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π -Extended and Curved Anti-Aromatic Polycyclic Hydrocarbons

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ABSTRACT: Synthesis of anti-aromatic polycyclic hydrocarbons (PHs) is challenging because the high energy of their highest occupied molecular orbital (HOMO) and low energy of their lowest unoccupied molecular orbital (LUMO) cause them to be reactive and unstable. In this work, two large anti-aromatic acene analogues, namely cyclopenta[*pqr*]indeno[2,1,7-*ijk*]tetraphene (**CIT**, **1a**) and cyclopenta[*pqr*]indeno[7,1,2-*cde*]picene (**CIP**, **1b**), as well as a curved anti-aromatic molecule with 48 π -electrons, dibenzo[*a,c*]diindeno[7,1,2-*fgh*:7',1',2'-*mno*]phenanthro[9,10-*k*]tetraphene (**DPT**, **1c**), are synthesized based on the corona of indeno[1,2-*b*]fluorene. These three anti-aromatic PHs possess a narrow energy gap down to 1.55 eV and exhibit high kinetic stability under ambient conditions. Moreover, these compounds display reversible electron transfer processes in both the cathodic and anodic regime. Their cation and anion radicals are characterized by *in-situ* vis-NIR absorption and electron paramagnetic resonance (EPR) spectroelectrochemistry. The X-ray crystallographic analysis confirms that while **CIP** and **CIT** manifest planar structures, **DPT** shows a curved π -conjugated carbon skeleton. The synthetic strategy starting from *ortho*-substituted benzene units to construct five-membered rings in this work, provides a unique entry to novel pentagon-embedding or curved anti-aromatic polycyclic hydrocarbons. In addition, besides the detailed chemical and physical investigations, microscale single-crystal fiber field-effect transistors were also fabricated.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) have attracted considerable attention over the last two decades because of their potential applications in organic field-effect transistors (OFETs), photovoltaics (OPVs), and light-emitting diodes (OLEDs).¹⁻⁷ Among various PAHs, acenes such as pentacene and its derivatives are remarkable semiconductor candidates due to their high intrinsic charge carrier mobilities.⁸ These acene-type molecules are, however, susceptible to oxidation under ambient conditions and photolytic degradation when further extended to higher acene homologues, thus hindering their physical investigations.⁹⁻¹¹ To circumvent this stability issue and simultaneously keep their fully conjugated skeletons, one avenue is to develop acene-based compounds containing five-membered rings rather than the traditional acenes solely consisting of six-membered rings. For instance, the zigzag-edged bistetracene has a moderate biradical character in the ground state and turns out to be highly unstable under ambient conditions,¹² due to the oxidation into corresponding diketone, tetrabenz[o*a,f,j,o*]perylene-9,19-dione; whereas replacing two of the traditional six-membered rings by five-membered rings, the resulting bistetracene analogue shows high stability and can be fully characterized.¹³

On the other hand, acene-type molecules in principle tend to form Kekulé diradicals with pro-aromatic¹⁴ structures or anti-aromatic cores. Anti-aromatic molecules are formally defined in terms of the existence of $4n$ π -electrons disposed in a planar cyclic arrangement.¹⁴ As a typical example of the anti-aromatic polycyclic hydrocarbons (PHs), indenofluorenes (**2** and **3**, Figure 1a),¹⁵ are prominent 20 π -electrons, fully conjugated analogue of acenes having 6-5-6-5-6 fused rings. Compared to the acene-type aromatic compounds, the fused polycyclic anti-aromatic systems usually have an elevated highest occupied molecular orbital (HOMO) level and a low lowest unoccupied molecular orbital (LUMO) level, leading to a narrower HOMO-LUMO energy gap. Although anti-aromatic systems are generally highly reactive and kinetically unstable, the introduction of bulky groups at the reactive sites would enhance the kinetic stability and, thus, allow for their solution processing toward device studies.^{16,17} Therefore, development of stable anti-aromatic analogues is of great demand for further application of such materials. However, to date, it remains a great challenge to develop the extended indenofluorene systems with more than 20 π -electrons.¹⁸⁻²⁸ Very recently, longitudinally extended anti-aromatic PHs (**4** and **5**, Figure 1a) based on indeno[1,2-*b*]fluorene were reported by the Haley group.^{29,30} However, the anti-aromatic PH based on fluoreno[3,2-*b*]fluorene (**6**) is still elusive.³¹ Moreover, the anti-aromatic PHs reported

