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Hydrindacene-Based Acetylenic Macrocycles with Horizontally and Vertically Ordered Functionality Arrays

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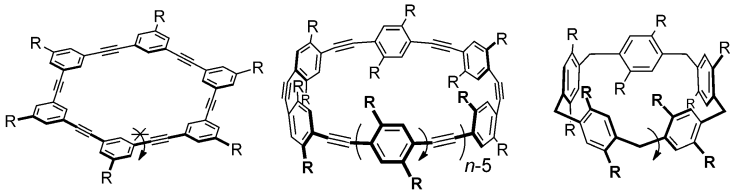
Abstract: The macrocyclization of 2,6-diethynyl hydrindacenes (**1**) with functional groups at mutually perpendicular positions results in the formation of novel macrocycles which, as a result of the hindered rotation of the hydrindacene units, possess directionally persistent peripheral functionalities. The two hydrindacene units in the dimer macrocycle (**2**) have been shown to interact electronically through their respective butadiyne moieties, whereas the trimer macrocycle (**3**) demonstrates a moderate degree of geometrical flexibility as a result of the five-membered hydrindacene rings. In addition, these trimer macrocycles contain a central cavity suitably sized for the inclusion of various solvent molecules. These new macrocycles can be further modified by introducing π-conjugated side groups, such as styryl and thienyl groups, as well as by attaching a variety of peripheral ester groups.

Keywords: alkynes · inclusion compounds · macrocycles · solid-state structures · through-bond interactions

Introduction

Macrocycles[1] that feature preorganized cavities and well-defined structures that are amenable to modification have attracted significant interest to date on account of their novel properties and potential applications.[2] Arylene and ethynylene units have often been used to form such shape-persistent macrocycles.[3–10] One example of a noteworthy property of some planar shape-persistent macrocycles, such as *m*-phenyleneethynylene macrocycles[4] and dehydrobenzo[*n*]annulenes,[5] is the formation of an internal void upon self-assembly based on π–π stacking. In addition, belt-shaped macrocycles[7–15] that consist of rotatable phenylene units—including *p*-phenyleneethynylene macrocycles (CPPAs[7,8] and their homologues[9]), cycloarylenes,[10] calixarenes,[11] and pillararenes[12]—all feature internal voids and thus might form molecular complexes with a variety of guest species. Further unique and interesting properties might be obtained by modifying the cyclic backbones of such macrocycles by attaching various peripheral functional groups oriented both horizontally and vertically relative to the plane defined by the macrocycle. However, additional structural modifications are also necessary to suppress rotation of the phenylene scaffolds, and thus to obtain a well-defined and persistent array of peripheral functional groups. Fixation of the rotational units within some macrocycles can be achieved by increasing their rotational energy barrier through attaching alkyl chains onto the phenylene units, or by the addition of covalently bound groups to form cyclic ladder-shaped structures,[13] as in the case with cavitands[14] and cucurbiturils.[2e] This approach to rotational fixation of the macrocycle, however, limits the options for any additional modifications of the molecules. An alternative approach to suppressing rotation is to connect the quaternary or tertiary carbon atoms on the individual ring units, as is the case in cyclodextrins and their analogues.[15]



m-phenyleneethynylene [*n*]CPPA [5]pillararene

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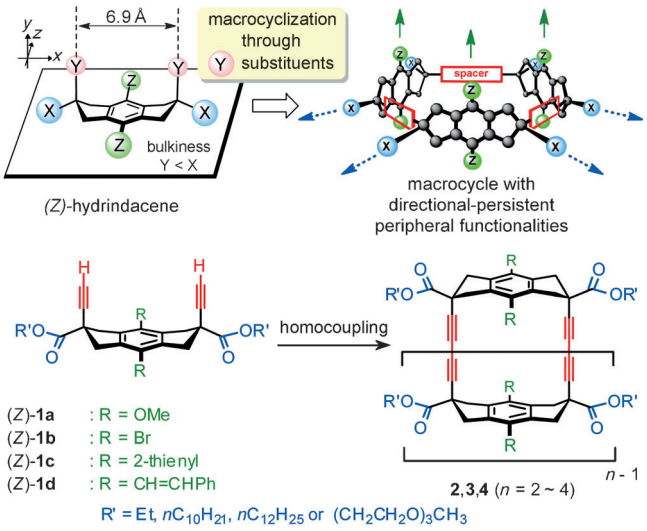
In this article, we report the design and synthesis of a series of novel macrocycles (**2**–**4**), all of which are functionalized in both the horizontal and vertical directions relative to the plane defined by the macrocyclic backbone (Scheme 1). These structures were prepared through Eglinton coupling reactions of the 2,6-diethynylhydrindacenes **1a**–**d**. The details of the synthetic procedures are presented herein, in addition to the results of X-ray structural analysis and the optical and redox properties of the resulting macrocycles.

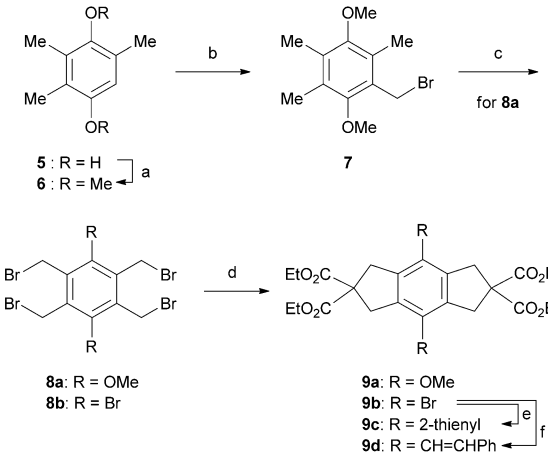


Scheme 1. Construction of hydrindacene-based macrocycles **2**–**4**.

Results and Discussion

Molecular design of hydrindacene-based macrocycles: This novel class of macrocycles, which consists of **2**–**4**, utilizes hydrindacene (1,2,3,5,6,7-hexahydro-*s*-indacene (**1**)) as the basic monomer unit. As shown in Scheme 1, the hydrindacene monomer is composed of a rigid aromatic ring with a five-membered alicyclic ring on either side. We recently reported that hydrindacene might be used as a versatile scaffold[16–18] for the synthesis of various supramolecular assemblies, including a rotaxane template[16] and allosteric[17] or functionality-selective receptors.[18] These varied assemblies result from the multidimensional modification of hydrindacene based on the addition of substituents X, Y, and Z (Scheme 1). Substituents X and Y, at the 2,6-positions on the five-membered rings, and substituent Z, at the 4,8-positions on the aromatic ring, are all mutually perpendicular to one another. The two Y substituents at the 2- and 6-positions are designed as linking groups to produce the macrocycle, whereas the two X groups at the 2- and 6-positions and the Z groups at the 4- and 8-positions remain in mutually perpendicular geometrical relationships and are used as the peripheral functionalities. Accordingly, we expected that the 2,6-diethynyl hydrindacene (*Z*)-**1** would function as a suitable monomer unit for the construction of macrocycles with directional-persistent peripheral functionalities. Macrocyclization was anticipated to proceed through the coupling of the ethynyl groups at the C2 and C6 quaternary carbon atoms of the hydrindacene units, thereby producing novel macrocycles with horizontally and vertically ordered functionality arrays, whereby rotation of the macrocycle units is effectively suppressed. At the same time, the five-membered rings of the hydrindacene units, each of which is puckered into an envelope conformation, confer a moderate degree of geometrical flexibility to the macrocycle as a result of ring flipping. In spite of the inherent flexibility of the five-membered ring on the basis of ring flipping, however, the structural stability that results from the formation of macrocyclic dimers and trimers is enough to maintain the planarity of the macrocycle, and therefore the mutually perpendicular directionality between the functional groups X and Z will be maintained.

