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ARTICLE

Contorted Aromatics via a Palladium-Catalyzed Cyclopentannulation Strategy

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We show that a new class of contorted polycyclic aromatic hydrocarbons containing five-membered rings can be prepared via a palladium-catalyzed cyclopentannulation followed by Scholl cyclodehydrogenation. The annulation chemistry can be accomplished between a di-arylethynylene and an appropriate aryl-dibromide to form 1,2,6,7-tetraarylcyclopenta[hi]aceanthrylenes and 1,2,6,7-tetraaryldicyclopenta[cd,jk]pyrenes. Scholl cyclodehydrogenation to close the externally fused aryl groups was accomplished only with properly arranged alkoxy substitutions and provides access to the pi-extended 2,7,13,18-tetraalkoxytetrabenzo[f,h,r,t]rubicenes and 2,7,13,18-tetraalkoxydibenzo[4,5:6,7]indeno[1,2,3-cd]dibenzo[4,5:6,7]indeno[1,2,3-jk]pyrenes. The final compounds each possess apparent [4]helicene-like arrangements with fused five-membered rings; however, only the 2,7,13,18-tetraalkoxytetrabenzo[f,h,r,t]rubicenes contort out of planarity owing to an additional [5]helicene like arrangement. Single crystal analysis of the contorted aromatic shows the PAHs stack in a lock-and-key like arrangement and pi-stack in a columnar arrangement. Solution-phase aggregation, as well as liquid crystalline mesophases, were found for derivatives with suitably attached solubilizing chains.

Introduction

Metal-catalyzed annulation reactions offer unique synthetic strategies to access complex and otherwise difficult to attain polycyclic aromatic hydrocarbons (PAHs).¹ The scope of substrates that undergo annulation transformations have increased substantially over the past decade largely owing to advances in catalyst design.^{2–8} One considerable benefit to an annulation strategy is the ability to quickly expand the aromatic core of a given PAH with minimal synthetic effort. The ring expansion increases the effective conjugation and often leads to significant modulation of the frontier orbital energies that can lead to beneficial properties such as reduced band gap energies. Furthermore, the larger surface area can be advantageous for pi – pi stacking that can improve charge transport characteristics.^{9,10} As a direct consequence of the ring expansions chemistry, the fused rings may be installed in such a way that leads to a congested arrangement of aromatic rings that result in PAHs that are distorted from planarity.¹¹ The resulting contorted aromatics^{12–27} are a unique class of compounds that diverge in structure from the more common planar arrangement of fused benzenoids in typical PAHs. In

these contorted systems, part of the conjugated ring system shifts out of planarity owing to steric congestion between near-spaced atoms that are projected by neighboring aromatic residues.²² Many of the non-planar arrangements in these larger pi systems can be compared to the well-known helicene compounds composed of benzenoids²⁸ or other sized rings.^{29–32} The contorted nature of these aromatics offers unique opportunities to access more soluble materials owing to their non-planar arrangement¹⁴ while still facilitating pi-pi stacking in the solid state through a lock-and-key like packing motif. In this contribution we demonstrate that a new class of contorted aromatics with five-membered ringed cores (Figure 1) can be prepared through cyclopentannulation followed by a Scholl cyclodehydrogenation, and the resulting materials participate in significant aggregation in the solid state and solution.

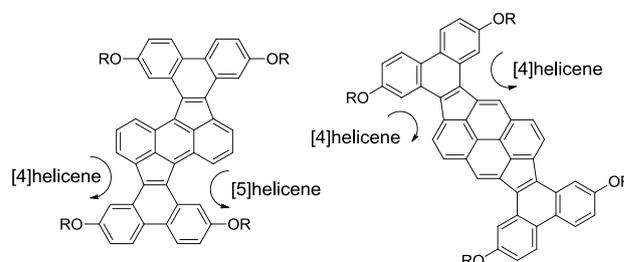


Figure 1. 2,7,13,18-tetraalkoxytetrabenzo[f,h,r,t]-rubicenes (left) and 2,7,13,18-tetraalkoxydibenzo[4,5:6,7]indeno[1,2,3-cd]dibenzo[4,5:6,7]indeno[1,2,3-jk]pyrenes (right)