till now mainly adopt a planar π -conjugated carbon skeleton (Figure 1a). Previous studies have revealed that not only the aromaticity, but also the geometry plays an important role in determining the electronic structures of PHs.^{32,33} Therefore, the development of anti-aromatic PHs bridged with novel π -expanded skeletons appears attractive.

Herein, in order to pursue the synthesis of novel π -extended, stable anti-aromatic PHs as well as to elucidate their molecular and electronic structures, we report the solution synthesis of air-stable 24 and 28 π -electron anti-aromatic analogues, namely cyclopenta[*pqr*]indeno[2,1,7-*ijk*]tetraphene (**CIT**, **1a** and **1a'**) and cyclopenta[*pqr*]indeno[7,1,2-*cde*]picene (**CIP**, **1b**) (Figure 1b), by laterally extending indeno[1,2-*b*]fluorene and fluoreno[3,2-*b*]fluorene, respectively. In addition, for the first time, we demonstrate that the combination of a **CIT** core and two phenanthrene units, exemplified by the synthesis of a curved 48 π -electrons anti-aromatic molecule dibenzo[*a,c*]diindeno[7,1,2-*fgh*:7',1',2'-*mno*]phenanthro[9,10-*k*]tetraphene (**DPT**, **1c**) (Figure 1b), which results from the steric hindrance of C-H bonds at the inner cove and fjord regions. The resulting molecules exhibit low LUMO levels, which are -3.50 , -3.70 and -3.55 eV for **1a**, **1b** and **1c**, respectively, and lead to a narrow HOMO-LUMO energy gap. These anti-aromatic PHs display reversible electron transfer properties in both the cathodic and anodic regime, and their cation and anion radicals are characterized by *in situ* vis-NIR absorption and electron paramagnetic resonance (EPR) spectroelectrochemistry. Moreover, the semiconductor properties of **CIT** (**1a'**) in microscale single-crystal fiber FETs is also investigated.

Figure 1. Structure of indeno[1,2-*b*]fluorene and its derivatives.

RESULTS AND DISCUSSION

Synthesis of 1a, 1a', 1b and 1c. The synthesis of **CIT** (**1a**, **1a'**) was achieved starting from the easily available 2,5-dibromoterephthalaldehyde (**7a**), as shown in Scheme 1. First, compound 2,2'-dimethyl-[1,1':4',1''-terphenyl]-2',5'-dicarbaldehyde (**8a**) was obtained by two-fold Suzuki coupling in 81% yield from **7a**. Subsequent Wittig reaction with 4-(*tert*-butyl)benzyltriphenylphosphonium bromide furnished 2',5'-bis((*E*)-3-(*tert*-butyl)styryl)-2,2'-dimethyl-1,1':4',1''-terphenyl (**9a**, *n*=0) in 77% yield. The key intermediate 5,12-bis(3-(*tert*-butyl)phenyl)-1,8-dimethylbenzo[*k*]tetraphene (**10a**) was synthesized from **9a** through photocyclodehydrogenation in 61% yield under UV-irradiation with the oxidant iodine and propylene oxide. The two methyl groups of **10a** were then transformed into aldehydes to afford 5,12-bis(3-(*tert*-butyl)phenyl)benzo[*k*]tetraphene-1,8-dicarbaldehyde (**11a**),^{13,34,35} via an benzylic bromination, substitution by acetate, hydrolysis and oxidation sequence in 32% yield over four steps. Afterwards, dialdehyde **11a** was treated with mesityl magnesium bromide, which was further subjected to a Friedel-Crafts alkylation reaction promoted by BF₃•OEt₂ to afford 6,12-bis(3-(*tert*-butyl)phenyl)-4,10-dimesityl-4,10-dihydrocyclopenta[*pqr*]indeno[2,1,7-*ijk*]tetraphene (**12a**). The desired product **1a** was obtained as a purple-red solid by oxidation of **12a** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene in 40% yield over three steps. Following a similarly efficient synthetic strategy, longitudinally extended **1b** (Scheme 1) was obtained as blue solid from 2,6-dibromonaphthalene-1,5-dicarbaldehyde (**7b**).

