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Communication

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Toward Full Zigzag-Edged Nanographenes: *peri*-Tetracene and Its Corresponding Circumanthracene

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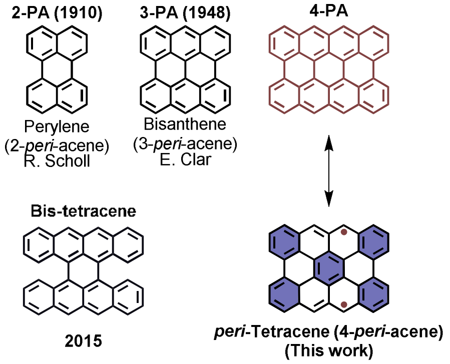
Supporting Information Placeholder

ABSTRACT: Zigzag-edged nanographene with two rows of fused linear acenes, called as n-*peri*-acene (n-PA), is considered as potential building unit in the arena of organic electronics. n-PAs with four (*peri*-tetracene, **4-PA**), five (*peri*-pentacene, **5-PA**) or more benzene rings in a row have been predicted to show open-shell character, which would be attractive for the development of unprecedented molecular spintronics. However, solution-based synthesis of open-shell n-PA has thus far not been successful because of the poor chemical stability. Herein we demonstrated the synthesis and characterization of the hitherto unknown **4-PA** by a rational strategy in which steric protection of the zigzag edges playing a pivotal role. The obtained **4-PA** possesses a singlet biradical character (y_0 = 72%) and exhibits remarkable persistent stability with a half-life time ($t_{1/2}$) of ~ 3 h under ambient conditions. UV-vis-NIR and electrochemical measurements reveal a narrow optical/electrochemical energy gap (1.11 eV) for **4-PA**. Moreover, the bay regions of **4-PA** enable the efficient two-fold Diels-Alder reaction, yielding a novel full zigzag-edged circumanthracene.

Atomically precise nanographenes and graphene nanoribbons (GNRs)[1,2] can be constructed with suitable oligophenylene and polyphenylene precursors[3] through oxidative intramolecular cyclodehydrogenation. Advantageously, such a rational bottom-up protocol can tune the energy gaps through the molecular size, edge structures or incorporation of appropriate heteroatoms.[4,5] Among the nanographenes, acene[6] and n-*peri*-acene[7] (n-PA) with rich zigzag edges are potential candidates for organic field effect transistors (OFETs), organic light-emitting diodes (OLEDs), organic spintronics, etc.[8] Acenes are linearly *cata*-condensed polycyclic aromatic hydrocarbons whereas n-PAs constitute two rows of *peri*-fused acenes (Scheme 1). Typically, the solution synthesis of longer acenes (larger than hexacenes) remains elusive due to their poor stability under ambient conditions.[9] Indeed, the longer acenes possess singlet biradical character (open-shell) in the ground state which can be explained by the formation of additional Clar π-electron sextets for rendering additional aromatic stabilization energy. Among n-PAs, perylene (2-*peri*-acene, **2-PA**) was achieved for the first time by Scholl *et al.* in 1910[10] and Clar reported the first synthesis of bisanthene (3-*peri*-acene, **3-PA**) in 1942.[11] Both **2-PA** and **3-PA**, as well as their derivatives, have since then become attractive targets of materials chemistry.[12-14] Higher n-PAs (n ≥ 4) are theoretically predicted to show strong open-shell properties by virtue of their narrow energy gaps, and, hence their synthetic realization remained challenging.[15] Despite the efforts from different research groups,[16,17] the next higher analogue, *i.e.*, *peri*-tetracene (4-*peri*-acene, **4-PA**, Scheme 1) has still remained elusive. Recently, *peri*-pentacene (5-*peri*-acene, **5-PA**) was accomplished under ultra-high vacuum (UHV) conditions on Au (III) surface,[18] nevertheless, its scalable synthesis in solution remains to be realized.

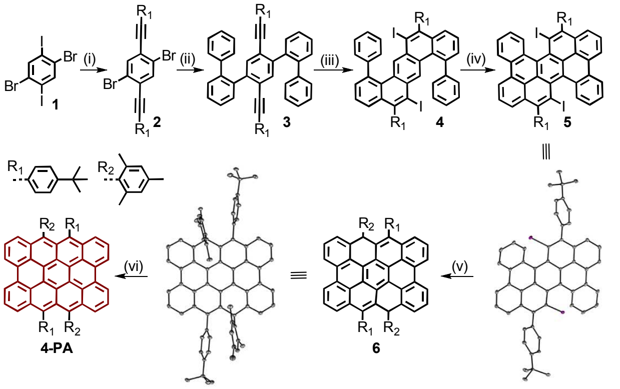
Scheme 1. Structures of perylene, bisanthene, bis-tetracene and *peri*-tetracene.