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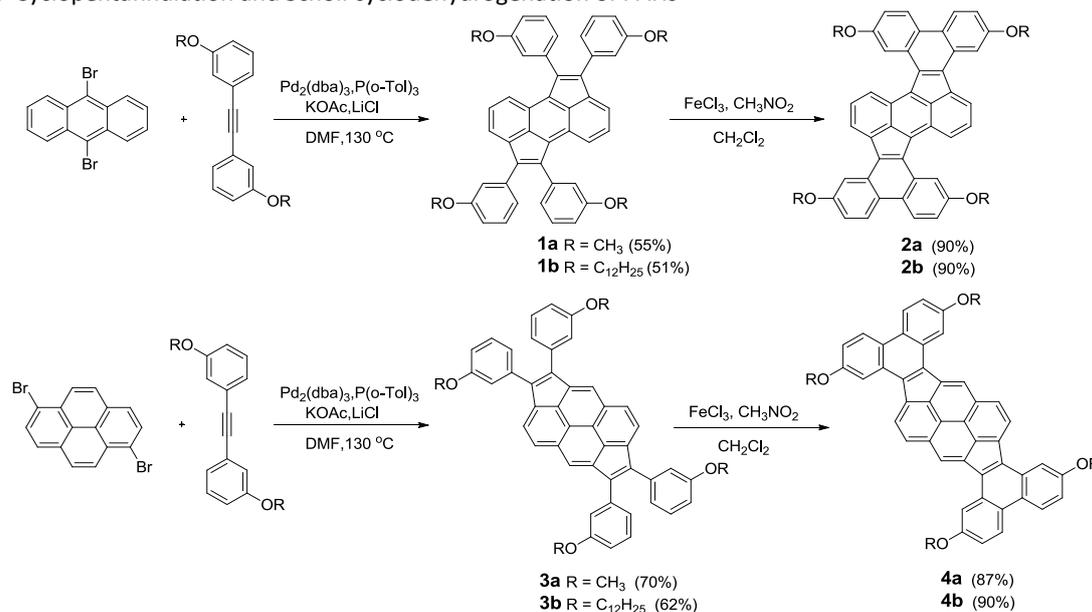
Results and Discussion

We have recently been interested in utilizing functionalizable cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) as electron accepting materials.^{33–36} To construct these five-member ring containing compounds, we have utilized the cyclopentannulation³⁷ chemistry developed by Garcia-Garibay^{38,39} to create trimethylsilyl (TMS) derivatives that could be easily modified via cross-coupling reactions upon ipso-bromination of the resulting CP-PAHs. Unfortunately, we have found the specific utilization of TMS-acetylene in the pentannulation reaction is PAH dependent and we have been unable to successfully apply those reaction conditions to other PAH scaffolds such as pyrene and perylene. Müllen,⁴⁰ and more recently Wu,⁸ have shown that the scope of pentannulation reactions can be extended to several new PAH cores including pyrene and perylenes via the utilization of di-substituted ethynyls and a more active catalyst system. Müllen's important contribution utilized a catalyst system of Pd₂(dba)₃ and P(o-Tol)₃ in a mixed solvent of toluene and acetonitrile with triethylamine as a base. With a goal of accessing these new CP-PAHs scaffolds and evaluating their ability to form new contorted aromatics upon subsequent modifications, we began to use this reported methodology. Although we were successful in reproducing the previously reported transformations, the yields in our hands were less than desirable after chromatographic separations. In search of alternative reaction conditions, we found the yields of the pentannulation reactions can be significantly increased by changing the solvent and base. We found that KOAc, with LiCl as an additive, in DMF is well suited to produce good yields of the cyclopentannulated products after a simple workup protocol. The compounds detailed in this contribution were prepared via this new methodology in a bimolecular reaction between a diarylethynylene and 9,10-dibromoanthracene or 1,6-dibromopyrene to give 1,2,6,7-

