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Synthesis and properties of conjugated thiophenes fused onto a dehydro[15]annulene scaffold

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Abstract

A short series of dehydrobenzothieno- and dehydropyridothieno[15]annulene ([15]DBTA and [15]DPTA) hybrids were assembled from thiophene, acetylene, and benzene/pyridine components. The molecules were constructed in a convergent manner and their properties examined optically, electrochemically, and thermally. In addition to lowered energy of electronic transitions of the 15-membered macrocycles, their emissive properties are discussed. The observed trends correspond with previously reported [14]annulenes, and are further rationalized using DFT (B3LYP/6-311G**) calculations. *To cite this article: M. J. O'Connor et al., C. R. Chimie 12 2009.*

1. Introduction

Highly unsaturated conjugated compounds have attracted substantial interest from synthetic, theoretical, and materials chemists in recent years [1]. Specifically, highly delocalized alkyne-containing systems [2] have elicited most of this attention for several reasons. First, the development of new synthetic procedures based on organometallic cross-coupling reactions [3] has provided access to a wide variety of compounds whose preparation was not previously possible. Second, many of these carbon-rich systems and macrocycles exhibit important materials

properties such as nonlinear optical (NLO) activity [4], liquid crystalline behavior [5], and molecular switching [6]. Recent developments have shown that dehydrobenzo-annulenes [7] and other related phenyl−acetylene macrocycles [8] are useful precursors to a number of carbon-rich polymeric systems, such as molecular tubes [9], ladder polymers [10], and novel allotropes of carbon [11]. Thus, it is essential to have easy access to these high carbon content molecules in sufficient quantities via straightforward synthetic methods if their technological potential is to be explored and eventually utilized.

We have been studying acetylene-rich dehydrobenzoannulenes (DBAs) [7,12] with the goal of examining their diverse chemical and physical properties. Our group has largely focused on the development of new or improved synthetic techniques for the assembly of such macrocycles. Our current

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methodologies allow us to introduce donor and/or acceptor functionalities on the phenyl rings of the DBA in a judicious manner, thus effectively "tuning" the optoelectronic properties of the annulene [12a]. To explore further DBA functionalization for detailed structure—property relationship studies, we chose to incorporate thiophene moieties onto the dehydroannulene skeleton [13]. The choice of thiophene as the fused aromatic ring was inspired by this moiety's materials applicability such as the chemical/electrochemical polymerizability of thiophene, the ability to form two-dimensional π-systems useful for electronics and photonics, the easier polarizability of thiophene, and the interaction among the individual macrocycles due to the lone pairs on the sulfur in each thiophene ring [14]. With respect to other heteroaromatics, thiophenes in general are easier to manipulate and to functionalize over pyrroles or furans, allowing easy access to tailored thiophene derivatives. Furthermore, by locking the conjugated system into planarity, thiophene-containing macrocycles [14d,e,15] and cyclic thiophene—acetylene hybrids [16—19] have the potential to be more efficient materials because of geometrically enforced π-orbital overlap with increased quinoidal character of the delocalized system and thus a decreased optical band gap [20].

Prior studies on thieno-fused dehydroannulenes such as **1** [17] and **2** [18] (Fig. 1) relied on metal-mediated intermolecular couplings for macrocycle construction. The structures of the starting materials, however, limited the resultant molecules to either C_{nh}- or D_{nh}-symmetry. In 2000 we reported the preparation of dehydrothieno[18]annulenes ([18]DTAs, e.g., **3**) having lower symmetries (C_{2v}, C_s) [13a,b]. While these macrocycles could be assembled in a systematic, stepwise manner, poor stability of the thienyldiyne intermediates necessitated exploration of other topologies. More recently, we described the
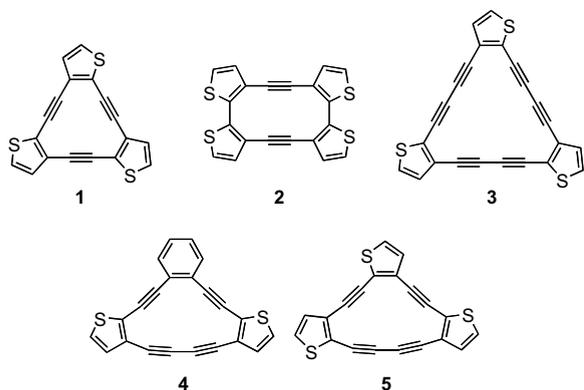
synthesis and optoelectronic properties of a series of thiophene-containing [14]DBA/DTA hybrids (e.g., **4**, henceforth [14]DBTAs) and the corresponding all-thiophene containing [14]DTAs (e.g., **5**) [13c]. That study showed that subtle changes in molecule symmetry can "tune" the properties of annulenes. For example, the UV—vis spectra of this class of macrocycles showed that the large transitions remain essentially the same, but displayed distinct differences in the low-energy vibronic region. Expanding on our success with [15]DBAs [12a,c,e] and our further understanding of thieno-fused annulenes, this report details the synthesis and characterization (thermal, optical, electro-chemical, computational) of [15]DBTA hybrids **6—9** (Fig. 2) and [15]DPTA (dehydropyridothieno annulene) hybrids **10** [12c] and **11**.