Scheme 2. Synthetic route towards the curved anti-aromatic **DPT (1c)**.

Structural Characterization. Crystals of **1a**, **1b** and **1c**, respectively, suitable for single-crystal X-ray analysis were obtained by slow evaporation of their solutions in a methanol/dichloromethane mixture. Notably, the planarity of the skeleton of **1a** and **1b** has not been affected by the extension of the indenofluorene core with additional annulated benzene rings at the bay positions. Both **1a** and **1b** possess a rigid, symmetrical and planar π -conjugated carbon skeleton (Figure 2a and 2b). The observed bond lengths of **1a** indicate that the central six-membered ring has two short $C(sp^2)$ - $C(sp^2)$ bonds (red one in Figure 3a: 1.381(4) Å) and four long $C(sp^2)$ - $C(sp^2)$ bonds (blue one in Figure 3a: 1.468(4) Å and 1.459(4) Å). These central core bond lengths are in agreement with a pronounced bond alternation for the *p*-quinodimethane³⁶ framework in **1a**. Similarly, compound **1b** is also completely flat with C_2 -point symmetry and exhibits large bond length alternation for the 2,6-naphthodimethene framework (Figure 3b). Moreover, it appears that the opposite rings of the five-membered ring in **1a** and **1b** contain a C-C double bond (brown one in Figure 3a and 3b), which are 1.396(4) and 1.389(2) Å, respectively.

Figure 2. X-ray crystal structures of compounds **1a** (a), **1b** (b) and **1c** (c) (from left to right: top views, side views and their packing, respectively). Hydrogen atoms and solvent molecules are omitted for clarity. Ellipsoids drawn at 50% probability level.

Interestingly, different from the planar structures of **1a** and **1b**, as well as the reported anti-aromatic PHs, the distinct feature of **1c** is its non-planar π -conjugated carbon skeleton (Figure 2c), which results from the steric hindrance of hydrogen atoms in the cove and fjord regions (Figure 1b). Furthermore, the distorted carbon framework makes **1c** chiral; the two enantiomers form a dimer packing in the crystals (Figure S6) and the double[4]helicene and double[5]helicene moieties have the same axial chirality. Figure 2c shows that the *P*-enantiomer of **1c** has its cove and fjord regions distorted with a torsional angle of 24.1° and 35.1° , respectively, which are larger than many reported non-planar PHs.^{33,37} In addition, the distance of the curved conjugated backbones in **1c** is

10.66 Å, decreased by 0.08 Å compared to **1a** (10.74 Å) with the same core due to its distortion. The X-ray diffraction data also disclose the detailed bond parameters of **1c** (Figure 3c), whereby the geometry of **1c** becomes asymmetric. The central core bond lengths are in agreement with a significant bond length alternation for the *p*-quinodimethane structure as in **1a**. The C-C bonds at the cove and fjord region (purple one in Figure 3c) are obviously longer (1.45-1.47 Å) due to the repulsive forces of congested hydrogen atoms.

Figure 3. Bond lengths (from their crystal structures) and nucleus-independent chemical shift (NICS(0)) values computed by using the GIAO approach at the PBE/TZ2P level of **1a** (a), **1b** (b) and **1c** (c). (d-f) show NICS isosurfaces at isovalues of ± 2 ppm of **1a** (d), **1b** (e) and **1c** (f) computed at the PBE/TZ2P level using the Priroda code³⁸ and visualized with VMD³⁹. (g-h) show normalized induced current flow in cross-section 1.0 Å above the joined rings plane of **1a** (g), **1b** (h). Blue and red color denote diatropic (shielding) and paratropic (deshielding) current contribution computed at the PBE/DZVP at DFPT level of theory^{41,42} using CP2k code⁴³⁻⁴⁵. Lines thickness scales with current magnitude.