tetraarylcyclopenta[hi]aceanthrylenes **1** and 1,2,6,7-tetraaryldicyclopenta[cd,jk]pyrenes **3**, respectively (Scheme 1 and Supporting Information). Of considerable significance, the reactions presented here are facile enough that pure products (50-80 %) were obtained by a simple precipitation and washing protocol that often eliminated the need for chromatographic separation.

The resulting set of CP-PAHs **1** and **3** are highly soluble, largely owing to the tilted arrangement of the aryl substituents, in relation to the aromatic core (Supporting Information). This substitution arrangement helps minimize aggregation via the disruption of pi-pi facial interactions. While the close arrangement of the aryl groups leads to the orthogonal conformations that minimize the steric congestion around the five-membered rings, it also offers an opportunity to access extended fused structures. To expand the delocalizable aromatic core in these systems, we attempted to use traditional Scholl cyclodehydrogenation conditions to fuse the aryl rings into a more planar arrangement. To our dismay, initial attempts at cyclizing the *para*-alkyl (in relation to CP-PAH core) substituted anthracene and pyrene derivatives with FeCl₃ were not successful giving back only starting materials (Supporting Information). As electron rich substituents are known to promote the Scholl cyclodehydrogenation,^{15,41} the *para*-alkoxy derivative was subjected to the same reaction conditions, but similarly to no avail. Other known Scholl conditions that utilized oxidants such as MoCl₅, DDQ/TFA, or AlCl₃, or the Katz-modified Mallory photooxidation^{42,43} were also ineffective. However, we were ultimately able to access the desired transformation by employing the *meta*-alkoxy derivatives (**1a**, **1b**, **3a**, **3b**) that project the alkoxy groups in a *para* arrangement to the desired ring closure location. Such pre-aligned Scholl reaction methodology is known to facilitate similar ring closures.⁴¹ Although the cyclodehydrogenation proceeded sluggishly the reaction could be completed upon