Herein we demonstrate the first solution synthesis of **4-PA** where steric protection of the zigzag periphery with appropriate phenyl substituents is essential. The successful formation of **4-PA** is supported by high-resolution (HR) matrix-assisted laser desorption/ionization time-of-flight (MALDI-

TOF) mass spectrometry, together with electron paramagnetic spectroscopy (EPR) and NMR analysis. Owing to its pronounced stability under inert conditions, **4-PA** is isolated and its optoelectronic properties are revealed by the aid of UV-vis-NIR spectroscopy and cyclic voltammetry (CV). **4-PA** displays a remarkable redox active nature and the optical/electrochemical energy gap is found to be only 1.11 eV. The strong open-shell character (y_0 = 72%) of **4-PA** is further rationalized by density functional theory (DFT) and Hartree–Fock (HF) calculations. Moreover, a two-fold Diels-Alder reaction is established between the bay regions of **4-PA** and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at room temperature (RT), yielding a novel electron deficient tetracyano-circumanthracene (**TC-4-PA**) with full zigzag-edged structure.[19]

Scheme 2: Synthesis of *peri*-tetracene (4-PA).



Reagents and conditions: (i) 4-*tert*-butylphenylacetylene, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, RT, 24 h, 87%; (ii) $Pd(PPh_3)_4$, K_2CO_3, *p*-dioxane/H_2O, 110 °C, 24 h, 92%; (iii) ICl, toluene, -78 °C, 3 h, 93%; (iv) DDQ, CF_3SO_3H, DCM, -10 °C, 30 min, 70%; (v) 1) *n*-BuLi, mesitaldehyde, toluene, -10 °C, 2 h; 2) $BF_3 \cdot OEt_2$, DCM, RT, 30 min, 50% (two steps); (vi) DDQ, toluene, RT, 1 h, quantitative yield. Crystal structures of **5** and **6** are shown where displacement ellipsoids are drawn at 20 and 50% probability level for **5** and **6**, respectively, and the hydrogen atoms and solvent molecules are omitted for clarity (grey, C; pink, I).

Recently, bis-tetracene (Scheme 1) has been synthesized by our group.[16c] However, due to its poor stability, its oxidative dehydrogenation to generate **4-PA** remained an arduous task. Therefore, we turned to a different design, where the fairly stable precursor (8,16-bis(4-(*tert*-butyl)phenyl)-7,15-dimesityl-7,15-dihydrotetrabenzo[*bc*,*ef*,*kl*,*no*]coronene, **6**) was synthesized firstly, which could afford **4-PA** upon dehydrogenation under mild reaction conditions (Scheme 2). It is also crucial to kinetically block the active zigzag edges of targeted **4-PA** by using phenyl substituents. Towards a detailed synthesis, we firstly prepared 4,4'-((2,5-dibromo-1,4-phenylene)bis(ethyne-2,1-diyl))bis(*tert*-butylbenzene) (**2**) from 1,4-dibromo-2,5-diiodobenzene (**1**) *via* Sonagashira coupling.[20] A two-fold Suzuki coupling of **2** with 2-biphenylboronic acid gave 1,4-bis(2'-biphenyl)-2,5-bis(4-(*tert*-butyl)phenyl)ethynylbenzene (**3**) in 92% yield. ICl-mediated benzannulation was performed to convert **3** into 5,12-bis(4-(*tert*-butyl)phenyl)-6,13-diiodo-1,8-diphenylbenzo[*k*]tetraphene (**4**) in 93% yield. Next, we carried out the Scholl reaction of **4** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and trifluoromethanesulfonic acid in dry dichloromethane (DCM) at 0 °C which afforded 6,15-bis(4-(*tert*-butyl)phenyl)-5,14-diiodotetrabenzo[*a*,*cd*,*j*,*lm*]perylene (**5**) in 70% yield. Despite the large steric hindrance generated by the iodine atoms, the Scholl reaction was successful and the formation of **5** was unequivocally confirmed by its crystal structure (Scheme 2, Fig. S1a). Afterwards, double nucleophilic additions were executed between *n*-butyllithium treated **5** and mesitaldehyde. Subsequent Friedel–Crafts cyclisation reaction promoted by $BF_3 \cdot OEt_2$ provided precursor **6** in 50% yield. Single crystals of **6** were grown by slow evaporation of its 1,1,2,2-tetrachlorethane/acetonitrile solution, and its structure was unambiguously confirmed (Scheme 2, Fig. S1b). It is noteworthy that the phenyl substituents at the periphery of **6** render a fair solubility in non-polar organic solvents.