NICS and Induced Current Calculations. The nucleus-independent chemical shift (NICS) calculations were performed by using the GIAO approach at the PBE/TZ2P level as implemented in the Priroda code³⁸ for **1a**, **1b** and **1c** to investigate the aromaticity of each ring. The obtained NICS (0) values of **1a** were –1.0 and –4.2 for the peripheral benzene rings, 10.8 and 7.5 for the five-membered and the central rings, respectively (Figure 3a). The values of the five-membered rings and the central naphthalene rings of **1b** are a little bit smaller than those of **1a** (Figure 3b). The central rings a and b in **1c** have similar values to **1a** due to the same *p*-quinodimethane core, while the peripheral benzene rings of **1c** have values of –2.1, –1.2, –7.3, –1.7 and –6.8 for rings c–g, respectively (Figure 3c). To achieve an overview of the NICS distribution around the molecules, we have computed NICS values on a dense grid of 51×51×51 points. NICS isosurfaces⁴⁰ with isovalues of ±2 ppm are plotted in Figure 3d–f. These plots illustrate that only pentagons and one (**1a**, **1c**) or two (**1b**) bridging hexagons have areas with positive NICS values. Peripheral hexagons do not exhibit such anomalies and show only negative NICS values. All these results are in accordance with the anti-aromatic nature of **1a**, **1b** and **1c**.

Density functional perturbation theory (DFPT) was used to compute the induced current flow in the systems as implemented in CP2k code. PBE/DZVP level of theory was employed with the position gauge for soft and step function for the local current parts to compute induced current within GAPW model. The induced current in the cross-section 1.0 Å above rings was separated into two components according to its rotation around the center of each ring (clockwise - shielding and counterclockwise - deshielding). When the molecules like **1a–1c** have rings with different degree of aromaticity, the statement on the definitive conclusion on the net aromatic or antiaromatic nature of the molecule as a whole cannot be reasonable. And although assignment of the current pathways in extended conjugated system (poly-ring) is still rather ambiguous especially for the diatropic contribution, the fragment analysis of individual rings gives a more sound background for the discussion. In Figure 3g and 3h, the blue and red colored stream plots encode diatropic and paratropic current contributions for the planar parts of **1a** and **1b**. One can justifiably state that the periphery largely unperturbed six-membered rings have bigger proportion of the diatropic current than its paratropic counterpart (stream density and current magnitude), which defines their aromatic nature. On the other hand, the five- and six-membered rings in the central region are paratropic current dominant and reassemble the patterns common for non-aromatic and anti-aromatic entities. These observations agree nicely with results of NICS modeling, which also show alternating aromatic/anti-aromatic nature of different rings in **1a–1c**. The non-planar topology of conjugated

segment of **1c** prevents reasonable ring current analysis, such as even the vector of magnetic perturbation would vary its orientation across the molecule.

Figure 4. (a) UV-Vis absorption spectra of **1a**, **1b** and **1c** in DCM (1×10^{-5} M). Insert: photo of their solutions. (b) Cyclic voltammetry of **1a**, **1b** and **1c** (0.1 M $n\text{Bu}_4\text{NPF}_6$ in DCM) at scan rate of 50 mV s^{-1} .

Optical and electrochemical properties. The UV-Vis absorption spectra were recorded for **1a**, **1b** and **1c**, as illustrated in Figure 4a. The purple, blue and red solution of **1a**, **1b** and **1c** were non-emissive when excited with UV light, which is in agreement with the $4n \pi$ -electron anti-aromatic character. The longest wavelength absorption maximum (531 nm) of **1a** was approximately 20 nm red-shifted in comparison to that of the reported indeno[1,2-*b*]fluorene.²¹ Notably, compounds **1a** and **1c** exhibit similarly shaped UV-Vis absorption patterns, with one major band (centered at 531 nm for **1a** and 564 nm for **1c**) and two shoulder peaks at 497 and 463 nm for **1a** and at 511 and 473 nm for **1c**, respectively. In contrast, compound **1b** shows a significant bathochromically shifted absorption maximum by 88 nm relative to that of **1a**, with an absorption maxima at 619 nm and two other shoulder peaks at 678 and 577 nm, respectively. The optical energy gaps (E_g^{opt}) of **1a**, **1b** and **1c** are determined from the onsets of the lowest energy absorption band of their UV-Vis absorption spectra, which are 2.14, 1.75 and 1.89 eV, respectively. This result suggests that the energy gap drastically decreases by the longitudinal extension of the central core from **1a** to **1b**. The electrochemical behavior of **1a**, **1b** and **1c** were investigated by cyclic voltammetry (CV) measurements (Figure 4b). Compound **1a** shows one reversible oxidation wave with half-wave potential $E_{1/2\text{ox}}$ at 1.29 V and two reversible reduction waves with half-wave potentials $E_{1/2\text{red}}$ at –

