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# Supertwistacene: A Helical Graphene Nanoribbon

Shuang Ma,<sup>†,#</sup> Jiajian Gu,<sup>†,#</sup> Chaojun Lin,<sup>†</sup> Zhixing Luo,<sup>†</sup> Yanpeng Zhu,<sup>†</sup> Jiaobing Wang<sup>\*,†</sup>

E-mail: wangjb5@mail.sysu.edu.cn

<sup>†</sup>School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, China

<sup>#</sup>These authors contribute equally to this work.

#### Abstract

This work describes a synthetic chiral graphene nanoribbon, named supertwistacene **1**. It has four superbenzene (HBC) units linearly fused in a helical manner. The structure of **1**, 4.3 nm in length, with an end-to-end twist of 117, was confirmed by single crystal X-ray diffraction. In contrast to various twistacene compounds and their analogues, **1** has a very stable configuration. It resists thermal isomerization even when being heated at 200 °C for 16 h. Enantiopure **1** obtained by chiral HPLC shows distinct CD signals in a broad spectral range until 600 nm. Additionally, two smaller congeners of **1**, the trimer **2** and the dimer **3**, were also prepared and systematically investigated. Combining theoretical and experimental studies on **1-3** presents a big picture on their (chir)optical and electronic characteristics.

Keywords: twistacene, chiroptical property, nanographene, helical aromatic compounds.

## Introduction

Twistacenes<sup>1,2</sup> are aesthetically pleasing polycyclic aromatic hydrocarbons (PAHs). They have straininduced helical chirality due to the presence of a stereogenic axis, which is identical to the main axis of their deformed ribbon-type structures. Many twistacenes have been known in literatures, showing attractive optical and electronic properties.<sup>3-10</sup> Impressively, Pascal and coworkers reported a highly luminescent dodecaphenyltetracene with an end-to-end twist of 97 (Figure 1).<sup>10</sup> It is an achievement after many years of efforts, and was selected among "molecules of year" in 2019.<sup>11</sup> Up to now, an **extraordinarily** twisted hexacene derivative, documented by Kilway group, sets a record longitudinal



**Figure 1**. Structures of dodecaphenyltetracene (top) and **1** (bottom). Note: only the *M*-form enantiomer of **1** was shown. The molecular models are optimized by DFT at the B3LYP/6-31G (d) level, consistent with their crystal structures.

However, in general, twistacene derivatives or analogues have low racemization barrier. For instance, the above-mentioned dodecaphenyltetracene will racemize quickly at room temperature with a half-life less

torsion of 184°.8

than one second.<sup>10</sup> In addition, some elegant twistacene-like helical nanoribbons featuring oligomeric porphyrin,<sup>12</sup> or  $\pi$ -extended naphthalene/perylene diimide<sup>13-16</sup> have been reported. But unfortunately, it seems that these compounds do not have sufficient thermal stability to allow chiral resolution and further explorations on their chiroptical properties.

Herein, by replacing the linearly fused benzene rings of twistacene with superbenzenes<sup>17</sup> (hexabenzocoronenes, HBCs), we report a large helical graphene nanoribbon, which might be called supertwistacene (Figure 1, 1).<sup>18</sup> It is 4.3 nm in length, and features an end-to-end twist of 117. The structure of **1** was identified by single crystal X-ray diffraction. Between adjacent superbenzene units, a pair of embedded [5]helicene with t-butyl substitution results in an extremely stable configuration.<sup>19,20</sup> As a result, optically pure enantiomer of **1** could be obtained via chiral high performance liquid chromatography (HPLC). It was studied systematically using various spectroscopic techniques, and showed strong Cotton effects in a broad spectral range. Moreover, two smaller homologues of **1**, the trimer **2** (a known compound)<sup>21</sup> and the dimer **3**,<sup>22</sup> were also synthesized (Figure 6). They were studied in comparison with **1** to provide a clear picture on how photophysical properties evolve for this kind of attractive helical graphene nanoribbons.