Scheme 1. Cyclopentannulation and Scholl cyclodehydrogenation of PAHs



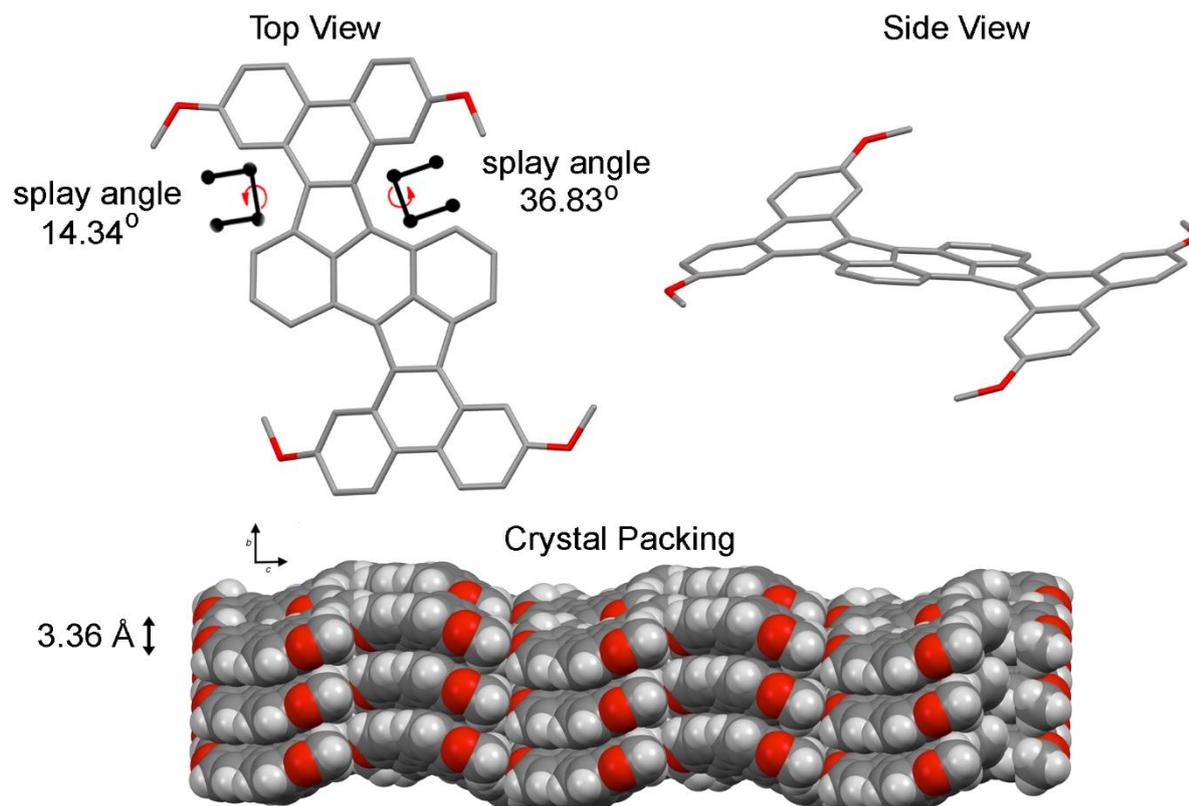


Figure 2. Crystal structure and packing of contorted aromatic **2a**.

stirring overnight to give either the methoxy (**2a**, **4a**) or dodecyloxy (**2b**, **4b**) derivatives. Attempts to access the parent PAHs (e.g., from **2a**) through a nickel-catalyzed dealkoxylation^{44,45} were unsuccessful and may be due to the requirement of four separate dealkoxylation to occur on a single molecular scaffold. However, this two-step synthetic method ultimately provides a new and convenient route to expanded rubicene^{46–48} and indenopyrene^{49–51} derivatives.

Obtaining suitable crystals for single crystal analysis turned out to be troublesome for this class of compound. First, only the dodecyloxy containing pyrene derivative **4b** was soluble in hot chlorinated solvents (**4a** was not soluble in any common solvent) and therefore presented challenges in growing crystals owing to the disordered alkyl chains. For the more soluble rubicene derivative **2a**, we were able to grow crystals from a variety of solvents; however, all crystallization attempts gave stacked platelets that easily sheared when manipulated. Only the smallest and most weakly diffracting crystals grown from chloroform gave diffraction data of sufficient quality for structure solution and refinement. Because of this, analysis of these crystals by X-ray diffraction required synchrotron radiation with high photon flux and a small beam size to match the size of the crystals ($\sim 100 \mu\text{m}$). X-ray data for **2a** was collected at beamline X10SA at the Swiss Light Source. The use of a multi-axis goniometer specially developed at the beamline enabled data collection of high accuracy and multiplicity, critical for successful structure solution.⁵² As seen in the crystal structure of **2a** (Figure 2), the compound has a center

of symmetry located at the middle anthracene ring and a contorted aromatic structure that cannot fully adopt a planar arrangement owing to interactions between the inner rubicene core and the outer phenanthrene subunits. The arrangement of fused rings gives rise to two [4]helicene-like and two [5]helicene-like fragments⁵³ in the compound (Figure 1). The two fragments generate two different splay angles in the compound, a phenomena seen in other thiophene-fused contorted aromatics.¹⁸ The [4]helicene arrangement gives an apparent splay angle of 14.34° (Figure 2), which is smaller than that of [4]helicene (19.9°).⁵⁴ This reduced angle would be expected as the internal angle⁵⁵ of the fused five membered ring is 35.4° , which is significantly compressed compared to that of a benzene ring (60°) and therefore results in a smaller turn in the helical arrangement and less crowding. Similar reduced angles and lower racemization barriers are known for other 5-membered rings containing systems including azahelicenes and thiahelicenes.^{27,56,57} However, this apparent torsion angle is not specifically due to the [4]helicene arrangement (as demonstrated discussing **4a** below), but is a remnant of its more distorted [5]helicene neighbor that induces it. The more sterically crowded [5]helicene gives a significantly larger splay angle of 36.83° , which coincides with the closer proximity of the terminal benzene rings. As it turns out, this [5]helicene arrangement is the entire driving force for the contortion in the molecule (discussed below) and a requirement for the distortion from planarity. The contorted disks arrange into columnar stacks with the contorted