2. Results and discussion

2.1. Macrocycle synthesis

All six macrocycles were constructed in a convergent fashion from the synthons given in Fig. 3. Dihaloarenes **12—14** are commercially available, whereas diynes **15—17** were prepared starting from the appropriate dihalothiophenes using our previously reported syntheses [12c,13c].

An example of symmetrical macrocycle synthesis is given in Scheme 1. Selective removal of the TMS group in diyne **16** with K_2CO_3 in MeOH/THF followed by cross-coupling to 1,3-diiodobenzene (**12**) afforded precursor **18** (**pre-6**) in 86% yield. Desilylation with TBAF and cyclization using modified Glaser—Eglinton conditions generated hybrid **6** in 55% yield.

Preparation of the only unsymmetrical macrocycle, **7**, is shown in Scheme 2. Selective desilylation of diyne **15** as described above and then cross-coupling to 1-bromo-3-iodobenzene (**13**) yielded **19**, which proved to be moderately sensitive to silica. After rapid

Fig. 1. Examples of known thieno-fused dehydroannulenes.
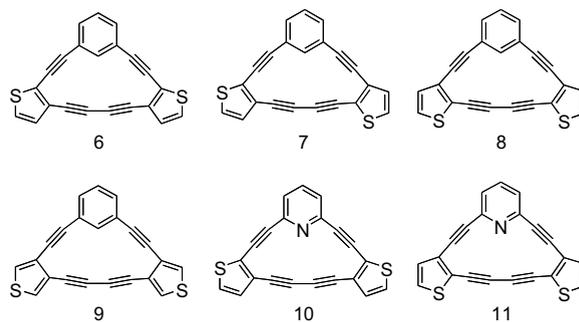
Fig. 2. Target thieno-fused dehydro[15]annulenes **6—11**.
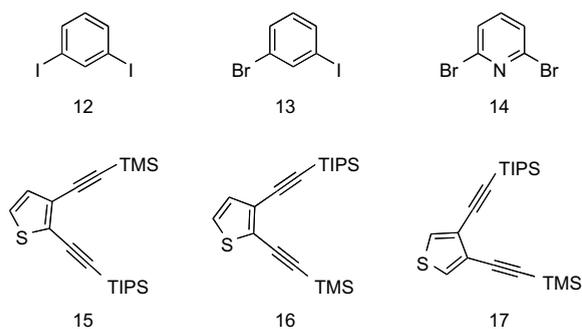
Fig. 3. Building blocks **12–17**.

purification, compound **19** was then cross-coupled to monodesilated **16** to furnish precursor **20** (**pre-7**), which was fully characterized. Desilylation and cyclization afforded **7** in 29% yield. A summary of the various syntheses is given in Table 1.

As with the previously reported [14]DBTAs, the thieno-fused [15]annulenes are only moderately stable during workup and are sensitive to acid, light, and silica, which accounts for the lower than normal cyclization yields. Workups were most successful when avoiding halogenated solvents and utilizing fast chromatographic methods (chromatotron or flash chromatography). NMR spectroscopic characterization of the annulenes was accomplished primarily in THF-d_8 for both stability and solubility. In general, those molecules with UV–vis absorptions past 400 nm and/or where both sulfurs are oriented 'down' (sulfur α to the diacetylene linkage), as is the case with **8** and **11**, showed the greatest sensitivity. Most could be stored in solution or in the solid state for several weeks if kept cold and dark sealed under argon. The most difficult macrocycle to work with was **9**, which was found to decompose gradually over 2–3 d. The instability is likely due to the more exposed α-positions of the 3,

Scheme 1. Synthesis of 'symmetrical' [15]DBTA **6**.

Scheme 2. Synthesis of 'unsymmetrical' [15]DBTA **7**.

