the solvent mixture and the hydrophobic solvation of **184d** by THF.[135b]

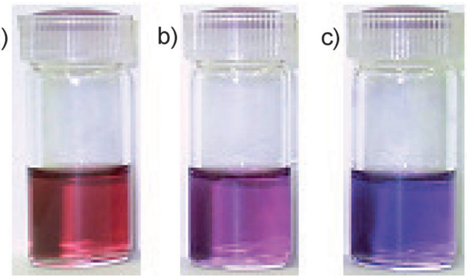


Figure 47. Solutions of **184d** at 25 °C. a) In THF. b,c) In a 1:1 THF/H_2O mixture after heating to 40 °C (b) and after cooling to 10 °C (c; adapted from Ref. [135b]).

8.2. Carbazole-Containing Macrocycles and Related Compounds

Since carbazole has prominent optical and electronic properties and is chemically stable, carbazole derivatives have been studied for use in a variety of applications, including organic light-emitting diodes (OLEDs),[136] nonlinear optics (NLOs),[137] and organic field-effect transistors (OFETs).[138] Furthermore, carbazoles have been used as electron-donating chromophoric units in photoinduced electron-transfer systems.[139]

Moore and co-workers reported the synthesis and the formation of nanofibrils of square carbazole-cornered arylene-ethynylene macrocycles.[140,141] Tetracycles **186a**,**b** were constructed from the corresponding monomeric precursors **185a**,**b** by alkyne metathesis in the presence of a highly active Mo^{VI} catalyst (Scheme 28). The nanofibril structure was constructed from **186a** by using a gelating process.[140b] The nanofibrils were thought to arrange in a tabular, nanoporous structure of stacked rings because of the rigid, planar, noncollapsible framework of **186a**. The nanofibril films fabricated from **186b** were shown to be efficient in detecting vapors of the explosive nitroaromatic compounds DNT and TNT,[140c] probably through a combination of the 1D extended

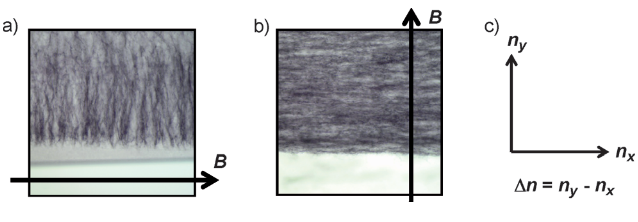
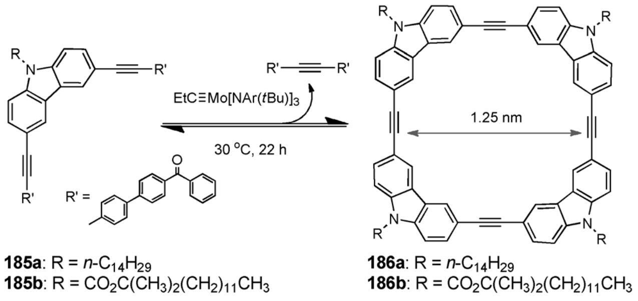


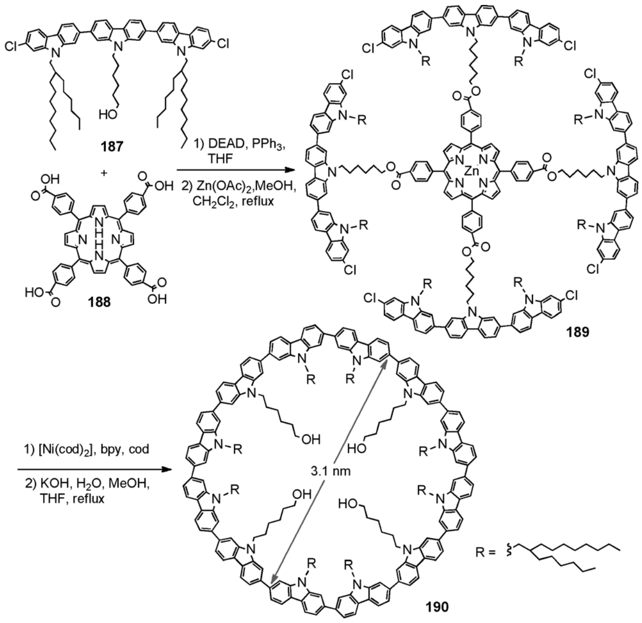
Figure 46. Optical micrographs of aligned **184c** fibers. The arrows *B* indicate the directions of the applied magnetic field (5 T). a) $\Delta n = -29\times10^{-6}$. b) $\Delta n = 58\times10^{-6}$. c) Directions of refractive index n_x and n_y (adapted from Ref. [135b]).