0.99 and -1.46 V (vs. Ag/AgCl). Two reversible oxidation waves with $E_{1/2\text{ox}}$ at 0.93 and 1.39 V, and two reversible reduction waves with $E_{1/2\text{red}}$ at -0.76 and -1.17 V were observed for compound **1b**. Compared with the same core of **1a**, compound **1c** manifests two reversible oxidation waves with half-wave potentials $E_{1/2\text{ox}}$ at 1.12 and 1.56 V and two reversible reduction waves with half-wave potentials $E_{1/2\text{red}}$ at -0.94 and -1.43 V. Thus, the HOMO/LUMO energy levels are estimated to be $-5.59/-3.50$, $-5.25/-3.70$ and $-5.43/-3.55$ eV for **1a**, **1b** and **1c**, respectively, based on the onset potentials of the first oxidation/reduction waves. The corresponding electrochemical energy gaps (E_g^{EC}) were estimated to be 2.09, 1.55 and 1.88 eV for **1a**, **1b** and **1c**, respectively, which are consistent with their optical energy gaps, which suggest that the energy gap drastically decreases by the longitudinal extension of the central core from the reported indeno[1,2-*b*]fluorene (2.22 eV)²¹ to **1b** (1.55 eV). All the extracted values are listed in Table S1 in the Supporting Information.

Figure 5 Vis-NIR absorption and EPR spectra of **1a** (a), **1b** (b), and **1c** (c) measured *in situ* during cyclic voltammetry at the first reduction step (blue lines) and the first oxidation step (red lines). Absorption spectra measured at each 0.05 V. The solvent is either *o*-DCB (**1a**) or CH_2Cl_2 (**1b**, **1c**) with 0.5 M Bu_4BF_4 as electrolyte salt, voltammetric scan rate $\nu = 2.5 \text{ mV s}^{-1}$. Absorption spectra are measured in a difference mode; the spectra of the non-charged compounds are taken as a reference. Insert: corresponding EPR spectra of monoanion (blue lines) and monocation (red lines) radicals for **1a**, **1b** and **1c**.

Stability. The kinetic stability of **1a**, **1b** and **1c** under ambient conditions and at higher temperatures was examined by means of NMR, EPR and UV-Vis analysis. There was no broadening in the ^1H NMR signals of **1a**, **1b** and **1c** and they remained EPR silent both at room and elevated temperature (up to 120°C) (Figure S2 and S3). Furthermore, no significant difference

was observed in the variable-temperature UV-Vis measurements from 30 to 60 °C in toluene (Figure S4). The time-dependent UV-Vis measurement of **1a**, **1b** and **1c** were conducted under ambient conditions to investigate their kinetic stabilities (Figure S5). During the measurement, the solutions of **1a**, **1b** and **1c** in CH₂Cl₂ were exposed to ambient air and sun light conditions up to 9 days. There were almost no change of the intensities of the UV-Vis absorption spectra of **1a**, **1b** and **1c** with the time. All these results support the air-stable feature of **1a**, **1b** and **1c**.