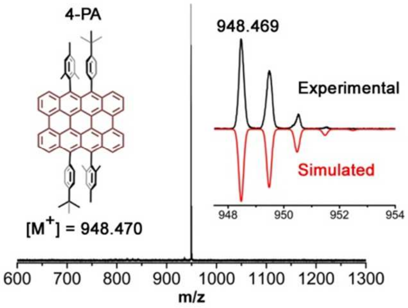


Figure 1: HR MALDI-TOF mass spectra of **4-PA**.

To examine the desired **4-PA** formation, precursor **6** was dehydrogenated with a slight excess of DDQ (~ 1.2 equiv.) in dry toluene at RT. The reaction mixture was purified by silica column chromatography with degassed DCM/acetonitrile as eluent under inert conditions and submitted for HR MALDI-TOF analysis (Fig. 1). At positive mode, an intense signal at 948.469 was obtained which is consistent with the calculated value of m/z 948.470 [M$^+$]. The isotopic distribution was in agreement with the simulated spectra and hence supported the formation of **4-PA**. To obtain a better insight, the reaction of **6** with 1-5 equiv. of DDQ was monitored by ^{1}H NMR spectroscopy (Fig. 2a and S4). With the addition of 1 equiv. DDQ in 1,1,2,2-tetrachloroethane-d_2 ($C_2D_2Cl_4$) solution of **6** under inert conditions and RT, the color of the solution instantly changed from bright yellow to dark brown and the aromatic signals of **6** had nearly vanished. The solution did not show any new signals in the aromatic region, which suggested the presence of open-shell **4-PA**. Cooling the solution of **6** with 1 or 2 equiv. of DDQ or the chromatographically isolated product over a temperature range from RT to –60 °C did not show significant changes, but rather remained silent in the aromatic region (Fig. S5-S8). Such a behavior can be expected for species with strong biradical character.[21] We also detected an intense EPR signal of solid **4-PA**, which we ascribed to its open-shell feature (Fig. S9). Notably, by treating **6** with excess equivalents of DDQ (5 equiv.) for an extended reaction time (~ 5 days) at RT, the ^{1}H NMR spectrum features a new set of resonance in the aromatic region (Fig. 2a). Based on our analysis, these peaks can be attributed to the formation of a novel full zigzag-edged circumanthracene (CA) derivative with four cyano groups (**TC-4-PA**, *vide infra*, Fig. 2b). The **TC-4-PA** (yield ~ 30%) was obtained *via* a two-fold Diels-Alder reaction between the bay regions of *in-situ* generated **4-PA** (dienes) and CN-C=C-CN (dienophiles) of DDQ (Fig. S10).[22]

The optoelectronic and electrochemical properties of **4-PA** were examined with UV-vis-NIR, CV and differential pulse voltammetry (DPV) measurements (Fig. 3 and S11). As shown in Fig. 3a, a solution of isolated **4-PA** in DCM showed clear vibronic structures with an intense absorption at 881 nm along with two shoulders at 788 and 1021 nm in the NIR region. The optical energy gap (E_g^{opt}) was determined to be 1.11 (±0.01) eV based on the lowest energy absorption onset. In order to investigate the stability of **4-PA** under ambient condition, we exposed the solution to air and continued to measure the absorption spectra at different time intervals. Notably, the pale brownish-green colored solution gradually changed to brown and the spectra displayed increasing absorptions in the region between 385-745 nm with concomitant decrease of the peak intensities in the UV and NIR regions. A plot of the absorbance change at 881 nm against time shows a gradual intensity decrease and the half-life ($t_{1/2}$) was found to be ~ 3 h. CV and DPV of **4-PA** (Fig. 3b) were performed in DCM solution containing 0.1 M of TBAPF$_6$ (*vs* Ag/AgCl). One reversible and one pseudo-reversible oxidation occurred at 0.21 (E^1_{ox}) and 0.73 V (E^2_{ox}), respectively, whereas one irreversible and one reversible reduction was seen at -0.90 (E^1_{red}) and -1.31 V (E^2_{red}), respectively. Each oxidation and reduction waves are accounted to respective one-electron redox process. Accordingly, the frontier orbitals are calculated as HOMO = -4.61 eV and LUMO = -3.50 eV, which gave an electrochemical energy gap (E_g^{EC}) of 1.11 eV that is consistent with the E_g^{opt}.