segments matching in a lock-and-key arrangement that propagates along the stacking directions with a pi-pi distance of 3.36 Å.

As mentioned above, the pyrene derivatives **4a** and **4b** were found to be considerably less soluble than the rubicene counterparts although each PAH core is fairly similar in overall surface area. While we were unable to obtain suitable single crystals due to solubility issues, the DFT minimized structure of **2d** (Supporting Information) gives a completely flat arrangement. This calculated result is in agreement with a recently reported crystal structure of a similar [4]helicene like fragments with five-member ring inclusion.^{8,47,58} Therefore, the marked solubility difference between **2a** and **4a** is directly related to the lack of the [5]helicene arrangements in the pyrene derivatives and results in the flat species that are more inclined to aggregate. These results suggest that the torsion angle present in the [4]helicene segment of **2a** is an artifact of the significant torsion angle of the [5]helicene neighbor.

Significant pi-pi stacking induced aggregation of the Scholl cyclodehydrogenated products with dodecyloxy chains, **2b** and **4b**, was detected in solution. While the non-cyclodehydrogenated compounds **1b** and **3b** did not show concentration dependent chemical shifting in the ¹H NMR spectra, **2b** and **4b** showed upfield shifting of the aromatic protons with increasing concentration (Supporting Information). These observations suggest significant dimerization or aggregation in solution with the upfield shifts resulting from the protons being shielded by neighboring aromatics in a stacked arrangement. As these chemical shifts were not found in the perpendicular aryl configured derivatives **1b** and **3b**, this aggregation behavior can be directly attributed to the more accessible aromatic core leading to a lower energetic barrier to stacking. Assuming a simple dimerization model, the concentration dependent chemical shifts could be quantitatively analyzed to provide dimerization association constants (K_2).^{59,60} The room temperature chemical shift data for **2b** in CDCl₃ gave an

association constant of $20.0 \pm 3.4 \text{ M}^{-1}$ (Supporting Information), which is of a similar value to other small extended PAH aggregations.^{14,61} As mentioned above, the pyrene derivative **4b** is insoluble in CDCl₃ at room temperature, suggesting significantly greater aggregation behavior. We therefore employed a higher boiling solvent, 1,1,2,2-tetrachloroethane-d₂ at 80 °C, to compare the aggregation behavior of **2b** and **4b**. As expected for a more energetic system, the measured association constant for **2b** at 80 °C was reduced to $1.88 \pm 0.78 \text{ M}^{-1}$, while **4b** at 80 °C gave a significantly greater value of $238 \pm 59 \text{ M}^{-1}$. The two orders of magnitude difference in aggregation can be most reasonably related to the significant difference in the contortion in the aromatic cores of the two compounds with **4b** being completely planar. In addition to the solution state, the cyclodehydrogenation ring closure in the dodecyloxy containing materials was also required to access ordered mesophases. As can be seen in Figure 3, **1b** displays only melting (173 °C) and crystallization (144 °C) transitions upon heating and cooling the sample via differential scanning calorimetry (DSC). Alternatively, **2b** gives a mesophases at 131 °C before melting at 171 °C. These results are consistent with a more accessible inner aromatic core that allows pi-pi stacking with a most likely columnar arrangement similar to the crystal packing of **2a**. The pyrene derivative **4b** showed no mesophases or melting under our DSC conditions up to 400 °C. With these results, it is clear that the ultimate fusion of the aryl rings via cyclodehydrogenation leads to materials that are more apt to undergo pi-pi stacking in the solid state or in solution.