Preparation of 4,8-disubstituted hydrindacene derivatives: A series of 2,2,6,6-hydrindacene tetraesters with vertical substituents at the 4,8-positions (**9a**–**d**) were prepared from the 1,4-disubstituted 2,3,5,6-tetrakis(bromomethyl)benzenes **8a**,**b**[19,20] (Scheme 2). Although several synthetic procedures for the preparation of methoxy derivative **8a** have been reported,[19] all required expensive starting materials such as duroquinone[19a] or 2,3-dimethylhydroquinone.[19b] For this reason, we developed a new synthetic route for **8a** as depicted in Scheme 2. Methylation of the relatively inexpensive starting compound 2,3,5-trimethylhydroquinone **5** with CH_3I gave methyl ether **6**,[21] and subsequent bromomethylation[22] of **6** with paraformaldehyde/HBr in AcOH produced monobromide **7**.[23] Treatment of **7** with NBS in CH_2Cl_2 under



Scheme 2. Preparation of 4,8-disubstituted hydrindacene derivatives **9a**–**d**. a) MeI, K_2CO_3, 2-butanone, 65 °C, 81 %; b) paraformaldehyde, 8 % HBr in AcOH, 50 °C, 83 %; c) *hv*, *N*-bromosuccinimide (NBS), CH_2Cl_2, 40 °C, 98 %; d) diethyl malonate, NaOEt, EtOH/PhH (for **9a**) or EtOH (for **9b**), reflux, 53 % for **9a**; 77 % for **9b**; e) 2-(tributylstannyl)thiophene, [$Pd(PPh_3)_4$], DMF, 100 °C, 95 %; f) *trans*-2-styreneboronic acid pinacol ester, $Pd(OAc)_2$, 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos), THF, 40 °C, 91 %.

photoirradiation with a halogen lamp afforded tetrabromide **8a**[19] in 66% total yield. Treatment of the tetrabromides **8a**,**b** with diethyl malonate along with NaOEt in EtOH[24] gave the tetraesters **9a**,**b**. The 4,8-dithienyl and distyryl derivatives **9c**,**d** were prepared by Stille or Suzuki–Miyaura coupling of the dibromo derivative **9b** with 2-(tributylstannyl)thiophene or *trans*-2-styreneboronic acid pinacol ester.[25] The molecular structures of **9a**,**c**,**d** were confirmed by crystallography and are given in Figure 1.

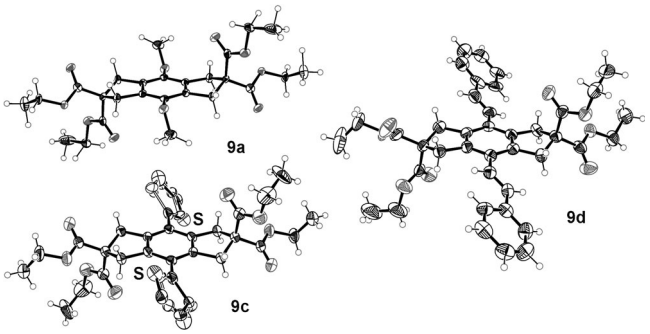
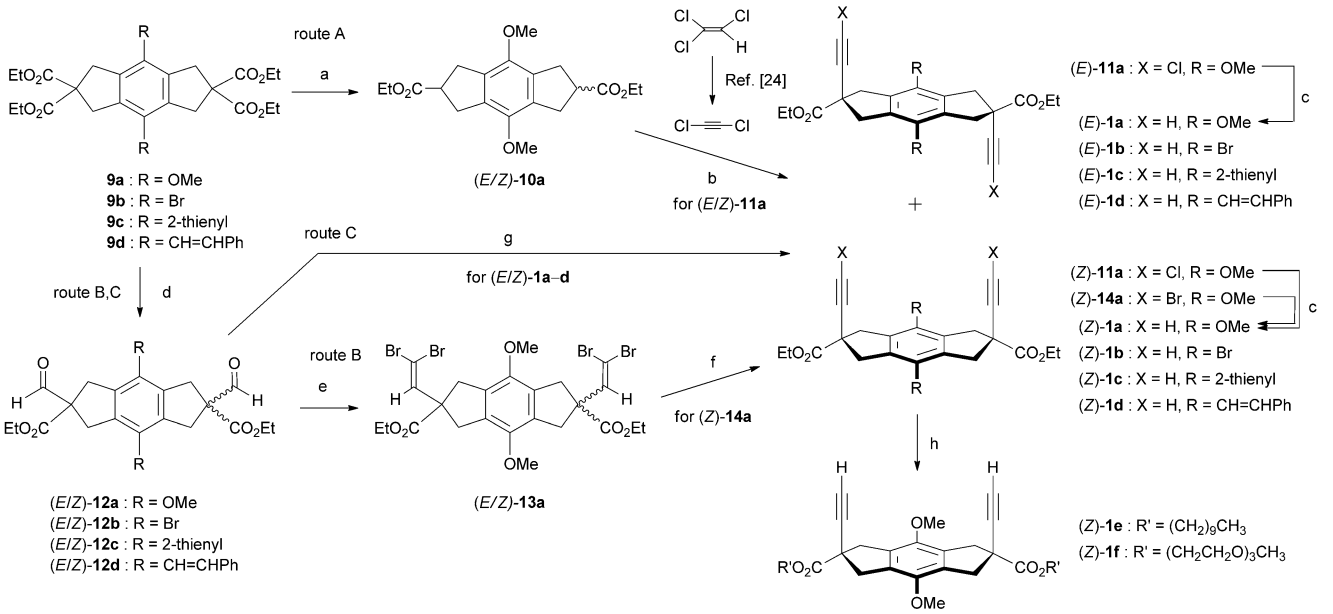


Figure 1. X-ray structures of 4,8-disubstituted hydrindacene derivatives **9a**, **9c**, and **9d**. Atoms in thienyl groups of **9c** are positionally disordered.

Preparation of 2,6-diethynyl hydrindacene monomer units: The monomer unit, 2,6-diethynyl derivative (*Z*)-**1a**, was prepared from the tetraester **9a** by using one of three possible methods for the introduction of the ethynyl groups, as shown in Scheme 3. These three routes were: A) the chloroethynylation of enolates as developed by Kende et al.,[26] B) the conversion of formyl groups to ethynyl groups by the Corey–Fuchs method[27] following selective reduction of the *gem*-diester to the monoaldehyde as developed by Burton and co-workers,[28] or C) the conversion of formyl groups to ethynyl groups by the Ohira–Bestmann method.[29]

Initially, 2,6-diethynyl derivative (*Z*)-**1a** was prepared by means of chloroethynylation at the 2,6-positions of (*E*/*Z*)-**10a** (route A). Decarboxylation of **9a** in DMSO gave the diester (*E*/*Z*)-**10a**. Treatment of (*E*/*Z*)-**10a** with lithium diisopropylamide (LDA) at −40°C and the subsequent addition of an excess amount of dichloroacetylene[26] in diethyl ether at −20°C gave an isomeric mixture of the 2,6-bis(-chloroethynyl) derivative (*E*)- and (*Z*)-**11a** in 20 and 15% yields, respectively. The structure of (*Z*)-**11a** was confirmed through X-ray crystallography after chromatographic separation of the isomers (Figure 2). Dechlorination[26] of (*E*)-**11a** and (*Z*)-**11a** with copper gave (*E*)-**1a** and (*Z*)-**1a** in 39 and 71% yields, respectively.

Secondly, (*Z*)-**1a** was also prepared by an alternative method through the selective reduction of the *gem*-diester to the monoaldehyde by means of the process developed by Burton et al.,[28] followed by Corey–Fuchs ethynylation[27] (route B). Reduction of the tetraester **9a** with an excess amount of diisobutylaluminium hydride (DIBAL-H) at −78°C gave an isomeric mixture of the 2,6-dialdehyde (*E*/*Z*)-**12a** in a ratio of 1:1. Treatment of (*E*/*Z*)-**12a** with CBr_4/



Scheme 3. Preparation of monomer units (*Z*)-**1a**–**d**. a) NaCl, H_2O, DMSO, 170°C, 69%; b) LDA, hexamethylphosphoramide (HMPA), THF, −78°C, then dichloroacetylene in Et_2O,[24] −20 to 25°C, 20% for (*E*)-**11a**, 15% for (*Z*)-**11a**; c) Cu powder, AcOH/THF, 70°C, 39% for (*E*)-**1a**, 71% for (*Z*)-**1a** (from (*Z*)-**11a**) and 71% for (*Z*)-**1a** (from (*Z*)-**14a**); d) DIBAL-H, CH_2Cl_2, −78°C; e) CBr_4, PPh_3, CH_2Cl_2, 0 to 25°C, 30% for (*E*)-**13a**, 31% for (*Z*)-**13a** (two steps, respectively); f) KHMDS, THF, −78°C, 92% for (*Z*)-**14a**; g) dimethyl 1-diazo-2-oxopropylphosphonate (Ohira–Bestmann reagent), EtONa, THF −78°C, then (*E*/*Z*)-**12a**–**d**, −78 to 25°C, 40% for (*E*/*Z*)-**1a**; 38% for (*E*/*Z*)-**1b**; 45% for (*E*/*Z*)-**1c**; 53% for (*E*/*Z*)-**1d** (1:1, two steps, respectively); h) 1) (*Z*)-**1a**, LiOH, H_2O/THF, 23°C; 2) $SOCl_2$, CH_2Cl_2, 40°C; 3) *n*-decanol or $CH_3(OCH_2CH_2)_3OH$, Et_3N, CH_2Cl_2, 21°C, 49% for (*Z*)-**1e**, 29% for (*Z*)-**1f** (three steps, respectively).