#### **Result and discussion**

The synthetic procedure of **1** was summarized in Figure 2. In particular, the bisketone **6** is a key intermediate, which sets the two unsubstituted phenyl rings of polyphenylene **7** at proper, opposite, positions via a Diels-Alder addition. *para*-Iodization of **7**, Scholl oxidation of **8**, and then Sonogashira coupling of **9** yielded the bisalkyne **10**, which was ready for a second Diels-Alder reaction to give precursor **11**. Its dehydrocyclization, facilitated by DDQ and CF<sub>3</sub>SO<sub>3</sub>H, offered **1**, the desired *helical* product, in 5% yield. Two other isomers of **1**, in the *waggling* (1%) or *mixed* (7%) configuration,<sup>23</sup> were

also generated (Figure S1), and they could be separated via preparative thin layer chromatography. It was found that the first Scholl oxidation from **8** to **9** to produce the central double-HBC core was an essential



step. In other words, a full polyphenylene analogue of precursor **11** could not be transformed into **1** under various oxidation conditions.

**Figure 2**. Synthesis of **1**. Structures of **7-11** were optimized using molecular mechanics. Stars on **7-10** show the positions of substituents. During the Diels-Alder addition from racemic **10** to **11** at 260 °C, the central double-HBC core might switch its helicity, but it would not affect the outcome of the reaction.

Note: Lower homologues 2 and 3 (see Figure 6) were synthesized using similar strategies, see the supporting information.

<sup>1</sup>H-NMR data (Figure 3A) is consistent with the expected structure of **1**, and all resonance signals can be assigned with the assistance of 2D-NMR techniques. H<sup>e</sup>, H<sup>f</sup>, and H<sup>i</sup>, at the edge of the "bay" area (see Figure 4), appeared at high field relative to other aromatic protons. This could be attributed to a shielding effect from their neighboring  $\pi$ -planes. These protons are degenerate ( $\delta = 9.21$ ) in the spectrum because of similar chemical environments nearby. The other two isomers of **1** (in the *mixed* or *waggling* configuration) manifest distinct resonance signals in accordance to their molecular symmetry (Figure S2). Matrix assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF MS) gives desired molecular weight (Calcd for C<sub>222</sub>H<sub>198</sub>, 2865.55; found, 2864.91 [M]<sup>+</sup>) with expected isotope pattern (Figure 3B).



**Figure 3**. (A) <sup>1</sup>H-NMR spectrum of **1** in CDCl<sub>3</sub>. Aromatic (a-i) or *t*-butyl (j-n) protons are labelled on Figure 4. (B) MALDI-TOF MS result of **1** with (*E*)-2-(3-(4-(tert-butyl)phenyl)-2-methylallylidene)-malononitrile as the supporting matrix.

High quality single crystal was obtained by vapor diffusing of hexane into a solution of **1** in carbon disulfide at 20 °C. X-ray diffraction study unambiguously confirms the helical structure of **1** (Figure 4. CCDC no. 2019940). It is deposited in the  $P2_1/c$  space group. The twist angles between adjacent HBCs are found to be 34°, 40°, and 43°, respectively. This nonuniform twisting was expected to be caused by the crystal packing effect. In total, an end-to-end twist of 117° (Figure 4, bottom) was observed, slightly lower



than the DFT reproduced deformation of 120°. The *P*- and *M*-isomers appeared alternately in the unit cell (Figure 5). In the crystal, they were stacked via van der Waals contacts without  $\pi$ - $\pi$  interaction.

**Figure 4.** X-ray crystal structure of **1**. Thermal ellipsoids are shown with 50% probability. Mean planes of the HBC units at the end intersect at 117. t-Butyl groups at the positions of j-n are not shown.

The C-C bonds around the crowded "bay" area were stretched evidently (e.g. C1-C2 = 1.50 Å), and the benzene ring shared by two HBC units (e.g. ring "s") experiences severe distortion with a nonplanarity value up to 0.114 Å. In general, distribution of bond lengths in **1** as well as the HOMA<sup>24</sup> (harmonic oscillator model of aromaticity) value suggested local aromaticity of individual rings can be understood by the "fully benzenoid" Clar structure of the HBC units (Figure S7).<sup>25</sup>



Figure 5. Orientations of (M)-1 (grey) and (P)-1 (blue) in the unit cell. t-Butyl groups are omitted for clarity.