In Situ Spectroelectrochemistry. To confirm the assignment of the redox processes, *in situ* Vis-NIR/EPR spectroelectrochemistry of **1a**, **1b** and **1c** was carried out. Remarkably enough, at the first reduction and oxidation steps, all three compounds formed stable anion and cation radicals with strong characteristic NIR absorptions and well-defined EPR spectra (Figure 5). The spectra of **1a** and **1c** in their charged forms are quite similar indicating that the central anti-aromatic moiety is mainly responsible for the spectral features (Figure 5a and 5c). In the absorption spectra, anion radicals exhibit strong NIR absorption pattern at 795 nm accompanied by lower-intensity absorption peaks at 717, 1001, 1135, and 1340 nm for **1a**^{•−} and a strong absorption peak at 854 nm with additional absorption shapes at 765, 1065, and 1230 nm for **1c**^{•−} (blue lines in Figure 5a and 5c). Interestingly, absorption patterns of **1c**^{•−} are red-shifted by ca 50 nm versus analogous absorption peaks in **1a**^{•−}. The cations also exhibit strong NIR absorption peaks at 869 nm with shoulders at 670 and 770 nm and a weak absorption peak at 1802 nm for **1a**^{•+} and similar pattern with a strong band centered at 934 nm and shoulders at 840 and 1120 nm and a weak band near 2000 nm for **1c**^{•+} (red lines in Figure 5a and 5c). Negative peaks due to depletion of neutral species can be found at 531 nm (**1a**) and 511 nm (**1c**). Anion radicals **1a**^{•−} and **1c**^{•−} display EPR spectra with quintet-shaped hyperfine pattern with apparent *a*(¹H) values of 2.5-2.8 G and a half-width of individual peaks in the multiplets near 1.4-1.5 G (Figure 5a and 5c). On the contrary, the EPR spectra of cation radicals **1a**^{•+} and **1c**^{•+} show a single broad line.

DFT calculations reveal that the spin densities of ion radicals of **1a** and **1c** are mostly delocalized over the anti-aromatic PH backbone (Figure 6). Compared to the **1a**^{•−} and **1a**^{•+}, fused phenanthrene moieties in **1c**^{•−} and **1c**^{•+} do not bear any significant difference in the spin density, which explains the similarity of the EPR spectra of the ion radicals of **1a** and **1c**. In anion radicals, only few protons bonded directly to the carbon atoms in PH moieties with considerable spin density have large *a*(¹H) hyperfine coupling constants (*hfc*) values. In particular, in both **1a**^{•−} and **1c**^{•−} there are two pairs of protons with large negative *a*(¹H) values near −3 G, which reasonably matches experimental

observations (Figure 6a and 6e). In cation radicals, the spin density is more localized on the central parts of PH fragments which do not bear protons (Figure 6b and 6f).

Figure 6. Spin density distribution in anion and cation radicals of **1a**, **1b**, and **1c** (red – positive, green – negative). The numbers near selected protons show DFT-predicted hyperfine coupling constants $a(^1\text{H})$ in Gauss (red), and the values obtained from experimental spectra (blue). The constants smaller than 0.4 G are not shown.

The charged states of **1b** are somewhat different, although the overall spectroelectrochemical behaviour is similar to those of **1a** and **1c** (Figure 5b). In the radical anion **1b**^{•-} strong absorption peaks are found at 831 and 1335 nm with additional weaker features at 745, 1140, and 1700 nm (blue lines in Figure 5b). Cation radical **1b**^{•+} exhibits two strong NIR absorption patterns at 953 and 1522 nm and a weaker band near 1320 nm (red lines in Figure 5b). In EPR spectra, **1b**^{•-} shows an apparent septet with $a(^1\text{H})$ value of 2.5 G, whereas **1b**^{•+} has a broad-line spectrum (ca 5 G) superimposed with unresolved hyperfine structure (multiple lines with the average distance of 0.28 G). The hyperfine structure of the anion can be well understood taking into account that the molecule has three pairs of protons bonded to carbons with large spin density (**1a** and **1c** have two such pairs). The fit of the experimental spectrum gives values of -2.24, -2.43, and -3.16 G for these protons (Figure 6c). In the cation radical **1b**^{•+}, the spin density is more uniformly distributed similar to the **1a**^{•+} and **1c**^{•+} (Figure 6d).