4-fused thiophenes, which have been shown to affect the integrity of samples [13c,21].

Thermal analysis of **6–9** by DSC revealed broad exotherms with onset after 200 °C and maxima ca. 225 °C, with decomposition above 300 °C. Thermal scans of pyridine macrocycles **10** and **11**, however, showed larger and sharper exotherms between 175 and 200 °C. Nonetheless, these data as a whole suggest random, disordered polymerizations that yield black amorphous materials.

2.2. Spectroscopic properties

NMR spectroscopic analysis of the [15]DBTAs shows only one significant difference between the macrocycles and their respective precursors: upon cyclization the triplet signal for the intraannular arene proton shifts from a range of 7.7–7.8 to 8.5–8.9 ppm. This large change is readily attributed to an increased anisotropic deshielding effect of the transannular triple

Table 1
Synthesis and yields of macrocycles **6–11**.

Haloarene	"Equivalents" of diyne			Precursor, yield	Annulene, yield
	15	**16**	**17**		
12	2			pre-**6** (**18**), 86%	**6**, 55%
13	1 (second)	1 (first)		pre-**7** (**20**), 67%	**7**, 29%
12		2		pre-**8**, 47%	**8**, 50%
12			2	pre-**9**, 79%	**9**, 53%
14	2			pre-**10**, 74%[a]	**10**, 73%[a]
14		2		pre-**11**, 67%	**11**, 38%

[a] Ref. [12c].

bonds [12a,c,e,22]; otherwise, the NMR data for the [15]annulenes are unremarkable.

Compared to the [14]DBTAs, the peaks in the electronic spectra of the [15]DBTAs (Fig. 4a) are bathochromically shifted, some up to 40 nm. For example, [14]DBTA **4** has its main peak at 329 nm with two low energy absorptions at 363 and 373 nm and cut-off by 390 nm. The analogous [15]DBTA, **6**, has a main peak at 337 nm and cut-off around 450 nm, with no readily discernable low energy bands. These bands do become apparent and grow in as thiophene orientation relative to the annulene ring changes from 'up' to 'down' (**6** → **7** → **8**), similar to the [14]DBTAs [13c]. In **8** the low energy bands are at 410 and 448 nm with a cut-off of ca. 465 nm. In comparison, the analogous bands in the 'down' [14]DBTA are 376 and 408 nm and a cut-off of ca. 425 nm. Compound **9** has an appreciable low energy absorption band at 349 nm and overall displays different features than **6**−**8**. This reflects the decreased conjugation in the macrocycle due to 3,4-fusion of the two thiophene moieties. Once again, the 15-membered ring of **9** affords a band that is lower in energy than the corresponding band in the 3,4-fused [14]DBTA (339 nm), though the magnitude of this difference is smaller than the 2,3-fused systems.

Replacing the benzene with a pyridine unit (Fig. 4B) yields only minor changes to the electronic absorption data. Compounds **6** and **10** have nearly identical electronic absorption spectra and thus identical band gaps, whereas [15]DPTA **11** red shifts to 465 nm compared to 448 nm for **8**. This 17 nm difference not only demonstrates that the orientation of the sulfurs plays an important role in the electronic properties of this class of compounds, but also suggests that direct conjugation of the sulfur to the benzene (or pyridine) is a driving factor in lowering the energy of the transition states. The addition of the electron-

Table 2
Photophysical parameters of [15]annulenes **6**−**11**.

	Lowest energy Abs. λ_{max} (cut-off) [nm]	Emission energy [nm] (CH_2Cl_2, PhMe)	Φ_f (CH_2Cl_2, PhMe)	Stokes shift, (CH_2Cl_2, PhMe) [cm^{-1}]
6	366 (450)	443, 447	0.11, 0.17	4975, 5028
7	440 (450)	449, 449	0.03, 0.03	507, 404
8	448 (460)	456, 455	0.06, 0.05	392, 244
9	349 (360)	363, 363	0.04, 0.05	1023, 1105
10	363 (460)	512, 510	0.04, 0.05	8017, 7789
11	465 (480)	524, 471	0.05, 0.06	2421, 228

withdrawing *N*-atom likely allows for a more charge separated excited state (vide infra). None of the reported macrocycles, however, displayed any appreciable solvatochromism.