1 is soluble in different organic solvents, such as ethyl acetate, tetrahydrofuran, and toluene. A red solution of 1 in dichloromethane (DCM) has a maximum absorption at 586 nm ( $\varepsilon = 205000 \text{ M}^{-1}\text{cm}^{-1}$ , Figure 6. For a visualized image, see Figure S10). In the shorter wavelength, a prominent band at 448 nm ( $\varepsilon = 354000 \text{ M}^{-1}\text{cm}^{-1}$ ) was observed. Based on the results of TD-DFT calculations, the 586 nm absorption was attributed mainly to the HOMO-to-LUMO transition (S<sub>1</sub>, oscillator strength, f = 1.53), and the 448 nm absorption was due to the degenerate S<sub>0</sub>-S<sub>19</sub> (f = 0.78) and S<sub>0</sub>-S<sub>20</sub> (f = 1.01) transitions. In addition, two

shoulders manifest at 544 and 419 nm, which should arise from the vibrational progression, because no prominent TD-DFT transition was found in the corresponding spectral range. **1** emits red fluorescence at 601 nm with a small Stokes shift of 15 nm (Figure 6A, inset).



**Figure 6**. (A) UV-vis absorption (5.0  $\mu$ M) of **1-3** in DCM. Inset: normalized emission with the maximum absorption as the excitation wavelength. <sup>max</sup> $\lambda_{abs}$  of **1-3**: 586, 577, and 554 nm; <sup>max</sup> $\lambda_{em}$  of **1-3**: 601, 594, and

 574 nm. (B-D) CD spectra of 1-3. The maximum CD intensity (red star) for 1-3 was 760, 575, and 160  $M^{-1}$  cm<sup>-1</sup>, respectively. Inset: structures of the (*M*)-form enantiomers.

Optically pure samples were obtained by chiral HPLC using a COSMOSIL cholester column (Figure S18). Two enantiomers of **1** display a series of mirror-image Cotton effects from 250 to 600 nm. Their helicities were assigned by theoretical studies (Figure S12). The strongest CD signal was found at 450 nm ( $|\Delta\varepsilon| = 760 \text{ M}^{-1} \text{ cm}^{-1}$ , Figure 6B, red star). While in the longer wavelength, CD signals were much weaker by comparison, e.g.  $|\Delta\varepsilon| = 60 \text{ M}^{-1} \text{ cm}^{-1}$  at 590 nm.

To probe the (chir)optical and electronic characteristics of this kind of helical graphene nanoribbons, two smaller congeners of **1**, the trimer **2** and the dimer **3** were also synthesized and investigated (inset of Figure 6C, 6D, S3, S5). Their helical structures were confirmed by using single crystal X-ray diffraction (Figure S8, S9), with an end-to-end twist of 61.9 and 45.9, respectively.<sup>26</sup>

The absorption and emission profiles of the tetramer **1** and the trimer **2** resemble each other closely (Figure 6A). It is not surprising that the higher congener shows red-shifted absorption and emission, larger extinction coefficient, and narrower Stokes shift. The fluorescence quantum yields of **1-3** are high and comparable (**1**:  $\Phi = 0.72$ ,  $\lambda_{em} = 601$  nm; **2**:  $\Phi = 0.72$ ,  $\lambda_{em} = 594$  nm; **3**:  $\Phi = 0.78$ ,  $\lambda_{em} = 574$  nm).