At the low voltammetric scan rate used in spectroelectrochemical measurements (2.5 mV s^{-1}), the reversibility of the second reduction and oxidation steps of the compounds is diminished. However, characteristic absorption band of the two-fold charged species could still be identified (see Supporting Information). Most importantly, second reduction and oxidation steps of all three compounds are accompanied by a diminishing of the NIR absorption patterns emerged in mono-charged ion radicals. None of the dications or dianions has absorption bands at wavelengths longer than 800 nm. Analysis of the difference in the absorption spectra in the shorter wavelength range is complicated due to overlap with the bands of neutral and mono-charged forms. EPR signals of mono-charged radical ions vanished upon further reduction or oxidation showing that diamagnetic species are likely to be formed.

Figure 7. Microscale single-crystal fiber field-effect transistor based on **1a'**. (a) A schematic illustration of the transistor, (b) polarized optical microscopy image of an FET, (c) transfer and (d) output characteristic of the transistor.

Field-Effect Transistor (FET). To evaluate the charge carrier transport behavior of **1a'**, microscale single-crystal fiber field-effect transistor was fabricated with a bottom-gate top-contact structure (Figure 7). Heavily doped silicon substrate covered by 300 nm-thick thermally grown oxide dielectric acted as a gate electrode. The dimensional parameters of fiber were obtained by polarized optical microscopy (POM) and atomic force microscopy (AFM) studies, whose width is $1.5 \mu\text{m}$ and thickness is 280-300 nm (Figure 7b and S17). Source and drain electrodes were deposited by Au evaporation. The transistor measurements were performed in glove-box and the transfer and output curves are shown in Figure 7c and 7d. According to the saturation regime of transfer curve, the hole mobility of **1a'** is $5.0 \pm 1.0 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $I_{\text{on}}/I_{\text{off}}$ around 5000, and a V_T

about -20 V. The transistor of **1a'** exhibits unipolar behavior since only the HOMO levels (-5.52 eV) of **1a'** is close to the work function of Au (-5.0 eV), meaning that holes can be injected from Au electrode into **1a'**.

CONCLUSION

In summary, we present a novel synthetic route towards two unprecedented π -extended anti-aromatic compounds **1a** and **1b** by extending indenofluorene both at lateral and longitudinal directions. In addition, for the first time, a curved anti-aromatic PH **1c** with 48 π -electrons was synthesized. The unambiguous crystallographic characterizations reveal that while **1a** and **1b** manifest planar structures, the cove-edge and fjord structure cause **1c** to deviate from planarity due to steric repulsion between the C-H bonds. The chemical, physical and optical properties of **1a**, **1b** and **1c** were elucidated by UV-Vis absorptions, CV, in-situ spectroelectrochemistry spectroscopies and DFT calculations. These findings demonstrated that **1a**, **1b** and **1c** represent a new type of air-stable, fully conjugated anti-aromatic PHs, which can be used as potential candidates in optoelectronic devices due to their narrow HOMO-LUMO energy gaps and excellent reversible electron transfer properties. Furthermore, the location of the unpaired electrons of the anion radicals of **1a**, **1b** and **1c** are identified from the EPR spectrum and interpreted by the aid of DFT calculations. These studies provide the conceptual basis of anti-aromatic PHs for a multitude of applications in an OFET device behaving as an n-channel materials or acceptors in OPVs. Phenyl-substituted CIT (**1a'**) was utilized in a microscale single-crystal fiber FET with Au source/drain contacts and exhibited p-type behavior. The synthetic strategy towards anti-aromatic PHs by building five-membered rings from the *ortho*-substituted benzene units and the combination of cove-edge structures, can be applied to the construction of other air-stable π -expanded and curved anti-aromatic PHs as well as even helical graphene nanoribbons.

ASSOCIATED CONTENT

Supporting Information

Experimental details, synthesis, characterizations, single-crystal data (CIF), computational studies, and NMR spectra. The Supporting Information is available free of charge on the ACS Publications website.

The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 1531485 (for **1a**), 1531484 (for **1b**) and 1531486 (for **1c**). These data can be obtained free of charge from CCDC via http://www.ccdc.cam.ac.uk/data_request/cif

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Notes

The authors declare no competing financial interests.

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