Scheme 28. Synthesis of carbazole-based macrocycles **186a**,**b**.

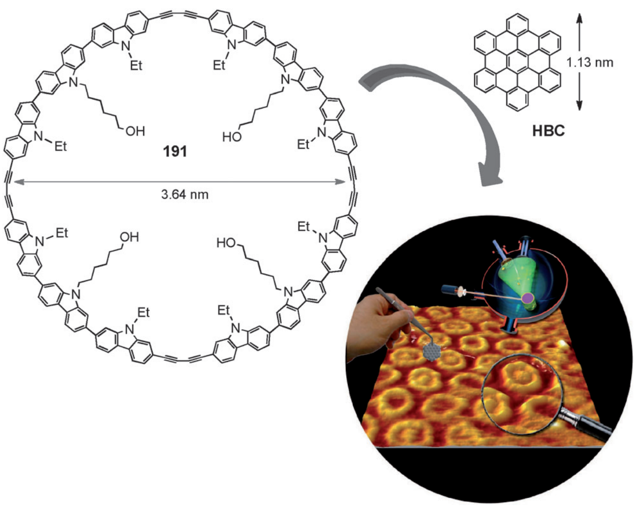
molecular stacking of the component molecules and the intrinsic nanoporous morphology within the film, which enables efficient quenching of the film's fluorescence by the gaseous nitroaromatic compounds.

Müllen and co-workers used a template approach for the construction of the fully conjugated, monodisperse macrocyclic cyclododeca-2,7-carbazole **190** (Scheme 29).[142] The cyclization of **189** was achieved through a nickel-mediated Yamamoto coupling reaction under highly dilute conditions in a microwave reactor. The porphyrin template was then readily removed from the ring by hydrolysis with KOH to generate the fully conjugated macrocyclic carbazole dodecamer **190**. AFM studies on a monolayer of **190** on HOPG showed that it had a hexagonal lattice composed of uniformly sized and distributed spots. STM studies provided additional evidence for the conjugated ring-shaped structure of **190**.



Scheme 29. Synthesis of the giant macrocyclic cyclododeca-2,7-carbazole **190**.[17] bpy = bipyridine, DEAD = diethylazodicarboxylate.

The formation of a host–guest complex of the carbazole dodecamer **191** with hexa-*peri*-hexabenzocoronene (HBC) was reported by Müllen and co-workers (Scheme 30).[143] The two-dimensional supramolecular structures of the host–guest complexes were obtained by physisorption of **191** on HOPG, followed by gas-phase deposition of HBC in a high vacuum. The macrocycle, visible by STM, self-assembled in a hexagonal lattice on HOPG. The design of the giant π-conjugated macrocyclic carbazole dodecamer **191** and the utilization of both deposition methods led to the insertion of one HBC molecule into the cavity of the ring to afford the 1:1 host/guest complex. Recently, the same research group also reported the synthesis of the completely π-conjugated cyclododeca-2,7-fluorene macrocycle.[144] STM studies showed that the macrocycle self-organizes on HOPG to form a well-defined hexagonal pattern.



Scheme 30. STM image of a monolayer of **191** after deposition of HBC molecules (adapted from Ref. [143]).