The DFT calculated HOMO of **1** (-4.56 eV) is slightly higher compared with that of **2** (-4.58 eV) and **3** (-4.64 eV), consistent with the cyclic voltammetry measurements (Figure S17), which show the first oxidation potential ( $E_{ox1}$  vs SCE) of **1-3** at 0.44, 0.51 and 0.56 V, respectively. The LUMO displays an opposite trend, with that of **1** (-2.13 eV) being lower relative to **2** (-2.10 eV) and **3** (-2.03 eV). As a result, the tetramer has a narrower HOMO-LUMO gap (2.43 eV), compared with the trimer (2.48 eV) and the dimer (2.61 eV), consistent with the red-shifted spectra for the higher congeners presented in Figure 6A.

Of particular interest was the much stronger Cotton effects for the tetramer ( $|\Delta\varepsilon|_{450nm} = 760 \text{ M}^{-1} \text{ cm}^{-1}$ ) and trimer ( $|\Delta\varepsilon|_{446nm} = 575 \text{ M}^{-1} \text{ cm}^{-1}$ ), relative to the dimer ( $|\Delta\varepsilon|_{441nm} = 160 \text{ M}^{-1} \text{ cm}^{-1}$ ), especially at the spectral range from 435 to 455 nm (Figure 6B-D, red star). According to previous studies, many helical aromatic compounds, such as helicenes<sup>27</sup> and chiral nanographenes, are subject to CD spectral saturation quickly for their higher congeners. For instance, higher [n]helicene (n = 8, 9) essentially has the same CD intensity compared with [7]helicene. Similar spectral characteristics were found for the multiple versions, for example, the hexapole [9]helicene<sup>28</sup> shows CD signals comparable to that of the hexapole [7]helicene.<sup>29</sup>

Theoretically, all chiroptical properties are related to the rotatory strength ( $R = |\mu_e| |\mu_m| \cos \theta$ )<sup>30</sup> which is the scalar product of the corresponding electric ( $\mu_e$ ) and magnetic ( $\mu_m$ ) transition dipole moments. A closer examination of the computational results (Table S8) suggests that an increased  $|\mu_m|$  in **1** is the major factor contributing to its high CD signals relative to **2** and **3**. While the differences in  $|\mu_e|$  and  $\theta$  are not significant. TD-DFT calculations indicates a steady increase of rotatory strength from the dimmer (308.8 × 10<sup>-40</sup> cgs) to the trimer (458.0 × 10<sup>-40</sup> cgs) and tetramer (643.1 × 10<sup>-40</sup> cgs), in accordance to the recorded experimental data. We noted that CD signal of the dimer was deviated from the theoretical value (weaker than expected). This might be caused by the offset of two close Cotton effects of opposite signs, i.e. transitions S<sub>0</sub>-S<sub>6</sub> and S<sub>0</sub>-S<sub>9</sub> (indicated with stars in Figure 6D, see Figure S16B also).

At last, we examine the thermal stability of **1** by prolonged heating at high temperature. There was no evident structural change when **1** was heated at 200 °C in diphenyl ether for 16 h, indicating an extremely

high thermal stability. Further increasing the temperature to 260 °C leads to a slow transformation from helical **1** to the other isomers, i.e. mixed-**1** or waggling-**1**, as demonstrated by HPLC and <sup>1</sup>H-NMR analysis (Figure S21). However, complicate interconversion between different isomers of **1** prohibits a more detailed analysis of the kinetic parameters.

Therefore, to determine the isomerization barrier, we turn to its lower congener, the enantiopure (*P*)-**3** (Figure 7). HPLC analysis of the samples after heating in diphenyl ether at 260 °C indicates a clean transformation from the (*P*)- to the (*M*)-isomer with a half-life ( $t^{1/2}$ ) of 35 h for the loss of enantiomeric excess. It gives a  $\Delta G^{\ddagger}$  (533 K) of 44.7 kcal/mol by using the Eyring equation. This value is even higher than that of [7]helicene ( $\Delta G^{\ddagger} = 42.6$  kcal/mol at 533 K).<sup>31</sup> It is much more favorable, in terms of thermal stability, compared with the previously resolved twisted pentacene ( $\Delta G^{\ddagger} = 23.8$  kcal/mol,  $t^{1/2} = 9.3$  h at 298 K).<sup>5,32</sup>

Notably, helical structures of most twistacene compounds,<sup>1,2</sup> such as dodecaphenyltetracene,<sup>10</sup> are induced by steric crowdedness around the peripheries of their acene frameworks, being dynamic and featuring low barriers to racemization. While for **1**, chiral configuration of its HBC units is formed and "locked" during dehydrocyclization, because of the newly generated [5]helicene subunits with bulky *t*-butyl substitutions.