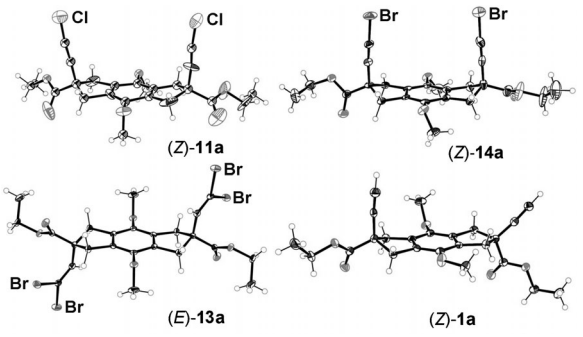
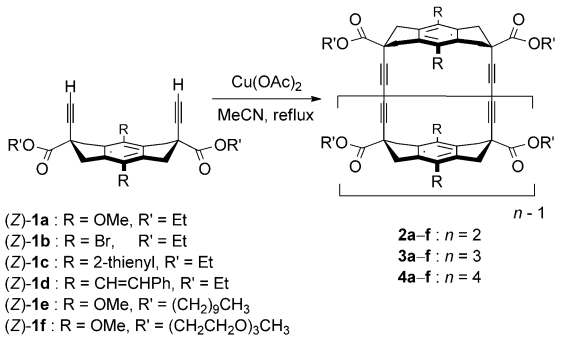


Figure 2. X-ray structures of hydrindacene derivatives.



Scheme 4. Macrocyclization of diethynylhydrindacenes (*Z*)-**1a–f**.

PPh_3[27] gave the 2,6-bis(dibromoethenyl) derivative (*E*)- and (*Z*)-**13a** in 30 and 31% yields, respectively. After chromatographic separation of the isomers, treatment of (*Z*)-**13a** with potassium bis(trimethylsilyl)amide (KHMDS) and the subsequent debromination of (*Z*)-**14a** with copper gave (*Z*)-**1a** in 92% yield. The structures of (*E*)-**13a**, (*Z*)-**14a** and (*Z*)-**1a** were confirmed through X-ray crystallography and are presented in Figure 2.

Table 1. Reaction conditions and yields for macrocycles **1a–f**.

	c [mM]	Isolated yields[a] [%]				
		2 (*n*=2)	**3** (*n*=3)	**4** (*n*=4)	Oligomer (*n*=5–6)	Total
1a	1	31	12	4	8	55
1a	10	42	35	5	8	91
1a	100	3	13	6	6	29
1b	10	39	26	12	13	90
1c	10	52	22	8	8	90
1d	5	64	13	–	–	77
1e	10	56	25	–	–	81
1f	10	18	11	–	–[b]	29

[a] The product ratios were determined by GPC separation and quantitation. [b] The oligomer could not be obtained due to its solubility to water.[32]

Lastly, (*Z*)-**1a** was more readily prepared by treating the dialdehyde (*E*/*Z*)-**12a** with Ohira–Bestmann reagent[29] (route C). Upon addition of (*E*/*Z*)-**12a** to a solution of Ohira–Bestmann reagent pretreated with NaOEt in THF at −78 °C,[30] a 1:1 isomeric mixture of the 2,6-diethynyl derivative (*E*/*Z*)-**1a** was successfully produced. A similar reaction scheme that uses K_2CO_3 as a base in MeOH at room temperature only gave the retro-Claisen product (*E*/*Z*)-**10a**. The 4,8-dibromo-, 4,8-bis(2-thienyl)-, and 4,8-distyryl derivatives (*E*/*Z*)-**1b–d** were also prepared by route C. The *E* and *Z* isomers of **1a–d** were separated by high-performance liquid chromatography (HPLC).

Modification of the ester groups on the hydrindacene units of (*Z*)-**1a** offers an opportunity to add a wide variety of moieties to these macrocycles. Saponification of ethyl ester groups of (*Z*)-**1a** with LiOH and subsequent treatments with $SOCl_2$ and 1-decanol or triethyleneglycol monomethyl ether gave the decyl ester **1e** or the triethyleneglycol (TEG) ester **1f**.

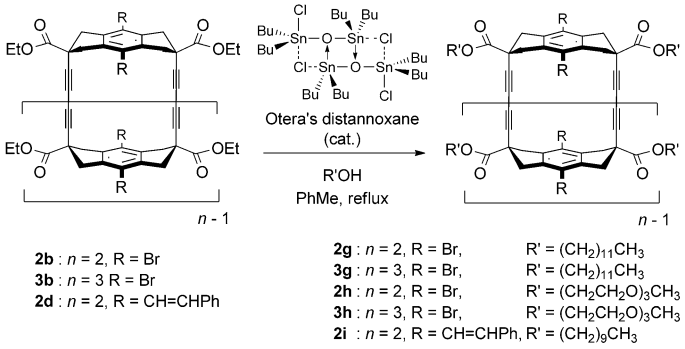
Macrocyclization of 2,6-diethynyl hydrindacenes (*Z*)-1a–d: Macrocyclization of the methoxy monomer (*Z*)-**1a** (10 mM) under modified Eglinton coupling[31] conditions using $Cu(OAc)_2$ in MeCN successfully produced a series of macrocycles including dimer **2a**, trimer **3a**, and tetramer **4a**, as well as higher oligomers in good total yields (Scheme 4, Table 1). The size distribution of the resulting macrocycles in these crude mixtures varied according to the concentration of the starting material (*Z*)-**1** used in the macrocyclization reaction, an effect that is highlighted by the relatively high proportion of dimer formed in the case of **1d**, for which a concentration of only 5 mM was employed. When either 1 or 10 mM solutions of (*Z*)-**1a** were used, the dimer **2a** was the major product, although the total yield of macrocycles was lower with the 1 mM solution. At a higher concentration of (*Z*)-**1a** (100 mM), a greater proportion of the larger oligomers resulted, with trimer **3a** as the major product. In contrast, treatment of (*Z*)-**1a** (10 mM) with $Cu(OAc)_2$ and CuCl in pyridine resulted in the formation of a complex mixture of products, and macrocycles **2a–4a** were isolated in low overall yields of 10%.

Macrocyclization of the bromo monomer (*Z*)-**1b** or thienyl monomer (*Z*)-**1c** (10 mM) produced mixtures that contained various sizes, including **2b–4b** or **2c–4c**, results that are somewhat similar to those observed when using (*Z*)-**1a**. Following the reaction of styryl monomer (*Z*)-**1d** suspended in MeCN, macrocyclic dimer **2d** was preferentially produced along with a smaller amount of trimer **3d**. This distribution of products was likely obtained because the macrocyclization of (*Z*)-**1d** proceeds under quasi-high dilution conditions due to the low solubility of this monomer in MeCN. Macrocyclization of monomers (*Z*)-**1e** and (*Z*)-**1f** under similar coupling conditions gave macrocyclic dimers **2e** and **2f** as the major products,[32] along with trimers **3e** and **3f**.

Dimers **2a–d** were less soluble than the other macrocycles in common organic solvents and were easily isolated by washing the reaction mixtures with $CHCl_3$. The mother liq-

uors were further separated by gel-permeation chromatography (GPC) and macrocycles **3** and **4** were thus also isolated and characterized by mass spectroscopy.

Peripheral modification of hydrindacene-based macrocycles: Modification of the ester groups on the macrocycles offers a means to vary some of the characteristic properties of these compounds. In this work, we chose to use transesterification, which allowed us to readily modify the ester groups by reaction with various alkanols. One result of such transesterification can be the tuning of the solubility of a macrocycle in various solvents. Although the macrocycles with long ester chains (**2e**,**f** and **3e**,**f**) were prepared by macrocyclization of the corresponding monomers (*Z*)-**1e** or (*Z*)-**1f** as shown in Scheme 4, we found that transesterification of macrocycles can be achieved using Otera's distannoxane catalyst[33] (Scheme 5). The ethyl groups on the ester substituents of



2b : *n* = 2, R = Br
3b : *n* = 3 R = Br
2d : *n* = 2, R = CH=CHPh

2g : *n* = 2, R = Br, R' = $(CH_2)_{11}CH_3$
3g : *n* = 3, R = Br, R' = $(CH_2)_{11}CH_3$
2h : *n* = 2, R = Br, R' = $(CH_2CH_2O)_3CH_3$
3h : *n* = 3, R = Br, R' = $(CH_2CH_2O)_3CH_3$
2i : *n* = 2, R = CH=CHPh, R' = $(CH_2)_9CH_3$

Scheme 5. Transesterification of macrocycles by using Otera's distannoxane.[33]

macrocycles **2** and **3** were easily modified by using Otera's distannoxane[33] and 1-dodecanol, 1-decanol, or triethyleneglycol monomethyl ether. The resulting peripherally modified macrocycles with long ester chains (**2g–i** and **3g**,**h**) demonstrated improved solubility in common organic solvents.