9. Summary and Outlook

Modern synthetic methods allow the preparation of many nanosized, shape-persistent macrocycles on a practical scale under mild conditions. Cyclic structures possessing shape-persistent, noncollapsible, and fully π-conjugated backbones have been employed in the construction of columnar 1D nanotubes, 2D porous surface networks, and 3D inclusion complexes by self-assembly. The complex supramolecular architectures have been created through π–π stacking or concave–convex interactions, and in some cases at a single-molecule level. Furthermore, these macrocycles show interesting photophysical properties such as large two-photon absorption cross-sections, light-havesting behavior, and luminescence detection of explosives.

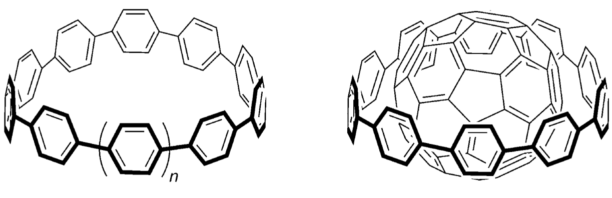
Shape-persistent and semi-shape-persistent heteromacrocycles form redox-active 1D, 2D, and 3D host–guest systems with new properties and applications in nanomaterials. These macrocycles have interior and exterior sites, and site-specific transformation at either or both sites can make the structure more attractive. In particular, the interior sites are usually dependent on the outer stimuli and solvents, and the site-specific host–guest interaction can create the possibility of forming functional superstructures for the recognition of appropriate guest molecules.

In summary, medium to giant conjugated macrocycles are molecules with unique structural, electronic, and optical properties that challenge the creativity and inventiveness of chemists in areas such as organic chemistry, polymer and material chemistry, surface chemistry, and supramolecular chemistry. The knowledge obtained during the 20 years of their existence paves the way for the development of their outstanding properties. Thus, conjugated macrocycles are without doubt a class of molecules to be exploited in depth.

Addendum A: Carbon-Rich Macrocycles

After this Review was accepted, many nanosized to giant macrocycles were reported in 2011. Since these compounds are closely related with this Review, we briefly summarize their syntheses and properties.

Cycloparaphenylenes (CPPs) **31** represent the smallest sidewall segment of carbon nanotube structures (Figure 48). Itami and co-workers reported the concise and effective synthesis of [12]CPP **31c** by using a nickel-catalyzed "shotgun" macrocyclization of a single monomer as the key step together with the first X-ray analysis of **31c**.[145a] The same research group also synthesized a segment of chiral carbon nanotube cyclo[13]paraphenylene-2,6-naphthalene by using a similar route as shown in Scheme 4.[145b] Yamago and co-workers reported the selective and random syntheses of [*n*]CPPs ($n = 8$–13) via tetranuclear platinum complexes based on the route shown in Scheme 5.[146a] Interestingly, although the UV/Vis spectra were rather insensitive to the size of the CPPs, the emission maxima of the [*n*]CPPs ($n = 8$–13) showed a red-shift as the ring size decreased. The encapsulation of C_{60} by [*n*]CPPs revealed that [10]CPP **31h** size-selectively forms a 1:1 complex **31h**$\supset C_{60}$.[146b] The diameter of [10]CPP **31h** (1.38 nm) is 0.67 nm larger than that of C_{60} (0.71 nm), and the distance between C_{60} and **31h** (0.335 nm) is favorable for a convex-concave interaction.

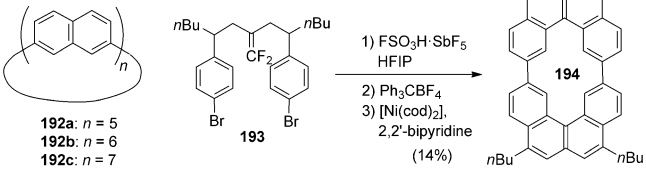


31a: [8]CPP ($n = -1$) **31h**: [10]CPP ($n = 1$)
31b: [9]CPP ($n = 0$) **31i**: [11]CPP ($n = 2$)
31c: [12]CPP ($n = 3$) **31j**: [13]CPP ($n = 4$)