**Figure 7**. Thermal racemization of (*P*)-**3** at 260 °C followed by chiral HPLC with a COSMOSIL cholester column (DCM/isopropanol, 70/30, v/v, 2.0 mL/min, detector: 550 nm). Note: in the Y-axis,  $\alpha$  stands for the mole ratio of the (*P*)-isomer. Inset, HPLC traces from 0 to 31 h. HPLC data indicates the absence of *meso-***3**, which is higher in energy (34.8 kJ/mol) relative to the helical isomer, as suggested by DFT calculations.

In summary, we report the synthesis and characterization of a 4.3 nm helical graphene nanoribbon, named supertwistacene. It is composed of four linearly fused superbenzenes with an end-to-end twist of 117, and has a remarkable thermostability. Structure and properties of **1** were thoroughly investigated using various spectroscopic techniques. Optically pure **1** displays strong Cotton effects without evident spectral saturation compared with its lower congeners **2** and **3**. Based on these results, one may conjecture the properties of higher congeners of **1**, such as the pentamer or the hexamer, but their synthesis should be a challenging task. Whether this work would have ramifications on the more extended polymeric-form<sup>33,34</sup> helical graphene nanoribbons remains an open question. We anticipate that this study, which intimately connects the fields of twistacene,<sup>1,2</sup> helicene,<sup>35</sup> and distorted nanographene,<sup>36</sup> might inspire further developments of these vibrant nonplanar PAHs.

#### **Experimental Section**

**6**: A mixture of **4** (1.20 g, 3.5 mmol) and **5** (3.60 g, 11.2 mmol) in EtOH (10 mL) was stirred at 90 °C until all solids were dissolved. Then, 1.0 mL of KOH solution in EtOH (3.5 mmol, 3.5 M) was added, and the reaction was refluxed for 15 min. After that, it was quenched by cooling in an ice bath, and the precipitate formed was collected by filtration and washed with cold EtOH (50 mL). The crude product was purified by silica gel column chromatography using petroleum ether (PE) and DCM (v/v = 1/5) as the eluent to give **6** as a violet solid (1.38 g, 43%, m.p. = 292-294 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.23

(s, 10H), 7.17 (s, 4H), 7.13 (d, J = 7.6 Hz, 8H), 6.83-6.74 (m, 8H), 1.26 (s, 18H), 1.25 (s, 18H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  200.9, 155.2, 154.8, 151.8, 151.7, 131.3, 130.3, 130.2, 129.8, 129.3, 129.2, 128.1, 127.3, 125.1, 124.8, 124.7, 124.6, 34.8, 31.4. MALDI-TOF MS calculated for C<sub>68</sub>H<sub>66</sub>O<sub>2</sub>, 914.50; found, 937.59 [M+Na]<sup>+</sup>.

**7: 6** (1.20 g, 1.31 mmol) and 1,2-bis(4-(tert-butyl)phenyl)ethyne (2.30 g, 7.93 mmol) were dissolved in diphenyl ether (8.0 mL). The reaction was stirred at 260 °C under a N<sub>2</sub> atmosphere for 48 h. After cooling to room temperature (RT,  $25 \pm 2$  °C), 50 mL of MeOH was added. The precipitate formed was collected and purified by silica gel column chromatography (PE/DCM, v/v, 10/1) to offer 7 as a white solid (1.43 g, 76%, m.p. > 300 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.05 (d, *J* = 6.6 Hz, 4H), 6.78 (m, 22H), 6.59 (t, *J* = 8.1 Hz, 12H), 6.41 (d, *J* = 8.0 Hz, 4H), 6.25 (s, 4H), 1.22 (s, 36H), 1.09 (s, 36H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  147.6, 147.5, 141.1, 140.8, 140.5, 139.9, 139.6, 138.1, 138.0, 136.8, 132.0, 131.8, 131.5, 131.1, 130.9, 130.5, 126.5, 124.9, 123.4, 123.2, 123.0, 34.3, 34.2, 31.6, 31.3. MALDI-TOF MS calculated for C<sub>110</sub>H<sub>118</sub>, 1439.93; found, 1440.07 [M]<sup>+</sup>.