X-ray structures of hydrindacene-based macrocycles 2–4: Single crystals of a quality suitable for X-ray crystallography were obtained for dimers **2a**,**b**, trimers **3a**,**b**,**c**, and tetramer **4b**, although attempts to obtain crystal samples from the styryl macrocycles **2d** and **3d** were unsuccessful. X-ray analyses of macrocycles **2a**,**b** and **3a**,**b**,**c** provided unambiguous confirmation of their structures and demonstrated a well-ordered array of functionalities that consisted of a peripheral ester along with methoxy (for **2a** and **3a**), bromo (for **2b** and **3b**), or thienyl groups (for **3c**) vertical to the macrocyclic ring.

The structures determined by X-ray analysis for the dimers **2a** and **2b** indicated two hydrindacene units facing one another in a parallel fashion with a distance between the two units of 7.86 (for **2a**) or 7.70 Å (for **2b**; Figure 3). The butadiyne moieties are arranged in pseudoaxial positions on the five-membered rings of the hydrindacene skeleton and are separated by a distance of 6.76 or 7.14 Å (for **2a** and **2b**, respectively). The resulting cavity in both **2a** and **2b** was found to be empty in the crystal structure, thus indicating that the cavity is too small to include any guest solvent molecules.

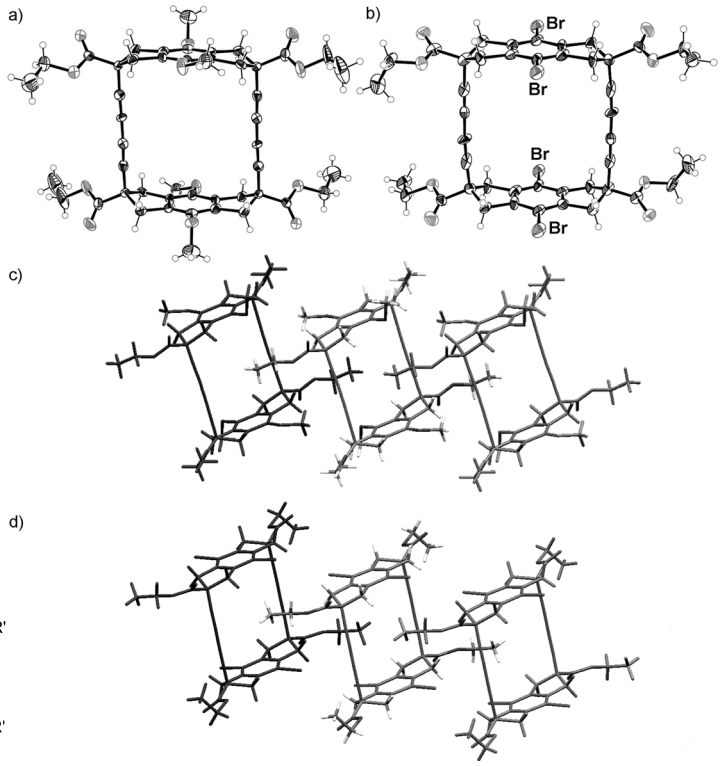


Figure 3. X-ray structures of a) **2a**·hexane solvate and b) **2b**, and c,d) their packing structures. A solvated hexane molecule in the crystal of **2a** is located outside the cavity and omitted for clarity.

In trimers **3a–c**, the macrocyclic frame adopts not a hexagonal shape with (pseudo-)D_{3h} symmetry, but rather a distorted rectangular conformation (Figure 4). Two hydrindacene units face one another nearly in parallel at a distance of 7.70, 8.47, or 8.04 Å for **3a**, **3b**, and **3c**, respectively, and are positioned at close to right angles to the third hydrindacene unit. The distances spanned by the hydrindacene and butadiyne units along the long axis of the void are 14.0, 13.4, and 13.8 Å for **3a**, **3b**, and **3c**, respectively. The butadiyne moieties along the central portion of the long axis occupy pseudoequatorial positions, thereby resulting in the rectangular shape of the macrocycles. X-ray analysis further demonstrated that one or more solvent molecules, such as hexane, $CHCl_3$, or cyclohexane, were captured within the cavities of these trimers. Macrocycles **3a**,**c**, with methoxy or thienyl groups as vertical substituents, stacked into a columnar structure with an offset packing, thus avoiding intermolecular contact between the methoxy or thienyl groups (Figure 4a,c). Solvent molecules in the **3a** crystals appear to be strongly held within the macrocycle cavity and were not removed even under vacuum, presumably due to buttressing effects by the neighboring methoxy groups. Interestingly, the

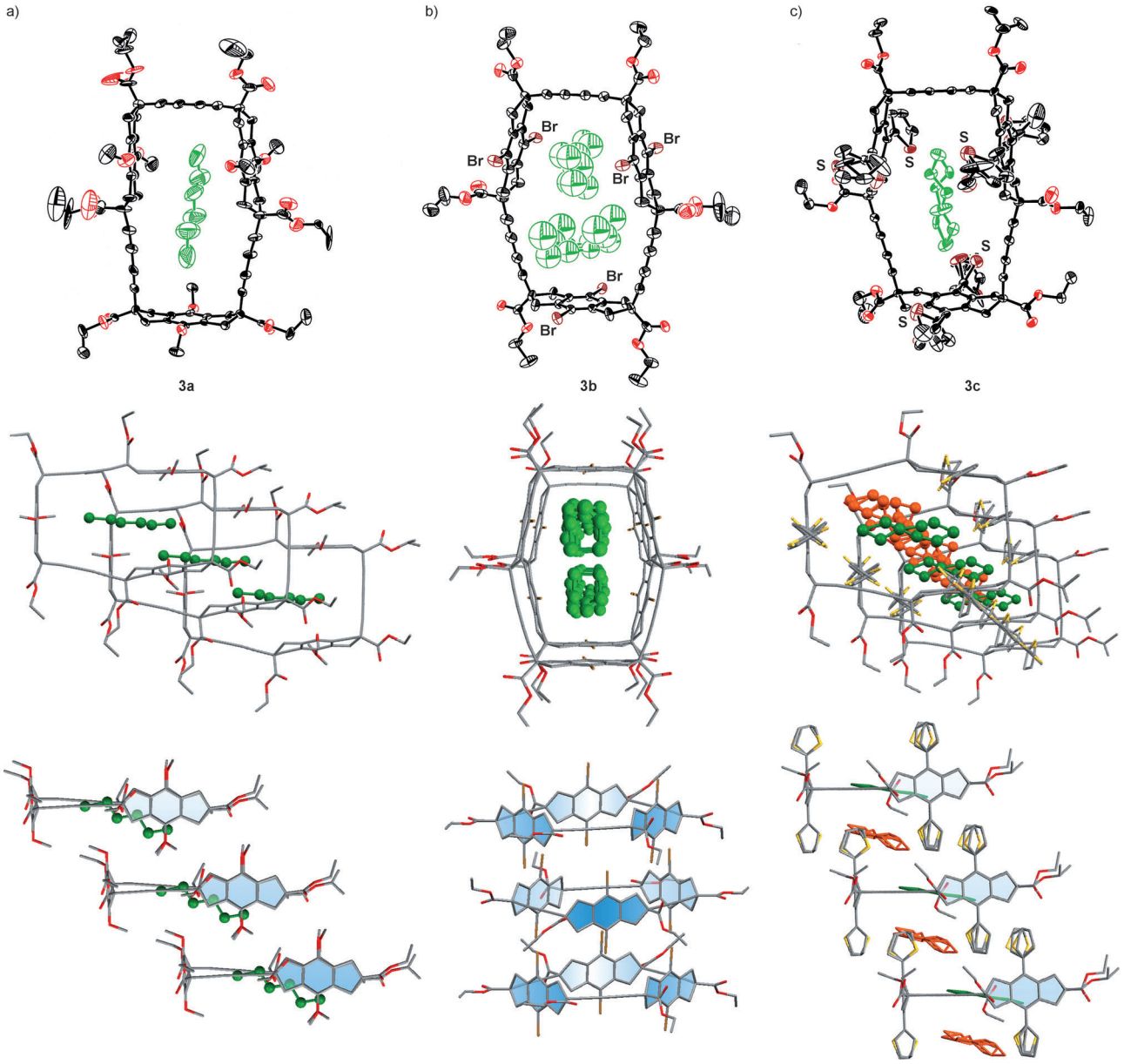


Figure 4. X-ray structures (top) and their packing structures (middle and bottom) of a) **3a**·hexane solvate, b) **3b**·(cyclohexane)$_2$ solvate, and c) **3b**·(hexane)$_{2.5}$·(benzene)$_{2.5}$ solvate. One methoxy group and one of the ethyl groups of **3a** are disordered. Cyclohexanes in **3b** are disordered. Five thienyl groups and one of the ethyl groups of **3c** and solvated hexanes are disordered. Hydrogen atoms are omitted for clarity.

macrocycle **3b** instead stacked into a tubelike structure with a 1D channel-like cavity, in which the three butadiynes and six bromo groups of neighboring macrocycles are in close proximity at distances of 3.30 to 3.66 Å (Figure 4b). The highly disordered packing of cyclohexane molecules within this cavity indicates that such solvent molecules do not undergo specific interactions with the columnar channel.