[10]CPP **31h** $\supset C_{60}$

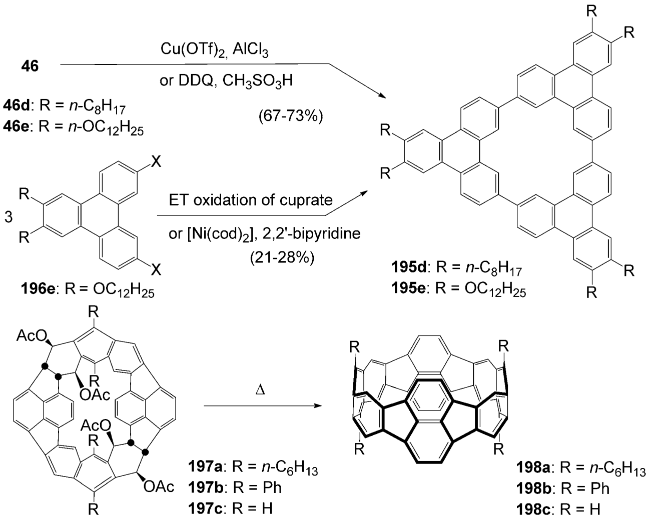
Figure 48. Cycloparaphenylenes (CPPs) and the formation of the smallest fullerene-peapod **31h**$\supset C_{60}$.

Isobe and co-workers reported two types of cyclic phenylene macrocycles, [*n*]cyclo-2,7-naphthalenes ([*n*]CNAP ($n = 5$–7)) **192** and cyclobis[4]helicene **194** (Scheme 31).[147] CNAPs **192a–c** were synthesized by a nickel-mediated Yamamoto coupling of 2,7-dibromonaphthalene. Although **192a–c** are composed solely of sp^2-hybridized carbon atoms and hydrogen atoms, these compounds show a bipolar carrier transport ability.[147a] In the case of **194**, an illusory structure such as "penrose stairs" with unique caracole topology has been suggested.[147b] Bo and co-workers developed an effective synthesis of shape-persistent macrocycles by a one-pot Suzuki–Miyaura coupling by using $[Pd_2(dba)_3]$ and P*t*Bu$_3$.[148]



Scheme 31. Cyclic phenylene macrocycles, [*n*]CNAP ($n = 5$–7) **192a–c** and cyclobis[4]helicene **194**.

Cyclic triphenylene trimers **195** are stable triangular-shaped molecules having potential liquid-crystalline and unique optoelectronic properties. Recently, **195d**,**e** were synthesized independently by the research groups of List and Müllen as well as by Iyoda and co-workers by dehydrogenative cyclization of **46d**,**e** or cyclotrimerization of **196e** (Scheme 32).[149,150] It is worth noting that the self-association of **195d** composed solely of carbon and hydrogen atoms produced oligomers in solution and fibrous material in the solid state, and that **195d** afforded with 2,4,7-trinitrofluorenone a 1:3 CT complex with a microball structure and a dendritic interior.[149] Furthermore, **195e** showed liquid crystallinity, and the hexaphenyl derivatives worked as blue emitters in organic light-emitting diodes.[150] Quite recently, Schlüter and co-workers synthesized the fully conjugated, double-stranded cycles **198a–c** by the thermolysis of **197a–c**.[151] The formation of **198a**,**b** was confirmed by mass spectrometric analysis and trapping reactions.



Scheme 32. Synthesis of cyclic triphenylene trimers **195d**,**e** and fully conjugated, double-stranded cycles **198a–c**.

Concerning dehydroannulenes, Navarrete, Casado, Diederich, and co-workers reported enantiopure, monodisperse alleno-acetylenic cyclooligomers such as **16** and suggested that the research is useful for designing carbon-rich compounds with intense chiroptical properties.[152] Rubin and co-workers synthesized the tetra(hydroxymethyl) derivative of dehydro[24]annulene which formed tightly packed nanotubular channels in the solid state.[153]

Höger and co-workers reported the synthesis and STM images of shape-persistent oligo(phenylene-ethynylene-butadiynylene)s and triphenylene-butadiynylene macrocycles.[154] The STM images showed the formation of empty helical nanochannels, tubelike superstructures, and related nanoscale patterns. Toyota and co-workers used a cyclic 1,8-anthrylene-ethynylene tetramer to synthesize chiral macrocycles **100–102** with a diamond-prism structure. The structures, dynamic behavior, and chiroptical properties of these macrocycles were investigated.[155]