**8**: A mixture of [bis(trifluoroacetoxy)iodo]benzene (PIFA, 507 mg, 1.18 mmol), 7 (1.42 g, 0.986 mmol), I<sub>2</sub> (300 mg, 1.18 mmol), and dry DCM (30 mL) was stirred at RT under a N<sub>2</sub> atmosphere for 4 days. After that, the reaction was quenched with cold MeOH (150 mL), and the precipitate formed was collected and purified by silica gel column chromatography (PE/DCM, v/v, 10/1) to give **8** as a white solid (1.52 g, 91%, m.p. > 300 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.14 (d, *J* = 8.3 Hz, 4H), 7.06 (d, *J* = 7.8 Hz, 4H), 6.86 (d, *J* = 8.0 Hz,4H), 6.79 (t, *J* = 7.8 Hz, 8H), 6.64 -6.49 (m, 16H), 6.40 (d, *J* = 7.6 Hz, 4H), 6.25 (s, 4H), 1.24 (s, 36H), 1.14 (s, 36H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  147.8, 147.6, 140.8, 140.5, 139.7, 138.6, 137.7, 137.6, 136.6, 135.5, 133.6, 131.8, 131.2, 130.9, 130.7, 130.3, 123.4, 123.2, 123.1, 122.9, 90.6, 34.2, 34.1, 31.4, 31.2. MALDI-TOF MS calculated for C<sub>110</sub>H<sub>116</sub>I<sub>2</sub>, 1691.72; found, 1713.86 [M+Na]<sup>+</sup>.

**9:** A mixture of **8** (1.48 g, 0.875 mmol) and DDQ (4.76 g, 21 mmol) in freshly distilled DCM (300 mL) was stirred at 0 °C for 15 min under a N<sub>2</sub> atmosphere. Then TfOH (3.0 mL) was added. After being stirred at 0 °C for 4 h, the reaction was quenched with triethylamine (5.0 mL). The solvent was removed under reduced pressure and MeOH (300 mL) was added. The precipitate formed was collected and dried in air, providing **9** as a red solid (1.25 g, 72%), which was used without further purification. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  9.59 (s, 4H), 9.45 (s, 4H), 9.39 (s, 4H), 9.27 (s, 4H), 9.15 (s, 4H), 1.87 (s, 36H), 1.35 (s, 36H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  149.9, 148.6, 133.2, 131.0, 130.9, 130.8, 130.4, 129.2, 127.6, 126.6, 124.2, 124.0, 121.8, 121.1, 119.9, 119.7, 119.6, 119.5, 36.1, 35.4, 32.2, 31.8. MALDI-TOF MS calculated for C<sub>110</sub>H<sub>22</sub>L<sub>2</sub>, 1667.53; found, 1667.69 [M]<sup>+</sup>.

**10:** A mixture of **9** (1.25 g, 0.744 mmol), CuI (14 mg, 0.0744 mmol), 1-(tert-butyl)-4-ethynylbenzene (706 mg, 4.46 mmol), and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (25 mg, 0.037 mmol), suspended in toluene (40 mL) and triethylamine (10 mL) was stirred at 55 °C for 12 h under a N<sub>2</sub> atmosphere. After cooling to RT, the solution was diluted with 300 mL of MeOH, and the precipitate formed was collected and dried in air, providing **10** as a red solid (1.19 g, 93%, m.p. > 300 °C), which was used without further purification. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  9.46 (s, 8H), 9.38 (s, 8H), 9.16 (s, 4H), 7.82 (s, 4H), 7.56 (s, 4H), 1.89 (s, 36H), 1.43 (s, 18H), 1.36 (s, 36H). <sup>13</sup>C NMR of **10** could not be collected because of its poor solubility in CDCl<sub>3</sub>. MALDI-TOF MS calculated for C<sub>134</sub>H<sub>118</sub>, 1727.93; found, 1728.11 [M]<sup>+</sup>.