The tetramer **4b** has a tub-shaped structure, in which all butadiyne moieties are located at a pseudoaxial position on the cyclopentene rings (Figure 5). Four molecules of CH_2Cl_2 are trapped in the cavity of the tub. Interhalogen interactions between adjacent bromo groups (at a distance of 5.09 and 5.31 Å), as well as a preferred conformation for the structure in which the orientation of the butadiyne groups is pseudoaxial, could account for the observed shrunken tub structure taking precedence over an open-extended structure with a larger cavity.

Spectroscopic characterization of the hydrindacene-based macrocycles

^1H NMR spectra: ^{1}H NMR spectra of all macrocycles in $CDCl_3$ indicated a high degree of symmetry (D_{nh}) in these species (Figure 6). Evidently the high symmetry (D_{3h}) of the trimer **3a** in solution differs from the pseudo-C_{2v} symmetry adopted in the crystal. Although the ^{1}H NMR spectrum of

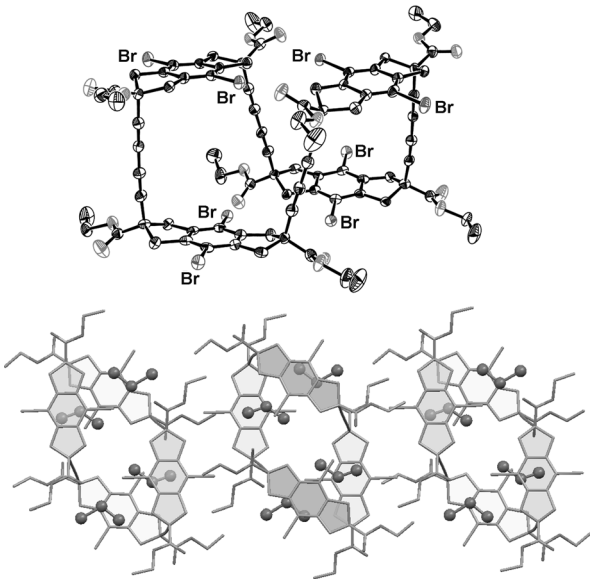


Figure 5. X-ray structure of **4b**·$(CH_2Cl_2)_4$ and its packing structure. Hydrogen atoms are omitted for clarity.

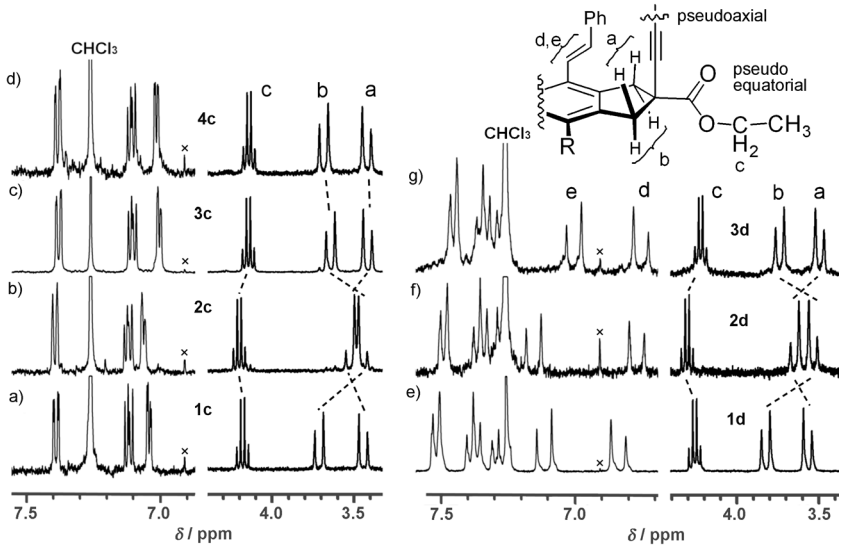


Figure 6. ^{1}H NMR spectra of a) monomer (*Z*)-**1c**; b) macrocycles **2c**, c) **3c**, and d) **4c**; e) monomer (*Z*)-**1d**; f) macrocycles **2d**; and g) **3d** in $CDCl_3$ at 295 K.

3a did not change upon lowering the solution temperature to −92 °C in CD_2Cl_2, the most stable conformer of **3a** is likely to adopt a rectangular shape with C_{2v} symmetry. Accordingly, this apparent D_{3h} symmetry is achieved by means of a rapid degenerate conformational change accompanied by flipping of the alicyclic rings of the hydrindacene units, since a hexagonal shape would force all alicyclic rings to adopt an unstable flattened conformation and thus is not favored for this macrocycle (see Figure S1 in the Supporting Information). The apparent high symmetry of the tetramer **4a** also originates in the rapid conformational changes between two degenerate folded tub forms.

It should be noted that the signals from dimers **2a–d** appear at shifted positions relative to the corresponding signals of the larger macrocycles **3a–d** and **4a–c**, as well as those of the precursor species **1a–d**. Notably, one of the signals from the protons of the five-membered ring of **2a–d** (H_b) appears at an upfield-shifted position around $\delta =$ 3.5 ppm, an effect that can be attributed to the conformational rigidity of the hydrindacene units in the dimer. When the ester group is located at the pseudoaxial position on the five-membered ring of a hydrindacene unit, the protons (H_b) of five-membered rings near the ester group experience a stronger deshielding effect from the carbonyl of the ester group than from the alkyne group, thereby causing those signals to appear at lower-field positions (see the Supporting Information). The larger macrocycles **3a–d** and **4a–c**, as well as the precursor species **1a–d**, all of which have moderately flexible five-membered rings, exhibit this effect, although the rigid macrocycles **2a–d** with ester groups at the pseudoequatorial position do not. Our conclusion that the population of ester groups that actually occupies pseudoaxial positions is greater in the monomers **1**, trimers **3**, and tetramers **4** than in the dimers **2** was also confirmed by observing that the methylene protons (H_c) of the ethyl ester groups of **1a–d**, **3a–d**, and **4a–c** appear at upfield-shifted positions (at $\delta = 4.1$ to 4.2 ppm) due to shielding from the benzene rings of the hydrindacene unit relative to the same protons in **2a–d** (at $\delta = 4.2$ to 4.3 ppm). These observations indicate that dimers **2a–d** possess a rigid macrocyclic framework, whereas trimers **3** and tetramers **4**, as well as monomers **1**, have a moderately flexible structure based on flipping of the five-membered rings.

UV-visible and fluorescence spectra: The spectroscopic properties of the macrocyclic dimers **2c**,**d**, trimers **3c**,**d**, and monomers **1c**,**d** are shown in Figure 7. The molar absorption coefficients for each species show multiplication by the number of chromophoric units in the structure. From the normalized data obtained by instead dividing by the number of chromophoric units (see the Supporting Information), it is evident that the molar absorption per hydrindacene unit shows a hypochromic shift in dimers **2c**,**d** relative to monomers **1c**,**d**. Slight blueshifts were observed in the UV-visible spectra of the dimers **2a–d** relative to **1a–d** (3, 1, 5, and 5 nm for **2a**, **2b**, **2c**, and **2d**, respectively; Table 2). Additionally, slight redshifts were observed in the fluorescence spectrum of dimer **2c** relative to **1c** and **3c**

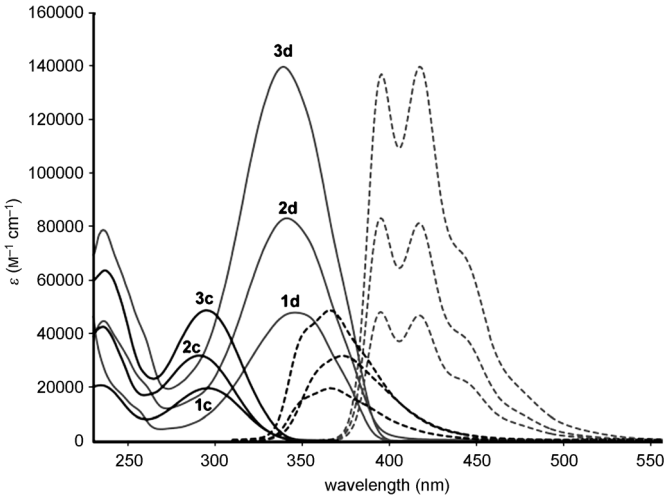


Figure 7. UV/Vis (solid line) and fluorescence spectra (dashed line) of a) (*E*)-**1c**, **2c**, and **3c**; and b) (*E*)-**1d**, **2d**, and **3d** in CH_2Cl_2.

Table 2. Optical data of monomers **1a–d** and macrocycles **2a–d** and **3a–d**.