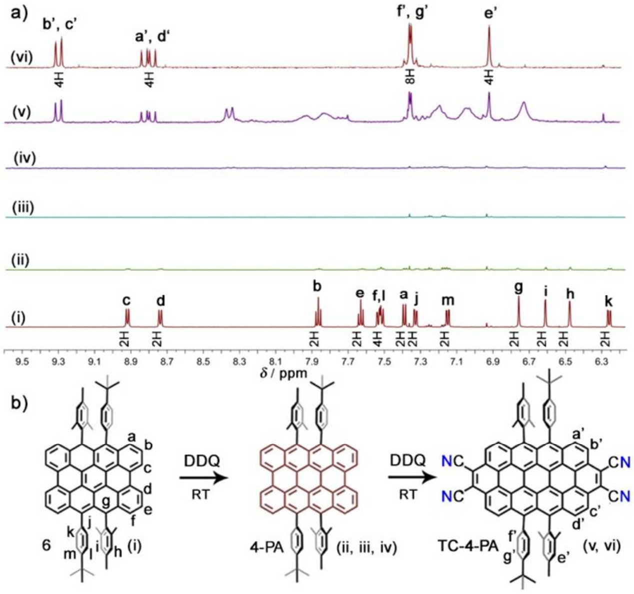


Figure 2: a) ^{1}H NMR spectra (600 MHz, RT, $C_2D_2Cl_4$) of **6** and DDQ-treated **6** (i, **6**; ii, **6** + 1 equiv. DDQ, 20 min; iii, **6** + 2 equiv. DDQ, 20 min; iv, **6** + 5 equiv. DDQ, 20 min; v, **6** + 5 equiv. DDQ after 5 days, vi, isolated **TC-4-PA**). b) Reaction pathway shows the formation of **4-PA**, from **6** with 1 equiv. of DDQ, and its two fold Diels-Alder reaction capability with excess of DDQ that yields **TC-4-PA**.

For a deeper insight into the electronic nature of **4-PA**, density functional theory (DFT) analysis was performed using Gaussian 09. The occupation numbers of the natural orbitals revealed the singlet biradical index (y_o) of 72% (UHF/6-31G*), which is significantly larger than the previously reported bistetracene (y_o = 61%).[16c] As depicted in Fig. S36, the singly occupied molecular orbital (SOMO) profiles of α and β display a disjoint feature. The zigzag C atoms, which are blocked with phenyl substituents, possess the highest spin densities (0.44) compared to the unprotected ones (0.23) (Fig. S36). In addition, the singlet-triplet energy gap (ΔE_{S-T}) of **4-PA** is -0.994 kcal mol^{-1} (UCAM-B3LYP/6-31G*), indicating the singlet biradical ground state.

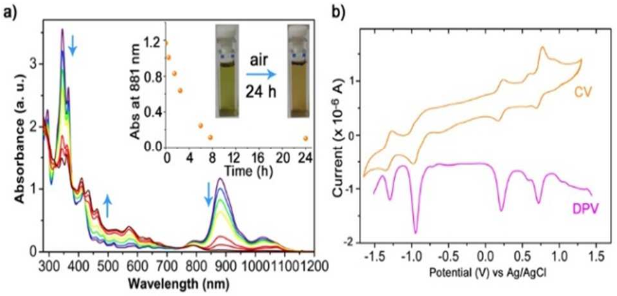


Figure 3: a) UV-vis-NIR spectra of isolated **4-PA** and its time-dependent absorption changes under ambient conditions in DCM. Inset shows the absorbance change at 881 nm with respect to time, and color change of the solution before and after air exposure. b) CV and DPV of **4-PA** in a 0.1 M solution of TBAPF$_6$ in DCM.