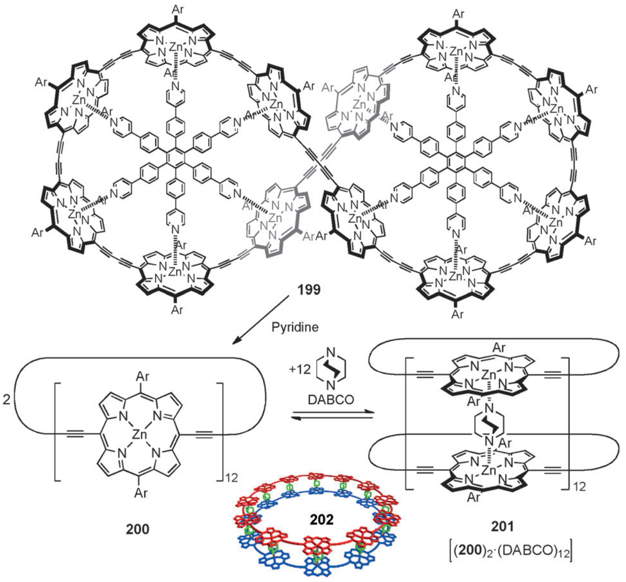
Addendum B: Oligoheteroarylene Macrocycles

The chemistry of porphyrinoids shown in Figure 29 has been very rapidly expanded, and a number of new porphyrinoids and related compounds have been reported.[156] Stępień et al. and Saito and Osuka recently summarized reviews on the synthesis, structures, aromaticity, electronic properties, coordination chemistry, and reactivities of expanded porphyrins.[157,158] Rambo and Sessler also summarized a review of oligopyrrole macrocycles as receptors and chemosensors for hazardous materials.[159]

Bäuerle and co-workers recently reported the X-ray structure and electronic properties of cyclo[10]thiophene **119a**.[160] Furthermore, **119a** was oxidized to produce the polaron-pair **119**$^{2(\cdot+)}$, whose structure was supported by absorption and ESR spectroscopies. Singh et al. synthesized meso-substituted tetrathia[22]annulene[2,1,2,1], which displayed porphyrin-like Soret and Q bands in the absorption spectrum.[161] Interestingly, tetrathiaannulene showed p-type FET behavior, with a mobility as high as 0.63 $\mathrm{cm^2\,V^{-1}\,S^{-1}}$.

Moore and co-workers developed a new synthesis of carbazole-ethynylene macrocycle **186a** and related compounds by a depolymerization/macrocyclization procedure.[162a] The solid-state packing of carbazole-ethynylene macrocycles **186** is sensitive to the length of the alkyl side chain owing to the maximization of the van der Waals interactions between the alkyl chains and aromatic parts of the macrocycles.[162b] Ceroni and co-workers revealed that shape-persistent macrocycles **170** are good ligands for Nd^{3+} and Gd^{3+} lanthanoide ions, and the Nd^{3+} complexes are candidates for luminescent probes with potential applications in the field of sensors and photonics.[163]

Anderson and co-workers reported the Vernier templating and the synthesis of a 12-porphyrin nanoring **200** (Scheme 33).[164a] By using the hexapyridyl template shown in Scheme 25, palladium-mediated oxidative coupling of the linear porphyrin tetramer produced the figure-of-eight complex **199** in a moderate yield. Treatment of **199** with pyridine afforded the 12-porphyrin nanoring **200**. It is worth noting that a cooperative self-assembly of the 12-porphyrin nanoring **200** forms a stable 2:12 sandwich complex **201** with a large excess of DABCO.[164b] Quite recently, [4]- and [7]catenanes based on 6- and 12-porphyrin nanorings, respectively, have been reported.[164c]



Scheme 33. 12-Porphyrin nanoring **199** with two hexapyridyl template, the formation of the sandwich complex **201** from **200** and DABCO (Ar = 3,5-dioctyloxyphenyl), and the calculated structure **202** of **201**.

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