The [15]DBTAs and [15]DPTAs do exhibit modest emissive properties (quantum yields of 0.03−0.17), unlike the [14]DBTAs (quantum yields < 0.01). The emissive properties of cross-conjugated systems over directly conjugated systems are a phenomenon often observed elsewhere [23] and have been observed in many of our previous studies [12a,e,24]. Emission spectra and quantum yields were taken in both toluene and dichloromethane, and are summarized along with the absorption data and Stokes shifts in Table 2. [15]DPTA **11** is the only system to exhibit appreciable solvatochromism in the emission spectrum with the emission peak shifting from 471 nm to 524 nm when changing solvent from toluene to CH_2Cl_2.

2.3. Electrochemistry

Cyclic voltammograms were obtained of the [15]annulenes using a Pt disk electrode, Ag wire reference, and Pt swirl auxiliary in CH_2Cl_2 solutions of Bu_4NPF_6 and referenced to ferrocene. Electrochemical
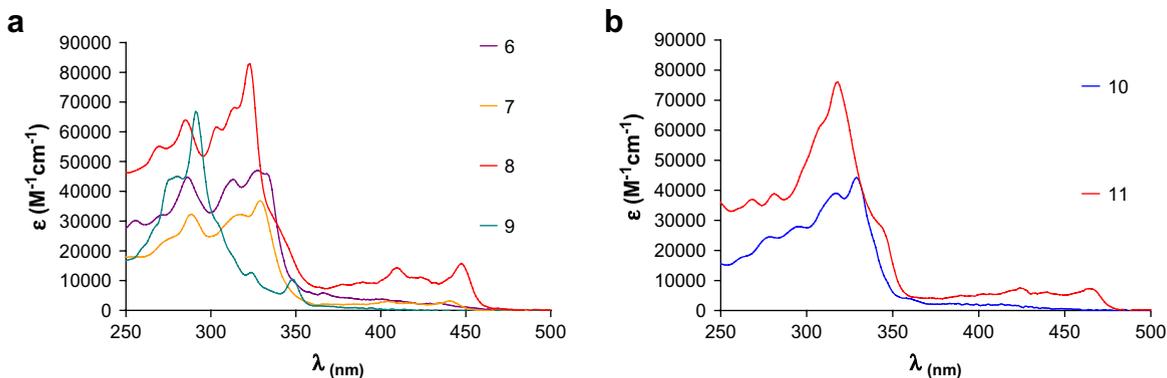
Fig. 4. UV−vis absorption spectra of (a) **6**−**9** and (b) **10**−**11**. All spectra recorded in CH_2Cl_2 at analyte concentrations of 15−25 μM.

Table 3
Electrochemical data and band gaps.

Compound	E_{pa} (ox) (vs. Fc) [V]	E_{pa} (red) (vs. Fc) [V]	Electrochemical band gap [eV]	Optical band gap [eV]	DFT calculated band gap [eV]
6	1.14	−1.71	2.85	3.39	3.18
7	1.14	−1.64	2.78	2.82	3.09
8	1.13	−1.57	2.70	2.53	3.02
9	–	–	–	3.55	4.03
10	1.20	−1.86	3.06	3.42	3.06
11	0.97	−1.76	2.73	2.66	2.93

Data obtained in CH_2Cl_2 solutions of Bu_4NPF_6 and referenced to ferrocene.

band gap values for compounds **6**–**8**, **10**, and **11** were discerned using previously described methods [13c,25]. Table 3 lists the oxidation and reduction onsets and the electrochemical band gap, along with the optically estimated and DFT calculated band gap values. Compound **9** was not tested, as it was too difficult to handle and thus garner reliable CV information. The CVs showed irreversible oxidation peaks and multiple irreversible and sometimes quasi-irreversible reduction waves. In certain instances, however, multiple oxidations were found to occur. This could be due to an increased HOMO energy, allowing more electron transfer reactions to happen outside the solvent window. As was the case with the [14]annulenes, no polymer films were deposited on the electrode. The electrochemistry results match the relative trends observed in the UV–vis absorption data. For example, sulfurs 'up' macrocycles have wider band gaps (e.g., **6**, 2.85 eV) than sulfurs 'down' (e.g., **8**, 2.70 eV), in agreement with the [14]DBTA series [13c]. Similarly, the optical and electrochemical band gaps of the [15]DPTAs are larger than those of the corresponding [15]DBTAs.

2.4. Computational results

DFT calculations (B3LYP/6-311G**) [26] were performed on both the [15]DBTAs and [15]DPTAs. The computed HOMO/LUMO gaps are also given in Table 3, and show excellent relative agreement with the empirical trends. For instance, the largest band gap, [15]DBTA **6** (2.85–3.39 eV), corresponds well to the calculated value (3.18 eV). In most cases the DFT computed energies are larger than the experimentally determined ones, as was found for all of the [14]DBTAs and [14]DTAs [13c]. The two exceptions in the current study are sulfurs 'up' annulenes **6** and **10**. Given their UV–vis spectra in Fig. 4, we can easily attribute this difference to unresolved low energy peaks in the data.