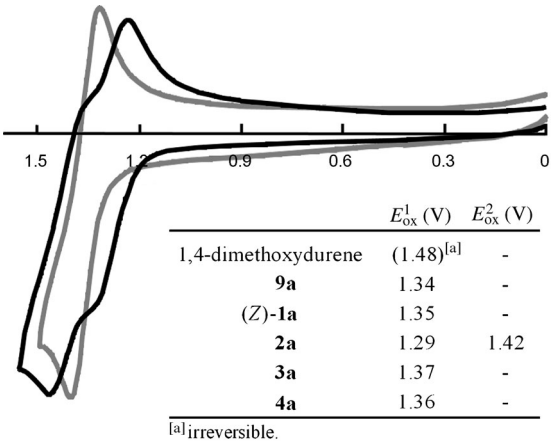
	Absorption λ_{max} [nm]	Emission λ_{em} [nm]	Stokes shift [nm]
3a	284	–	–
2a	284	–	–
(*Z*)-**1a**	283	328	49
3b	286	–	–
2b	286	–	–
(*E*)-**1b**	285	–	–
3c	295	353, 366	58
2c	291	360, 374	69
(*E*)-**1c**	296	352, 366	56
3d	339	395, 417	56
2d	341	395, 417	54
(*E*)-**1d**	346	395, 417	49

(8 nm redshifted from both **1c** and **3c**). The methoxy and bromo derivatives **2a**,**b** and **3a**,**b** are nonfluorescent.

Since the distances of 7.7 to 7.9 Å between the two hydrindacene units in the dimers **2a–d** are too great to allow direct interaction in a through-space manner,[34] the larger Stokes shift observed in **2c** relative to trimer **3c** might be attributed to the excited-state coupling of the hydrindacene chromophores of **2** and the butadiyne units arranged vertically between the two hydrindacene units. Due to the overlapping of the absorption band of the butadiyne and the hydrindacene chromophore in **1a–c** (at $\lambda_{max} \approx 270$ nm for each relevant compound[35,36]), their excited states might be effectively delocalized over the entire molecule in the dimer structure (see the calculated molecular orbitals (MOs) in Figure 9 below).[37]

A coupled excited state appears to be energetically unfavorable in the case of the styryl macrocycles **2d** and **3d**. Interactions among hydrindacene units were not observed even in dimer **2d**, although a series of styryl-substituted hydrindacene derivatives (**1d**, **2d**, **3d**, and **9d**) efficiently emit fluorescence bands in the region of 400 nm both in solution and in the solid state ($\phi = 0.89$ for **1d**, 0.92 for **2d**, approximately 1.0 for **9d** in CH_2Cl_2, 0.17 for **2d**, 0.61 for **9d** as a solid, respectively). These differences might be due to the fact that the excited-state energy of the distyrylbenzene chromophore is lower than that of the butadiyne unit.[37]

Cyclic voltammetry: The interunit interactions[34] within the macrocyclic dimer were also evident in the redox properties of the methoxy macrocycles **2a–4a**. These macrocycles, along with reference compounds **1a**, **9a**, and 1,4-dimethoxydurene, were analyzed by cyclic voltammetry in CH_2Cl_2 that contained 0.1 M Bu_4NPF_6 as a supporting electrolyte (Figure 8). The 4,8-dimethoxyhydrindacene derivatives **1a–4a** and **9a** show reversible oxidation waves around +1.35 V ($E_{1/2} = +1.29$ and +1.42 V for **2a**, +1.37 V for **3a**, +1.36 V for **4a**, +1.35 V for **1a**, and +1.34 V for **9a** versus SCE). In contrast, 1,4-dimethoxydurene shows irreversible oxidation peaks at a higher potential ($E_{1/2} = +1.48$ V). This can be accounted for by considering that the methoxy groups in this species cannot adopt coplanar arrangements with the benzene nuclei in the cationic state due to steric hindrance, so that a positive charge cannot be delocalized over the methoxy lone pair.[39] Thus, the reversibility upon oxidation of the hydrindacene derivatives **1a–4a** and **9a** can be attributed to the decrease in steric hindrance around the methoxy groups on the benzene ring, which is achieved by binding neighboring alkyl groups on the aromatic ring into alicyclic structures.[39a–c]



	E^1_{ox} (V)	E^2_{ox} (V)
1,4-dimethoxydurene	(1.48)[a]	-
9a	1.34	-
(*Z*)-**1a**	1.35	-
2a	1.29	1.42
3a	1.37	-
4a	1.36	-

[a] irreversible.

Figure 8. Cyclic voltammograms of a) **2a** (black line) and b) **3a** (gray line) measured in CH_2Cl_2 containing 0.1 M nBu_4NPF_6 (Pt electrode, scan rate: 100 mV s^{-1}).

It is interesting to note that dimer **2a** shows two well-resolved and reversible waves at $E_{ox} = +1.29$ and +1.42 V, whereas trimer **3a** and tetramer **4a** show only one reversible wave around +1.36 V. Because each hydrindacene unit should undergo one-electron oxidation at this potential, it is highly likely that there is an electronic interaction between the two hydrindacene units in the cation radical $\mathbf{2a}^{+\bullet}$, which makes further oxidation of $\mathbf{2a}^{+\bullet}$ to the dication $\mathbf{2a}^{2+}$ difficult. Considering that the analogous tetramethoxy-

[7.7]paracyclophane derivative, with an interplanar distance of 7.38 Å, shows only one reversible peak,[34c] the potential difference of 0.13 V observed in dimer **2a** (with an interplanar distance of 7.86 Å between its two hydrindacene units) presumably does not stem from through-space interaction,[34] but rather from through-bond interaction. The absence of such bond interactions in trimer **3a** or tetramer **4a** can be explained by considering their flexible structures. Thus, a rigid macrocycle framework that favors through-bond interactions is necessary for the stepwise oxidation observed in the dimer.

Theoretical calculation: To elucidate the observed electronic interactions between the two hydrindacene units in dimer **2a**, we performed density functional theory (DFT) calculations with regard to both dimers **2a** and **2c**, as well as radical cation $\mathbf{2a}^{+\bullet}$. The optimized geometric parameters of these macrocycles calculated at the B3LYP/6-31G* level[40,41] are in good agreement with the experimental data obtained for their solid-state structures. Orbital-coefficient contours of the HOMOs and LUMOs of dimers **2a**,**c** demonstrate that a significant interaction exists between the two hydrindacene units through the butadiyne units (Figure 9). The through-bond coupling between the orbitals of the substituted benzene portions of the hydrindacene units and those of the butadiyne units yields the following: bonding HOMO−1, *anti*-bonding HOMO, bonding LUMO, and *anti*-bonding LUMO+1. The calculated gaps between HOMO and HOMO−1 are 0.10 eV (LUMO and LUMO+1: 0.11 eV) for **2a** and 0.04 eV (LUMO and LUMO+1: 0.07 eV) for **2c**. In the optimized structure of radical cation $\mathbf{2a}^{+\bullet}$, orbital-coefficient contours of the singly occupied molecular orbital (SOMO) demonstrate that a similar interaction exists between the two hydrindacene units through the butadiyne units, thus suggesting electronic delocalization in the one-electron-oxidated state (Figure S3 in the Supporting Information).

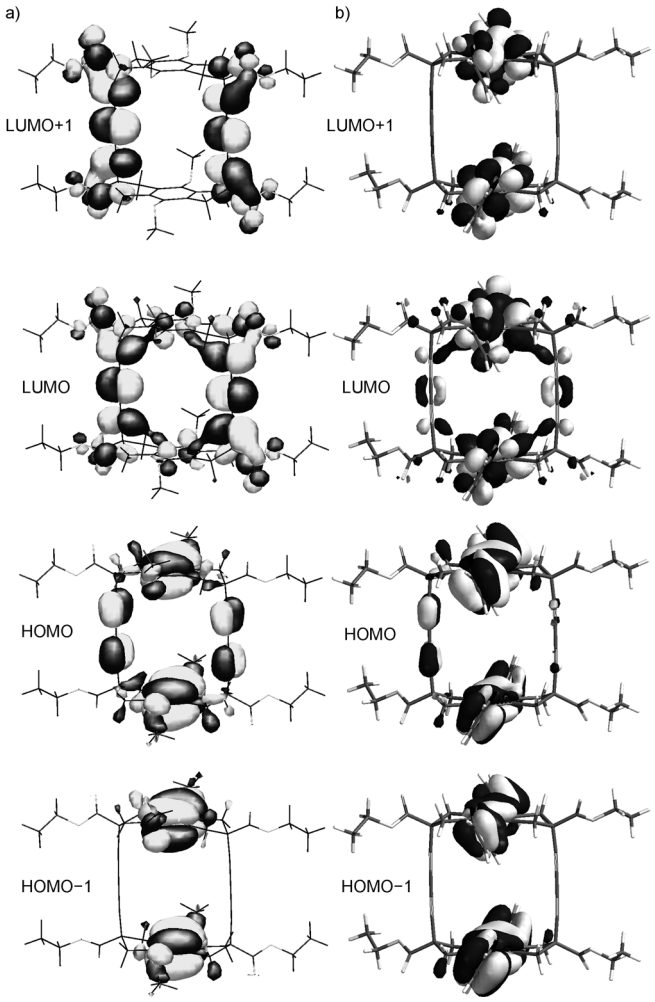


Figure 9. Pictorial presentations of HOMOs and LUMOs in a) macrocyclic dimers **2a** and b) **2c** calculated at the B3LYP/6-31G* level.