After cyclodehydrogenation, the photophysical and electrochemical properties of the compounds are modulated mildly and can be seen visually in solution via a color change from emerald green (**1b**) to purple (**2b**) or reddish brown (**3b**) to red (**4b**). As shown in Figure 4, **2b** gives a mild hypsochromic shift of the longest wavelength absorption (λ_{max}) after ring closure of **1b** although it maintains an overall similar

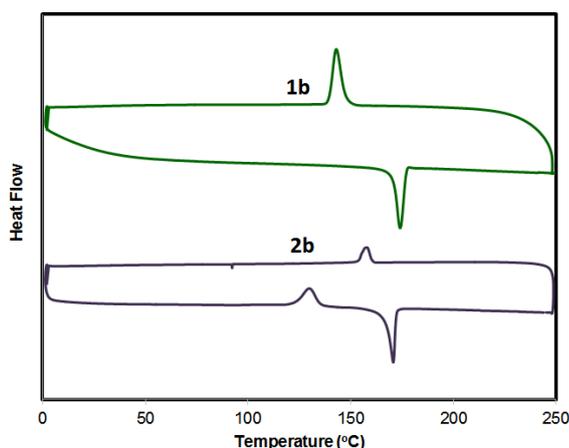


Figure 3. Differential scanning calorimetry of **1b** (top) and **2b** (bottom).

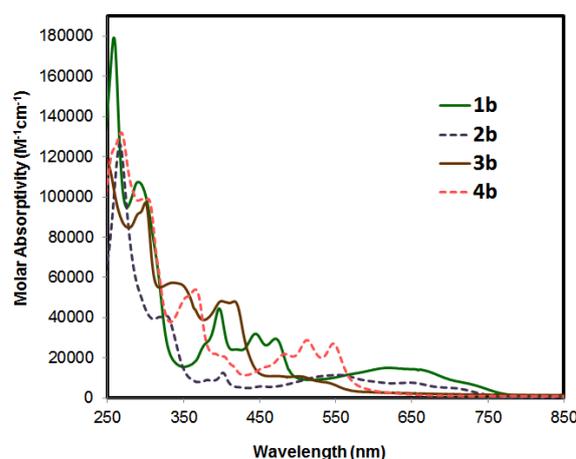


Figure 4. UV-Vis spectra of **1b** (green), **2b** (purple-dotted), **3b** (brown), and **4b** (red-dotted).

absorption profile. The greater absorption at ~550 nm of **2b**

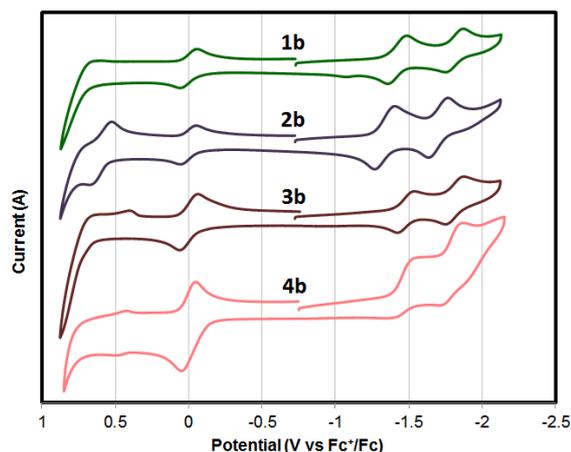


Figure 5. Cyclic voltammetry of **1b**, **2b**, **3b**, and **4b** (top to bottom) in 0.1 M tetrabutylammonium hexafluorophosphate in THF with glassy carbon working electrode, platinum counter electrode, and an Ag/AgCl reference electrode. Scan rate = 50 mV/sec. Ferrocene added as internal standard and referenced to 0 V.

leads to the change in color from green to purple.⁶² Both compounds show relatively reduced bandgaps that are similar to those shown previously for other cyclopenta[hi]aceanthrylene derivatives.^{15,33,34} In contrast, the ring closure of **3b** to **4b** leads to a slight bathochromic shift upon ring closure albeit both λ_{\max} values are reduced compared to the **1b** and **2b**.