The computed HOMO/LUMO plots for **6**–**11** are given in Fig. 5. These show little if any difference in topology with respect to the sulfur orientation in [15]DBTAs **6**–**8**, similar to what was observed in the [14]annulene series (e.g., **4**–**5**) when 2,3-fused thiophenes were incorporated into the macrocycle [13c]. Compound **9**, possessing 3,4-fusion, shows disruption
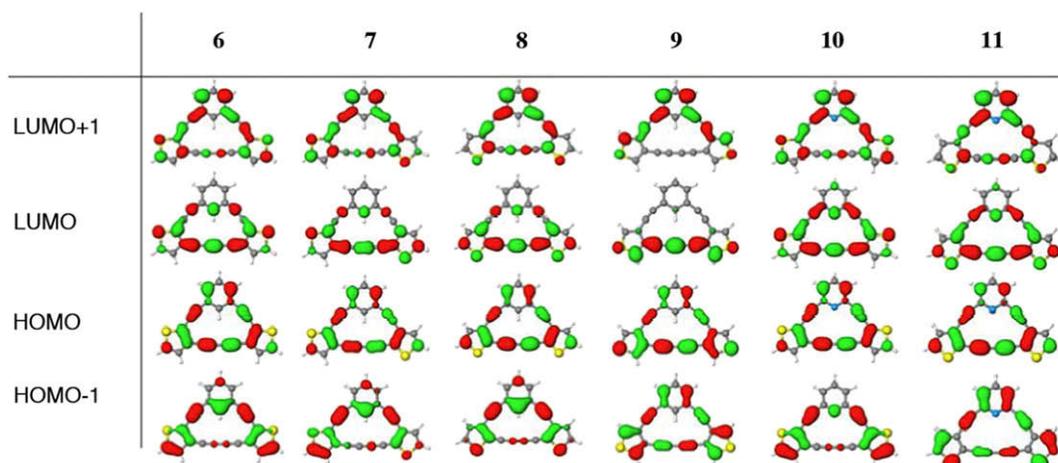
Fig. 5. Calculated HOMO and LUMO plots of [15]DBTAs **6**–**9** and [15]DPTAs **10**–**11**.

in the continuity of electron delocalization around the macrocycle; however, it is not as dramatic and well-defined as in the plots of the corresponding [14]DBTA [13c]. DPTAs **10** and **11** also show remarkable similarity to DBTAs **6−8** with the exception of some slight additional electron density at C4 of the pyridine.

The placement of the electron density on the carbon lying between the triple bonds in the LUMOs of **6−8** and **10−11** alludes to perhaps some charge transfer effects. Furthermore it is serendipitous that the lowering of energy of the UV absorption for the pyridine, sulfurs 'down' DPTA **11** occurs when the sulfurs are directly in conjugation with the pyridine nitrogen atom, in contrast to **10**, when the sulfur is not conjugated with the nitrogen, where no discernable change in the UV−vis spectrum is observed. This could imply that there is some level of charge transfer component to **8** and **11**.

3. Conclusions

A short series of [15]DBTA and [15]DPTA hybrids composed of multiple fused thiophenes, benzenes, and/ or pyridines were successfully prepared. Planarizing the thiophenes into the [15]annulene scaffold was found to increase orbital overlap even in a cross-conjugated system. Concurrently, the same relative electronic trends were observed in both the 14- and 15-membered macrocycles that are contingent on the orientation of the sulfur. When the sulfur atoms is oriented 'down' (as in **8**), the absorption bands of the macrocycle red shift and intensify compared to when the sulfurs are oriented 'up' (as in **6**). When 3,4-fused onto the annulene scaffold, as in **9**, the net conjugation around the ring is disrupted by the increased single bond character. Incorporating pyridines in the macro-cycle (DPTAs **10−11**) can significantly red shift the UV−vis absorptions of the molecule, but only when the sulfurs are oriented down (**11**). These results as a whole are supported by DFT-B3LYP calculations of the HOMO−LUMO energy gap. Overall, the [15]annulene scaffold offers some benefits over the [14]scaffold with a wider dispersion of UV−vis absorption energies, and increased emissive properties despite the loss of the 'aromaticity' found with the 14-membered macrocycle. Electrochemical measurements were performed and again failed to yield polymers typical of thiophenes, most likely due to the increased 'annulene' character of the compounds. Future reports will focus on stabilized α-alkylated thiophene targets in order to expand the scope of syntheses of these macrocycles by solubilizing the products and protecting against unwanted degradation.