11: A solution of 10 (994 mg, 0.575 mmol) and 2,3,4,5-tetrakis(4-(tert-butyl)phenyl)cyclopenta-2,4-dien-1-one (1.40 g, 2.30 mmol) in diphenyl ether (5.0 mL) was stirred at 260 °C under a N<sub>2</sub> atmosphere for 48 h. After cooling to RT, 80 mL of MeOH was added. The precipitate formed was collected and purified by silica gel column chromatography (PE/DCM, v/v, 8/1) to give 11 as a red solid (684 mg, 41%, m.p. > 300 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  9.39 (s, 4H), 9.20 (s, 4H), 9.07 (s, 4H), 8.83 (s, 4H), 8.81 (s, 4H), 7.06 (m, 8H), 6.89 (m, 28H), 6.76 (d, *J* = 7.5 Hz, 4H), 1.79 (s, 36H), 1.33 (s, 36H), 1.17 (s, 54H), 0.74 (s, 36H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 149.1, 148.1, 148.0, 147.8, 141.5, 141.3, 141.1, 140.7, 139.2, 138.3, 138.1, 131.5, 131.4, 131.0, 130.8, 130.6, 129.5, 127.1, 126.9, 126.5, 126.3, 123.9, 123.8, 123.4, 121.4, 121.0, 120.9, 119.2, 118.8, 118.5, 35.9, 35.3, 34.3, 34.1, 32.3, 31.8, 31.4, 30.9. MALDI-TOF MS calculated for C<sub>222</sub>H<sub>222</sub>, 2889.74; found, 2890.00 [M]<sup>+</sup>.

1: DDQ (281 mg, 1.24 mmol), **11** (150 mg, 0.0517 mmol), and dry DCM (150 mL) were added to a 250 mL Schlenk flask under a N<sub>2</sub> atmosphere. The solution was stirred at 0 °C for 15 min, then TfOH (1.5 mL) was added. After stirring at 0 °C for another 2.5 h, the reaction was quenched with triethylamine (3.0 mL) and washed with water (100 mL × 3). The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was first purified by silica gel column chromatography (PE/DCM, v/v, from 20/1 to 5/1) and then recrystallized from DCM/EtOH (1/5, v/v, 5.0 mL) to give pure **1** as a deep red solid (7.5 mg, 5%, m.p. > 300 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  9.61 (s, 8H), 9.52 (s, 4H), 9.46 (d, 8H), 9.41 (s, 4H), 9.21 (s, 12H), 1.94 (s, 18H), 1.93 (s, 36H), 1.49 (s, 36H), 1.48 (s, 36H), 1.43 (s, 36H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  149.5, 148.5, 148.4, 131.3, 131.2, 131.1, 131.0, 130.9, 130.8, 130.7, 130.2, 129.9, 127.4, 127.1, 126.8, 126.7, 126.5, 124.3, 124.2, 121.8, 121.7, 121.0, 120.0, 119.7, 119.5, 119.3, 119.2, 119.0, 36.1, 36.0, 35.5, 35.4, 32.3, 31.9, 31.8, 31.7. MALDI-TOF MS calculated for C<sub>222</sub>H<sub>198</sub>, 2865.55; found, 2864.91 [M]<sup>+</sup>.

#### **Supporting Information**

Synthesis and characterization of **1-3**, X-ray structures, computational results, chiral resolution, electrochemical data, and studies on thermal stability (PDF).

Single crystal X-ray diffraction data (CIF).

### Notes

The authors declare no conflict of interest.

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## **TOC Graphic**