The electrochemical properties of the CP-PAHs were probed by cyclic voltammetry (Figure 5). Each compound gave

calculated via standardization with ferrocene and can be found in Table 1. The LUMO levels are low lying owing to the ability to form cyclopentadienyl anions in the reduced state. To look at the electronic structures and the frontier orbitals of these compounds, DFT calculations of all four derivatives with methoxy substituents (e.g., **1a**, **2a**, **3a**, and **4a**) were investigated at the B3LYP/6-311g(d,p) level (Figure 6). As can be visualized in the contour plots of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) some variation occurs between the ring open and closed forms. For example, the HOMO of **1a** and **2a** maintains a line of high electron density from the CP-PAH core to the fused aryl rings that are in a diagonal arrangement, which is similar to previous difunctionalized cyclopenta[hi]aceanthrylenes.³³ In contrast, the two additional aryl rings possess very little electron density in **1a** and a mild increase upon cyclodehydrogenation to form **2a**. The disparity between the electron densities for **1a** is supported further by the torsion angles (Supporting Information) that show a 47.7° angle for the more interacting aryl ring and a larger 66.6° angle for the non-interacting ring. The HOMO in **3a** is more symmetrically extended to all four attached aryl rings with the torsion angles being a more favorable 47.4° and 49.2° owing to the lack of steric interactions with the pyrene core. Upon full planarization to **4a**, the HOMO is fully delocalized over the aromatic core. The LUMOs of all compounds are found to reside most prevalently on the inner CP-PAH cores where the cyclopentadienyl character of the reduced material is located. The predicted absolute values (Table 1) for the frontier orbitals show the greatest DFT calculated energy errors arise in the LUMO and optical band gap, which is partially due to the difficulties in accurately calculating CP-PAHs energies with charge-transfer characteristics. However, the general TD-DFT predicted

Table 1. Summary of optoelectronic properties of **1b-4b**.^a

Cmpd	$E_{\text{ox/onset}}$ (V)	$E_{\text{red/onset}}$ (V)	HOMO (eV)	LUMO (eV)	E-chem gap (eV)	Optical gap (eV)
1b	0.66	-1.32	-5.46 (-5.48)	-3.48 (-3.29)	1.98 (2.19)	1.63
2b	0.52	-1.24	-5.32 (-5.41)	-3.56 (-3.35)	1.76 (2.06)	1.67
3b	0.63	-1.38	-5.44 (-5.45)	-3.41 (-3.23)	2.03 (2.22)	2.17
4b	0.43	-1.39	-5.20 (-5.48)	-3.44 (-3.21)	1.76 (2.27)	2.13

^aMeasurements taken at sample concentration of 0.2 mM and potentials measured relative to a ferrocenium/ferrocene redox couple used as an internal standard (Figure 5). $E_{\text{ox/onset}}$ is the onset of oxidation potential, $E_{\text{red/onset}}$ is the onset of reduction potential. HOMO and LUMO values calculated on the basis of the oxidation of the ferrocene reference in vacuum (4.8 eV). DFT predicted values are in parenthesis and calculated based on methoxy derivatives **1a-4a**.

two reversible reductions at relatively low potential. For the non-fused systems **1b** and **3b** the oxidations were irreversible, while the cyclodehydrogenated compounds **2b** and **4b** showed reversible oxidations. The HOMO and LUMO values were

absorption spectra (Supporting Information) were in reasonable agreement with the experimental results and provide support and confidence in the calculation method.