4. Experimental

4.1. General methods

These are described in Ref. [12a]. Diynes **17** [12c], **18** [13c], and **19** [13c] and annulene **10** [12c] were prepared according to known procedures.

4.2. General procedure for preparation of 'symmetrical' annulene precursors

To a solution of diyne (2.5 equiv.) dissolved in MeOH/THF (10:1, 0.05 M) was added K_2CO_3 (10 equiv.) and the mixture was stirred for 30 min. The solution was filtered and then Et_2O was added. The solution was washed successively with H_2O, 10% NaCl solution and water, and then dried ($MgSO_4$). Solvent was removed in vacuo and the residue was added to a solution of THF/DIPA (1:1, 0.1 M) and dihaloarene (1 equiv.). The mixture was degassed under Ar for 30 min after which CuI (6 mol%) and $Pd(PPh_3)_4$ (3 mol%) were added. The sealed vessel was stirred at room temperature until TLC showed the reaction complete (12 h−2 d). The solvent was removed in vacuo and the crude product chromato-graphed on silica to afford the annulene precursor.

4.2.1. Precursor to 6 (18/pre-6)

Chromatography on silica (10:1 hexanes:CH_2Cl_2) furnished **18** (**pre-6**, 334 mg, 85%) as an orange oil. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.20$ (s, 42H), 7.08 (d, $J = 5.3$ Hz, 2H), 7.21 (d, $J = 5.3$ Hz, 2H), 7.33−7.39 (m, 1H), 7.48−7.54 (m, 2H), 7.69 (t, $J = 1.5$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 11.6$, 19.0, 82.9, 95.7, 96.4, 100.9, 123.5, 126.3, 127.0, 127.6, 128.7, 130.3, 131.5, 134.9; MS (APCI): m/z (%) 650.8 (MH$^+$, 50); IR (NaCl): $v = 2149, 2202, 2864, 2891, 2942$ cm^{-1}.

4.2.2. Precursor to 8 (pre-8)

Chromatography on silica (10:1 hexanes:CH_2Cl_2) furnished **pre-8** (184 mg, 47%) as an orange oil. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.17$ (s, 42H), 7.09 (d, $J = 5.3$ Hz, 2H), 7.16 (d, $J = 5.3$ Hz, 2H), 7.34−7.39 (m, 1H), 7.47−7.53 (m, 2H), 7.71 (t, $J = 1.4$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 11.3$, 18.7, 84.4, 92.2, 98.2, 100.4, 132.4, 125.8, 126.7, 126.8, 128.2, 129.3, 131.2, 134.8; MS (APCI): m/z (%) 721.3 (MH$^+$ + THF, 100); IR (NaCl): $v = 2142, 2213, 2891, 2864, 2942$ cm^{-1}.

4.2.3. Precursor to 9 (pre-9)

Chromatography on silica (10:1 hexanes:CH_2Cl_2) furnished **pre-9** (913 mg, 79%) as an orange oil. [1]H

NMR (300 MHz, CDCl$_3$): δ = 1.07 (s, 42H), 7.41−7.47 (m, 5H), 7.67 (t, J = 1.4 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 11.3, 18.7, 83.7, 90.4, 93.2, 100.0, 123.4, 125.0, 125.3, 128.1, 128.2, 129.0, 131.2, 135.0; MS (APCI): *m/z* (%) 721.3 (MH$^+$ + THF, 100), 791.3 (M$^+$ + 2THF, 10); IR (NaCl): v = 2155, 2219, 2960, 2863, 3109 cm^{-1}.

4.2.4. *Precursor to* **11** (**pre**-**11**)

Chromatography on silica (10:1 hexanes:CH$_2$Cl$_2$) furnished **pre-11** (153 mg, 56%) as an orange oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.34 (s, 42H), 7.11 (d, J = 5.3 Hz, 2H), 7.15 (d, J = 5.3 Hz, 2H), 7.41 (d, J = 7.6 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 11.2, 18.7, 84.0, 91.7, 97.9, 100.8, 125.9, 126.0, 126.2, 127.9, 129.7, 136.1, 143.7; MS (APCI): *m/z* (%) 651.9 (MH$^+$, 100); IR (NaCl): v = 2143, 2214, 2942, 3109 cm^{-1}.