Conclusion

We have shown that the macrocyclization of a series of (*Z*)-2,6-diethynyl hydrindacenes ((*Z*)-**1**) with functional groups at mutually perpendicular positions results in the formation of novel macrocycles with directionally persistent peripheral functionalities as a result of rotational fixation of the hydrindacene units. Analysis of the resulting macrocycles has demonstrated several interesting characteristics, including that the two hydrindacene units in the macrocyclic dimers (**2**) might interact electronically through their butadiyne moieties. The macrocyclic trimers (**3**) exhibit moderate geometrical flexibility and possess a central cavity that is large enough to accommodate molecules of common organic solvents. Furthermore, peripheral ester groups were readily modified to introduce hydrophobic or hydrophilic chains through the use of Otera's distannoxane catalyst. Some of these modified macrocycles could have the capacity for tunable solubility and subsequent assembly into tubelike structures when in solution, with the result of adjusting their affinity towards membranes[2b,i,42] or other substrate surfaces.[2d] The introduction of π-conjugated groups, such as styryl and thienyl groups (as in **2c**,**d** and **3c**,**d**), or hydrogen-bonding groups such as amides[17,18] to the 4,8-positions of the hydrindacene unit could allow the possibility of π-conjugated or self-assembled nanotubes. We are currently studying various functionalization options with the goal of assembling such macrocycles into tubular structures.

Experimental Section

General method for the macrocyclization of (*Z*)-1: A mixture of (*Z*)-**1** and $Cu(OAc)_2$ (20 equiv) in CH_3CN was heated at reflux for 25 h. After the mixture was cooled, water was added, and the solution was extracted with $CHCl_3$. The organic layer was washed with water and brine, dried over Na_2SO_4, and then filtered. A small amount of $CHCl_3$ was added to the white solid obtained by evaporation of the solvent to give a suspension. Macrocycles **2a**–**d** were obtained by filtration of the suspension.

Other macrocycles **3a–d**, **4a–c**, and higher oligomers were separated by GPC (eluting with $CHCl_3$) of the filtrate.

Methoxy macrocycles 2a–4a with ethyl esters: Macrocycles **2a–4a** were prepared from (*Z*)-**1a** (28 mg, 68 μmol) and $Cu(OAc)_2$ (220 mg, 1.22 mmol) in CH_3CN (5.0 mL). GPC separation of the crude product gave dimer **2a** (11.6 mg, 46%), trimer **3a** (9.8 mg, 39%), tetramer **4a** (1.5 mg, 6%), and higher oligomer (2.5 mg, 10%) as white solids, respectively.

Dimer 2a: M.p. 269.0–270.0°C; ^{1}H NMR: δ=4.27 (q, J=7.2 Hz, 8H), 3.73 (s, 12H), 3.44 (d, J=15.6 Hz, 8H), 3.38 (d, J=15.6 Hz, 8H), 1.34 ppm (t, J=7.2 Hz, 12H); ^{13}C NMR: δ=171.35, 148.23, 131.18, 79.27, 66.66, 62.21, 59.84, 50.13, 41.96, 14.15 ppm; IR (KBr): $\tilde{\nu}$=2978, 1740, 1482, 1290, 1264, 1236, 1090, 1050 cm^{-1}; MS (FD): *m*/*z* (%): 817 [M^++1] (55), 816 [M^+] (100), 408 [M^{2+}] (18); HRMS (FD): *m*/*z*: calcd for $C_{48}H_{48}O_{12}$: 816.3146; found: 816.3136; elemental analysis calcd (%) for $C_{48}H_{48}O_{12}$·H_2O: C 69.05, H 6.04; found: C 69.25, H 6.30.

Trimer 3a: M.p. 192.0–194.0°C; ^{1}H NMR: δ=4.22 (q, J=7.2 Hz, 12H), 3.74 (s, 18H), 3.56 (d, J=15.6 Hz, 12H), 3.31 (d, J=15.6 Hz, 12H), 1.29 ppm (t, J=7.2 Hz, 18H); ^{13}C NMR: δ=171.23, 148.06, 131.73, 79.72, 66.62, 62.29, 59.90, 49.11, 41.87, 14.05 ppm; IR (KBr): $\tilde{\nu}$=2980, 1738, 1482, 1292, 1234, 1184, 1090, 1048 cm^{-1}; MS (FD): *m*/*z* (%): 1226 [M^++2] (46), 1225 [M^++1] (85), 1224 [M^+] (100), 613 [M^{2+}] (25); HRMS (FD): *m*/*z*: calcd for $C_{72}H_{72}O_{18}$: 1224.4719; found: 1224.4695; elemental analysis calcd (%) for $C_{72}H_{72}O_{18}$·H_2O: C 69.55, H 6.00; found: C 69.46, H 6.26.

Tetramer 4a: ^{1}H NMR: δ=4.23 (q, J=7.2 Hz, 16H), 3.75 (s, 24H), 3.58 (d, J=15.6 Hz, 16H), 3.34 (d, J=15.6 Hz, 16H), 1.31 ppm (t, J=7.2 Hz, 24H); ^{13}C NMR: δ=171.28, 148.05, 131.69, 79.74, 66.6a, 62.30, 59.88, 49.02, 41.94, 14.07 ppm; IR (KBr): $\tilde{\nu}$=2928, 1738, 1480, 1292, 1234, 1186, 1090, 1038 cm^{-1}; MS (FD): *m*/*z* (%): 1634 [M^++2] (42), 1633 [M^++1] (100), 1632 [M^+] (66), 817 [M^{2+}+1] (39), 816 [M^{2+}] (27); HRMS (FD): *m*/*z*: calcd for $C_{96}H_{96}O_{24}$: 1632.6292; found: 1632.6259.

Bromo macrocycles 2b–4b with ethyl esters: Macrocycles **2b–4b** were prepared from (*Z*)-**1b** (35 mg, 69 μmol) and $Cu(OAc)_2$ (252 mg, 1.39 mmol) in CH_3CN (6.9 mL). $CHCl_3$ (3 mL) was added to the crude product after workup, and the mixture was filtered to give dimer **2b** (11.4 mg, 33%) as a white solid. GPC separation of the filtrate gave dimer **2b** (2.2 mg, 6%, total 39%), trimer **3b** (9.2 mg, 26%), tetramer **4b** (4.1 mg, 12%), and higher oligomer (4.6 mg, 13%) as white solids, respectively.

Dimer 2b: M.p. 240–242°C (decomp); ^{1}H NMR: δ=4.28 (q, J=7.1 Hz, 8H), 3.56 (d, J=15.4 Hz, 8H), 3.45 (d, J=15.4 Hz, 8H), 1.35 ppm (t, J=7.1 Hz, 12H); ^{13}C NMR: δ=170.41, 140.68, 115.53, 78.94, 67.20, 62.50, 48.38, 46.47, 14.13 ppm; IR (KBr): $\tilde{\nu}$=2977, 2925, 2172, 1740, 1443, 1066, 908, 857 cm^{-1}; MS (FD): *m*/*z* (%): 1016 [M^++8] (27), 1015 [M^++7] (33), 1014 [M^++6] (67), 1013 [M^++5] (42), 1012 [M^++4] (100), 1011 [M^++3] (31), 1010 [M^++2] (68), 1016 [M^+] (22); elemental analysis calcd (%) for $C_{44}H_{36}Br_4O_8$·H_2O: C 51.29, H 3.72; found: C 51.23, H 3.55.

Trimer 3b: M.p. 212–214°C (decomp); ^{1}H NMR: δ=4.25 (q, J=7.1 Hz, 12H), 3.67 (d, J=16.1 Hz, 12H), 3.42 (d, J=16.1 Hz, 12H), 1.31 ppm (t, J=7.1 Hz, 18H); ^{13}C NMR: δ=170.73, 140.57, 115.13, 79.48, 66.94, 62.60, 47.03, 46.75, 14.03 ppm; IR (KBr): $\tilde{\nu}$=2978, 2924, 2172, 1739, 1443, 1236, 1185, 1061, 799 cm^{-1}; MS (FD): *m*/*z* (%): 1524 [M^++12] (28), 1522 [M^++10] (59), 1520 [M^++8] (78), 1518 [M^++6] (100), 1516 [M^++4] (78), 1514 [M^++2] (41), 11512 [M^+] (13); elemental analysis calcd (%) for $C_{66}H_{54}Br_6O_{18}$: C 52.20, H 3.58; found: C 52.39, H 3.86.