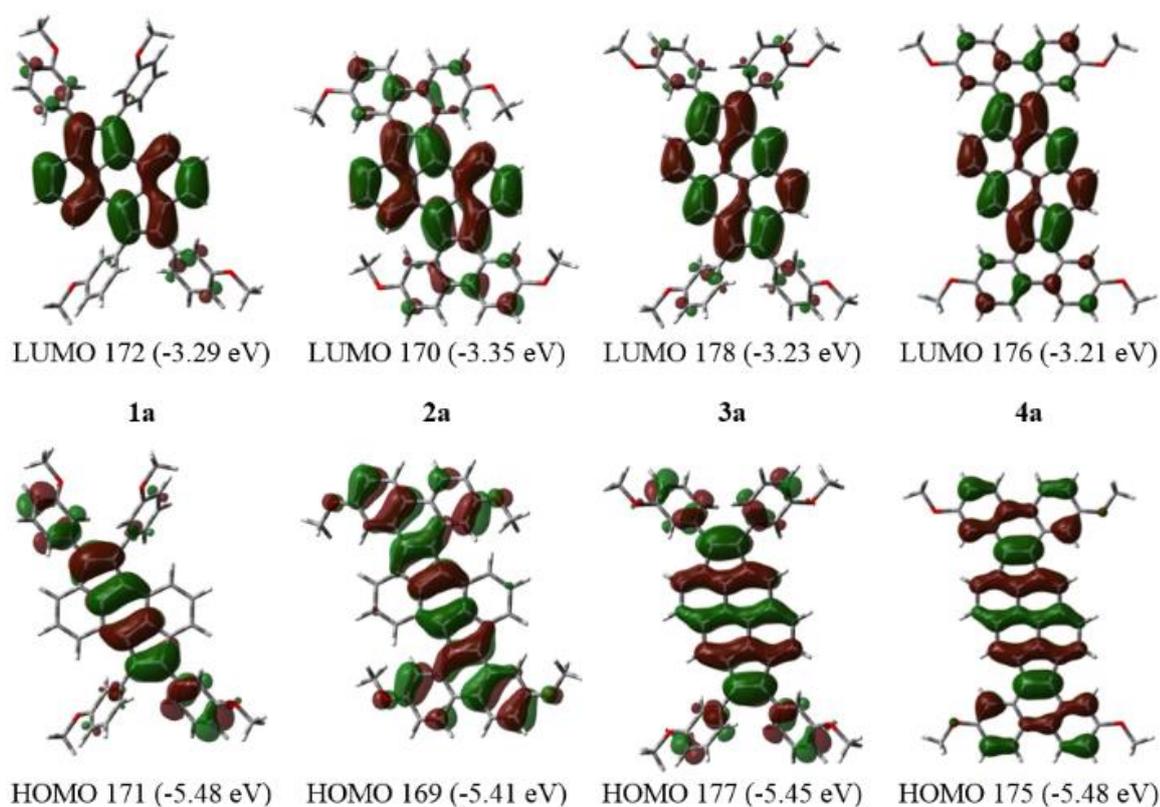


Figure 6. The B3LYP/6-311g(d,p) DFT calculated HOMO and LUMO contours of **1a**, **2a**, **3a**, and **4a**.

Conclusions

In conclusion, we have shown that a two-step cyclopentannulation followed by a Scholl cyclodehydrogenation can lead to a new class of contorted aromatics based on CP-PAHs. To access the contorted structures with five-member ring inclusion, a [5]helicene like arrangement of the fused rings is required while simple inclusion of a [4]helicene like arrangement results in planar structures. The contortion provides access to more highly soluble materials than their planar counterparts but still participate in significant pi-pi stacking. The optimized cyclopentannulation conditions presented here also provide efficient and easy access to the desired CP-PAHs and we are currently applying these reaction conditions to more complicated aromatic systems.

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A palladium-catalyzed cyclopentannulation provides access to contorted aromatics that afford solubility benefits while maintaining pi-pi stacking motifs.