The formation of **TC-4-PA** was unambiguously proven by X-ray crystallography (Fig. 4 and S2). The 4-*tert*-butylphenyl and mesityl groups are bent 8.37 and 4.57°, respectively, in opposite directions and severely twisted against the cores. Notably, the CN groups situated at the core positions show a torsional angle of 5.41°. The bond length analysis of **TC-4-PA** reveals that the C-C bonds at the *peri*-position, *i.e.*, a and b show stronger double-bond character compared to the other C-C bonds of the CA core, which is estimated to be 1.35 Å. The unusual lengthening of d bond (1.44 Å) could be due to the steric effects of the zigzag substituents. The optical properties of **TC-4-PA** in $C_2H_2Cl_4$ (1 μM) were examined by UV-vis and fluorescence spectroscopies (Fig. S12). The green solution of **TC-4-PA** shows absorption peaks at 396, 416, 594, 623, and 644 nm. Moreover, **TC-4-PA** exhibits moderate fluorescence emissions at 650 and 707 nm (quantum yield Φ_f = 15% by using rhodamine-6g as standard). **TC-4-PA** possesses an optical energy gap (E_g^{opt}) of 1.89 eV, which is extracted from the onset of λ_{max} = 644 nm. The electrochemical behavior of **TC-4-PA** (Fig. S13) was investigated by CV in dry DCM (*vs* Ag/AgCl). The HOMO and LUMO levels are estimated to be -5.48 and -3.60 eV, respectively, based on the first oxidation and the first reduction onset potentials. Hence, the electrochemical energy gap (E_g^{EC}) of **TC-4-PA** is 1.88 eV, in good accordance with E_g^{opt}.

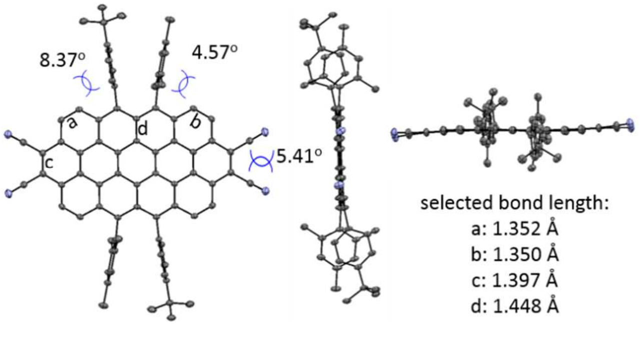


Figure 4: X-ray crystal structure of **TC-4-PA** (top and side views). Hydrogen atoms and solvent molecules are omitted for clarity. Ellipsoids are drawn at 50% probability level.

In conclusion, we have reported the efficient synthesis of **4-PA**. Our rational approach utilized suitable phenyl groups at the spin active zigzag positions rendering sufficient steric protection as well as adequate solubility in common organic solvents. The achieved **4-PA** possesses remarkable stability under ambient conditions, which facilitates in-depth characterizations. The singlet biradical character of **4-PA** is corroborated by the narrow optical/electrochemical energy gap (1.11 eV). Importantly, a novel full zigzag-edged **TC-4-PA** was obtained *via* a two-fold Diels-Alder reaction between **4-PA** and DDQ. The synthesis developed in the current work offers access not only to the next higher homologues of n-PAs, but also to the corresponding circumacenes (CA) under mild reaction conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental details, synthesis, X-ray crystallography details, HR mass spectra, NMR spectra and computational studies.

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Notes

The authors declare no competing financial interests.

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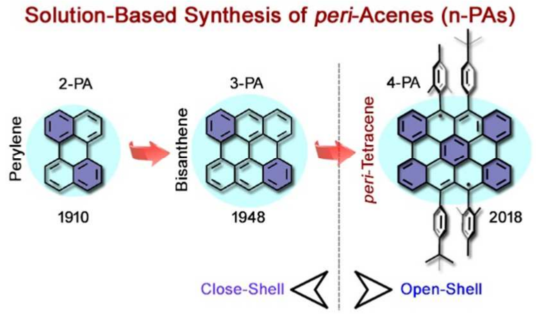
TOC:


Solution-Based Synthesis of *peri*-Acenes (n-PAs)
2-PA
Perylene
1910
3-PA
Bisanthene
1948
4-PA
peri-Tetracene
2018
Close-Shell
Open-Shell