4.3. *Procedure for preparation of 'asymmetrical' annulene precursor* **20** (**pre**-**7**)

To a solution of diyne **15** (111 mg, 0.311 mmol) dissolved in MeOH (6 ml) and THF (0.5 ml) was added K$_2$CO$_3$ (106 mg, 0.78 mmol) and the mixture was stirred for 30 min. The solution was filtered and then Et$_2$O was added. The solution was washed successively with H$_2$O, 10% NaCl solution and water, and then dried (MgSO$_4$). Solvent was removed in vacuo and the unstable crude material (**19**) was added to a solution of THF (1.5 ml), DIPA (1.5 ml) and 1-bromo-3-iodobenzene (**13**, 80 mg, 0.282 mmol). The mixture was degassed under Ar for 30 min after which CuI (3 mg, 0.017 mmol) and Pd(PPh$_3$)$_4$ (10 mg, 0.008 mmol) were added. The sealed vessel was stirred at room temperature until TLC showed the reaction complete (ca. 2 d). The solvent was removed in vacuo and the crude product chromatographed on a short plug silica to afford the halodiyne precursor. This material was redissolved in THF (1.5 ml) and DIPA (1.5 ml), and then diyne **16** (153 mg, 0.429 mmol), desilylated in the manner described above, was added. The solution was degassed under Ar for 30 min and then CuI (4 mg, 0.019 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (7 mg, 0.0086 mmol), and Pd(PPh$_3$)$_4$ (5 mg, 0.0043 mmol) were added. The reaction mixture was transferred to a sealed pressurized tube and heated at 85 °C for 18 h. The solvent was removed in vacuo and the crude product was chromatographed on silica (6:1 hexanes:CH$_2$Cl$_2$) to afford **20** (**pre-7**, 191 mg, 67%) as a dark orange oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.14 (s, 42H), 7.04 (d, J = 5.3 Hz, 2H), 7.16 (d,

J = 5.3 Hz, 1H), 7.17 (d, J = 5.3 Hz, 1H), 7.28−7.36 (m, 1H), 7.43−7.48 (m, 2H), 7.68 (t, J = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 11.3, 18.7, 84.5, 84.5, 92.2, 95.4, 96.3, 98.1, 100.5, 100.6, 123.1, 123.5, 125.8, 126.0, 126.8, 126.9, 127.2, 128.3, 129.3, 130.0, 131.0, 131.2, 131.4, 134.7; MS (APCI): *m/z* (%) 757.4 (M$^+$ + THF + 2H$_2$O, 80); IR (NaCl): v = 2145, 2209, 2891, 2865, 2943 cm^{-1}.

4.4. *General procedure for annulene formation*

To a solution of annulene precursor (1 equiv.) in THF (0.1 M) was added TBAF (20 equiv., 1.0 M THF). The mixture was stirred for 5 min and then Et$_2$O was added. The solution was washed 4−6 times with brine and then water, and the organic layer was dried (MgSO$_4$). The solution was diluted with Et$_2$O (to ca. 50 ml total volume) and then slowly injected over 8 h into a pyridine solution (0.01 M) of CuCl (10 equiv.) and Cu(OAc)$_2$ (10 equiv.) with stirring at 45 °C. Once TLC showed completion of the reaction, the solvent was removed under reduced pressure and the residue was run through a silica plug (1:1 hexanes:CH$_2$Cl$_2$). The product was further purified on a chromatotron (8:1 hexanes:EtOAc).

4.4.1. *[15]DBTA* **6**

Obtained **6** (8 mg, 55%) as a pale yellow solid. ^{1}H NMR (300 MHz, THF-d_8): δ = 7.14 (d, J = 5.3 Hz, 2H), 7.25−7.40 (m, 3H), 7.47 (d, J = 5.3 Hz, 2H), 8.52 (t, J = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, THF-d_8): δ = 79.6, 80.0, 87.5, 101.9, 125.1, 127.1, 127.9, 129.5, 129.7, 130.1, 130.4, 146.1; MS (APCI): *m/z* (%) 406.7 (MH$^+$ + THF, 85); IR (KBr): v = 2105, 2198 cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 285 (4.67), 327 (4.67), 333 (4.65), 366 (3.77) nm.