Tetramer 4b: M.p. 180–183°C (decomp); ^{1}H NMR: δ=4.27 (q, J=7.1 Hz, 16H), 3.65 (d, J=16.1 Hz, 16H), 3.48 (d, J=16.1 Hz, 16H), 1.34 ppm (t, J=7.1 Hz, 24H); ^{13}C NMR: δ=170.77, 140.53, 115.25, 79.65, 66.93, 62.63, 47.09, 46.80, 14.11 ppm; IR (KBr): $\tilde{\nu}$=2925, 2172, 1740, 1631, 1442, 1236, 1058, 799 cm^{-1}; MS (FD): *m*/*z* (%): 2024.4 [M^+] (100), 1013.1 [M^{2+}] (43); HRMS (FD): *m*/*z*: calcd for $C_{88}H_{72}Br_8O_{16}$: 2015.8287; found: 2048.4442.

Thienyl macrocycles 2c–4c with ethyl esters: Macrocycles **2c–4c** were prepared from (*Z*)-**1c** (17.6 mg, 34 μmol) and $Cu(OAc)_2$ (124 mg, 0.68 mmol) in CH_3CN (3.4 mL). GPC separation of the crude product gave dimer **2c** (9.2 mg, 53%), trimer **3a** (3.7 mg, 21%), tetramer **4a** (1.9 mg, 11%), and higher oligomer (0.7 mg, 4%) as white solids, respectively.

Dimer 2c: M.p. 255.0–259.0°C; ^{1}H NMR: δ=7.39 (d, J=5.1 Hz, 4H), 7.12 (dd, J=3.6 Hz, 5.1 Hz, 4H), 7.06 (d, J=3.6 Hz, 4H), 4.20 (q, J=7.1 Hz, 8H), 3.52 (d, J=15.4 Hz, 4H), 3.45 (d, J=15.4 Hz, 8H), 1.28 ppm (t, J=7.1 Hz, 12H); ^{13}C NMR: δ=171.12, 139.01, 138.96, 128.19, 127.18, 127.05, 125.70, 79.82, 67.14, 62.17, 49.41, 44.59, 14.07 ppm; IR (KBr): $\tilde{\nu}$=3101, 2977, 2924 1736, 1235, 1042, 701 cm^{-1}; MS (FD): *m*/*z* (%): 1027 [M^++3] (23), 1026 [M^++2] (47), 1025 [M^++1] (72), 1024 [M^+] (100); HRMS (FD): *m*/*z*: calcd for $C_{60}H_{48}O_8S_4$: 1024.2253; found: 1024.2232.

Trimer 3c: M.p. 186.0–189.0°C; ^{1}H NMR: δ=7.38 (dd, J=0.75 Hz, 5.1 Hz, 6H), 7.10 (dd, J=3.6 Hz, 5.1 Hz, 6H), 7.00 (dd, J=0.75 Hz, 3.6 Hz, 2H), 4.15 (q, J=7.1 Hz, 12H), 3.64 (d, J=15.8 Hz, 12H), 3.42 (d, J=15.8 Hz, 4H), 1.22 ppm (t, J=7.1 Hz, 18H); ^{13}C NMR: δ=171.22, 138.92, 138.78, 127.54, 127.18, 127.07, 125.71, 79.73, 66.57, 62.20, 48.54, 44.86, 13.40 ppm; IR (KBr): $\tilde{\nu}$=3106, 2977, 1736, 1235, 1046, 699 cm^{-1}; MS (FD): *m*/*z* (%): 1540 [M^++4] (27), 1539 [M^++3] (55), 1538 [M^++2] (90), 1538 [M^++1] (100), 1537 [M^+] (100), 1463 [M^+−CO_2Et] (22); HRMS (FD): *m*/*z*: calcd for $C_{90}H_{72}O_{12}S_6$: 1536.3348; found: 1536.3356.

Tetramer 4c: M.p. 220.0–223.0°C; ^{1}H NMR: δ=7.38 (dd, J=0.72 Hz, 4.9 Hz, 8H), 7.11 (dd, J=3.5 Hz, 4.9 Hz, 8H), 7.01 (dd, J=0.72 Hz, 3.5 Hz, 8H), 4.14 (q, J=7.1 Hz, 16H), 3.68 (d, J=15.9 Hz, 16H), 3.42 (d, J=15.9 Hz, 16H), 1.22 ppm (t, J=7.1 Hz, 24H); ^{13}C NMR: δ=171.21, 139.02, 138.67, 127.33, 127.23, 127.07, 79.50, 66.52, 62.25, 48.56, 44.91, 14.00 ppm; IR (KBr): $\tilde{\nu}$=3101, 3074, 2976, 2925, 1736, 1236, 1041, 701 cm^{-1}; MS (FD): *m*/*z* (%): 2054 [M^++5] (30), 2053 [M^++4] (50), 2052 [M^++3] (80), 2051 [M^++2] (100), 2050 [M^++1] (100), 1540 [M^+] (65), 1977 [M^++1−CO_2Et] (33), 1976 [M^+−CO_2Et] (30); HRMS (FD): *m*/*z*: calcd for $C_{120}H_{72}O_{16}S_8$: 2048.4464; found: 2048.4442.

Styryl macrocycles 2d–3d with ethyl esters: Macrocycles **2d–3d** were prepared from (*Z*)-**1d** (24.7 mg, 45 μmol) and $Cu(OAc)_2$ (165 mg, 0.91 mmol) in CH_3CN (9.0 mL). Benzene (5 mL) was added to the crude product after workup, and the mixture was filtered to give dimer **2d** (10.5 mg, 43%) as a white solid. The filtrate was re-precipitated from $CHCl_3$/hexane to give **2d** (2.9 mg, 12%). GPC separation of the filtrate gave dimer **2d** (2.3 mg, 9%, total 64%), trimer **3d** (3.2 mg, 13%), and higher oligomer (3.6 mg, 15%) as white solids, respectively.

Dimer 2d: M.p. 241.5–242.5°C; ^{1}H NMR: δ=7.49 (d, J=7.3 Hz, 8H), 7.36 (t, J=7.1 Hz, 8H), 7.28 (d, J=7.1 Hz, 4H), 7.16 (d, J=16.8 Hz, 4H), 6.77 (d, J=16.8 Hz, 4H), 4.30 (q, J=7.1 Hz, 8H), 3.64 (d, J=15.0 Hz, 8H), 3.53 (d, J=15.0 Hz, 8H) 1.36 ppm (t, J=7.1 Hz, 12H); ^{13}C NMR: δ=171.47, 137.74, 137.33, 133.07, 129.65, 128.73, 127.96, 126.55, 125.41, 79.38, 66.65, 62.32, 49.59, 44.39, 14.18 ppm; IR (KBr): $\tilde{\nu}$=3055, 3025, 2922, 2853, 2169, 1736, 1631, 1448, 1232, 1046, 968 cm^{-1}; MS (FD): *m*/*z* (%): 1106 [M^++2] (41), 1105 [M^++1] (94), 1104 [M^+] (100), 553 [M^{2+}+1] (24), 552 [M^{2+}] (46); HRMS (FD): *m*/*z*: calcd for $C_{76}H_{64}O_8$: 1104.4601; found: 1104.4632.

Trimer 3d: M.p. 213.5–214.5°C; ^{1}H NMR: δ=7.45 (d, J=7.1 Hz, 12H), 7.36 (t, J=7.1 Hz, 12H), 7.28 (d, J=7.1 Hz, 6H), 7.01 (d, J=16.5 Hz, 6H), 6.76 (d, J=16.5 Hz, 6H), 4.22 (q, J=7.1 Hz, 12H), 3.73 (d, J=15.5 Hz, 12H), 3.53 (d, J=15.5 Hz, 12H) 1.28 ppm (t, J=7.1 Hz, 18H); ^{13}C NMR: δ=171.47, 137.78, 137.34, 133.26, 129.15, 128.72, 127.92, 126.51, 125.19, 80.06, 66.59, 62.33, 48.67, 44.38, 14.04 ppm; IR (KBr): $\tilde{\nu}$=2925, 2172, 1736, 1629, 1598, 1448, 1250, 1231, 1186, 1038, 966, 751, 692 cm^{-1}; MS (FD): *m*/*z* (%): 1660 [M^++4] (30), 1659 [M^++3] (66), 1658 [M^++2] (81), 1657 [M^++1] (100), 1656 [M^+] (70), 829 [M^{2+}+1] (75), 828 [M^{2+}] (56); HRMS (FD): *m*/*z*: calcd for $C_{114}H_{96}O_{12}$: 1656.6902; found: 1656.6921.

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