4.4.2. *[15]DBTA* **7**

Obtained **7** (10 mg, 29%) as a yellow solid. ^{1}H NMR (300 MHz, THF-d_8): δ = 7.05 (d, J = 5.2 Hz, 1H), 7.15 (d, J = 5.2 Hz, 1H), 7.22−7.37 (m, 3H), 7.47 (d, J = 5.2 Hz, 1H), 7.52 (d, J = 5.2 Hz, 1H), 8.51 (bs, 1H); ^{13}C NMR (75 MHz, THF-d_8): δ = 78.1, 79.7, 82.4, 83.6, 87.5, 89.4, 98.9, 102.2, 125.3, 125.6, 127.2, 127.5, 128.1 (2), 129.6, 129.8, 130.2, 130.6, 132.4, 146.8; MS (APCI): *m/z*(%) 406.9 (MH$^+$ + THF, 85); IR (KBr): v = 2130, 2190 cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 288.0 (4.51), 328 (4.56), 406 (3.46), 441 (3.47) nm.

4.4.3. *[15]DBTA* **8**

Obtained **8** (23 mg, 50%) as a yellow solid. ^{1}H NMR (300 MHz, THF-d_8): δ = 7.05 (d, J = 5.3 Hz, 2H), 7.22−7.36 (m, 3H), 7.53 (d, J = 5.3 Hz, 2H), 8.51 (t,

$J = 1.5$ Hz, 1H); ^{13}C NMR (75 MHz, THF-d_8): $\delta = 79.2$, 82.4, 88.2, 98.0, 124.6, 126.5, 126.8, 127.1, 128.9, 129.1, 131.4, 146.2; MS (APCI): m/z (%) 407.0 (MH$^+$ + THF, 90); IR (KBr): $v = 2173$, 2205 cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 285 (4.81), 303.0 (4.78), 314 (4.83), 323.0 (4.92), 410 (4.15), 448 (4.19) nm.

4.4.4. [15]DBTA **9**

Obtained **9** (27 mg, 53%) as an unstable white solid. ^{1}H NMR (300 MHz, THF-d_8): $\delta = 7.27−7.36$ (m, 3H), 7.58 (d, $J = 2.9$ Hz, 2H), 7.82 (d, $J = 2.9$ Hz, 2H), 8.47 (t, $J = 1.5$ Hz, 1H); ^{13}C NMR (75 MHz, THF-d_8): $\delta = 77.0$, 77.8, 88.2, 94.9, 125.0, 126.2, 126.5, 127.6, 128.1, 130.0, 132.2, 145.3; MS (APCI): m/z (%) 407.0 (MH$^+$ + THF, 90); IR (KBr): $v = 2136$, 2200 cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 292 (4.83), 325 (4.16), 349 (4.08) nm.

4.4.5. [15]DBTA **11**

Obtained **11** (10 mg, 38%) as a yellow solid. ^{1}H NMR (300 MHz, THF-d_8): $\delta = 6.99$ (d, $J = 5.2$ Hz, 2H), 7.10 (d, $J = 7.8$ Hz, 2H), 7.45 (d, $J = 5.2$ Hz, 2H), 7.59 (t, $J = 7.8$ Hz, 1H); ^{13}C NMR (75 MHz, THF-d_8): $\delta = 78.9$, 85.3, 86.3, 99.2, 123.0, 129.2, 129.3, 130.3, 131.9, 138.1, 146.0; MS (APCI): m/z (%) 337.5 (MH$^+$, 100); IR (KBr): $v = 2145$, 2212 cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max} (log ϵ): 281 (4.85), 317 (4.87), 345 sh (4.27), 426 (3.87), 464 (3.86) nm.

4.5. Computational methods

Geometry optimizations were performed using the B3LYP [26] functional and 6-31G* basis set. HOMO−LUMO gaps and dipole moments were taken from single-point energy calculations which were carried out on the optimized structures using B3LYP/6-311G**, in a solvent modeled using the Cosmo reaction field model [27] with a dielectric corresponding to methylene chloride ($\epsilon = 9.08$). The set of atomic radii optimized by Stefanovich and Truong [28] was used for the solvation energy calculations. The NWChem (v4.7 and v5.0) [29] program was used for all geometry optimizations and single-point energy calculations. Building and modeling of all compounds were done using the program Ecce v3.2.4 [30].

4.6. Electrochemistry

Electrochemical measurements were taken in a CH$_2$Cl$_2$ solution of 100 mM Bu$_4$NPF$_6$ and 1 mM macrocycle using Pt disc working electrode, Pt wire auxiliary electrode, and silver wire reference. Measurements were then referenced with respect to an internal ferrocene standard.

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