Introduction

Nanographenes (NGs)\textsuperscript{[1–5]} have attracted increasing attention due to their intriguing electronic and optical properties, which render them as potential materials in carbon-based nanoelectronics.\textsuperscript{[6, 7]} Particularly, NGs can serve as molecular models for electronic applications. Accordingly, effective synthetic strategies are required towards the synthesis of highly stable zigzag-edged NGs with tailor-made magnetic properties.

Herein, we report the synthesis of zigzag-edged NGs with tailor-made magnetic properties through the controlled Diels–Alder reactions\textsuperscript{[12–34]} of 4-PA with suitable dienophiles (Scheme 1 b). The unprecedented benzo-peri-tetracenes (BPTs)\textsuperscript{[35,36]} possessed moderate open-shell biradical characters whereas the circumanthracenes (CAs)\textsuperscript{[28–30]} exhibited closed-shell or open-shell features depending on the dienophile employed. Among them, the open-shell BPTs (BPT 1, $\gamma_0 = 0.55$; BPT 2, $\gamma_0 = 0.61$) were synthesized (yields: 40% for BPT 1 and 20% for BPT 2) by one-side Diels–Alder reactions of 4-PA with $p$-chloranil (1) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 2), respectively (Scheme 1 b, route i). BPT 1 was able to execute further Diels–Alder reaction by virtue of its reactive

4-PA ($\gamma_0 = 0.72$; half-life, $t_{1/2} = 3$ h) was transformed into the unprecedented benzo-peri-tetracenes (BPTs) by a one-side Diels–Alder reaction, which featured a biradical character at the ground state ($\gamma_0 = 0.60$) and exhibited remarkable stability under ambient conditions for several months. In addition, the fully zigzag-edged circumanthracenes (CAs) were achieved by two-fold or stepwise Diels–Alder reactions of 4-PA, in which the magnetic properties could be controlled by employing the corresponding dienophiles. Our work reported herein opens avenues for the synthesis of novel zigzag-edged NGs with tailor-made magnetic properties.

Abstract: Nanographenes (NGs) with tunable electronic and magnetic properties have attracted enormous attention in the realm of carbon-based nanoelectronics. In particular, NGs with biradical character at the ground state are promising building units for molecular spintronics. However, most of the biradicaloids are susceptible to oxidation under ambient conditions and photolytic degradation, which hamper their further applications. Herein, we demonstrated the feasibility of tuning the magnetic properties of zigzag-edged NGs in order to enhance their stability via the controlled Diels–Alder reactions of peri-tetracene (4-PA). The unstable

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Controlled Diels–Alder Reactions

Tailoring Magnetic Features in Zigzag-Edged Nanographenes by

Tailoring Magnetic Features in Zigzag-Edged Nanographenes by Controlled Diels–Alder Reactions

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[Image 28x717 to 42x732]
bay region to afford open-shell CA 1 ($y_0 = 0.46$) in 25% yield (Scheme 1b, route ii). Furthermore, two-side Diels–Alder reactions of 4-PA with dienophiles, such as diethyl acetylenedicarboxylate (3), 1,4-diphenyl-2-butyne-1,4-dione (4) and N-phenylmaleimide (5), provided closed-shell CA 2, CA 3 and CA 4 (Scheme 1b, route iii), respectively, in moderate yields ($\approx 30\%$). The optical and electrochemical energy-gaps are estimated to be 1.1–1.5 eV for the open-shell BPT 1, BPT 2 and CA 1, among them, BPT 1 possesses the narrowest energy-gap (1.1 eV). Moreover, the magnetic properties of the open-shell BPT 1, BPT 2 and CA 1 were analyzed by electron paramagnetic resonance (EPR) and superconducting quantum interfering device (SQUID) measurements, as well as supported by the theoretical calculations. Importantly, all these open-shell BPT 1, BPT 2 and CA 1 displayed high air-stability, and there was no noticeable degradation over one month under ambient conditions. Our work demonstrated herein paves the way for the rational synthesis of open-shell zigzag-edged NGs with remarkable stability and tailor-made magnetic properties.

Results and Discussion

The synthetic procedure is based on the key precursor PA 1,[28] which can readily yield 4-PA through dehydrogenation with $p$-chloranil or DDQ (Scheme 1a). First, PA 1 was oxidized into 4-PA in the presence of $p$-chloranil at 105°C in toluene (Scheme 1a, path a), which further underwent Diels–Alder cycloaddition with the additional $p$-chloranil in the reaction mixture (Scheme 1a, route i).[28] The aromatization of the resultant Diels–Alder adduct (a plausible mechanism of the Diels–Alder reaction was proposed in Scheme S1) occurred by the elimination of two HCl molecules and afforded BPT 1 (along with the inseparable monochloro derivative as minor impurity, Scheme S1) in 40% yield. However, the large excess of $p$-chloranil did not prompt two-fold Diels–Alder reaction of 4-PA, instead it led to undesired chlorination of the BPT core (Scheme S1 and Figure S11). Furthermore, a slow addition of 2 equiv DDQ into the dichloromethane (DCM) solution of PA 1 at room temperature was carried out. The in situ generated 4-PA executed Diels–Alder reaction with the DDQ (Scheme S2),[28,40,41] and afforded BPT 2 as dark-brown solid (20% yield). Interestingly, further treatment of BPT 1 with diethyl acetylenedicarboxylate (3) dienophile at 105°C in toluene and followed addition of excess $p$-chloranil into the mixture gave CA 1 in 25% yield (Scheme 1a, route ii), in which the short-edges (Scheme S3) of the CA core were asymmetrically installed with the carboxylic esters and dichloro-$p$-benzoquinone.

Regarding the synthesis of CA 2, CA 3 and CA 4, two-fold Diels–Alder cycloadditions of 4-PA with various dienophiles were performed (Scheme 1b, route iii). The precursor PA
In dry toluene was treated with 2.5 equiv of p-chloranil in presence of excess dienophile 3 at 105 °C to afford 4-PA. The in situ formed 4-PA underwent two-fold Diels–Alder reaction with 3, and the successive aromatization of the adduct (Scheme S4) yielded CA 2 (32%) as dark green powder. Following the similar synthetic strategy, CA 3 (30%) and CA 4 (31%) were achieved using dienophiles 4 and 5, respectively. All of the BPTs and CAs were fully characterized by high-resolution MALDI-TOF mass spectrometry and NMR (1H, 13C and 2D) spectroscopy (see the Supporting Information).

Single crystals suitable for X-ray analysis were grown by slow diffusion of methanol into chloroform solution of CA 2 and CA 3. X-ray crystallographic analyses of CA 2 and CA 3 reveal that the CA cores are slightly non-planar due to the presence of zigzag-edge substituents (Figure 1). The planes of the tert-butylphenyl and mesityl groups are nearly parallel to each other, whereas perpendicular to the plane of the respective CA cores. The torsional angles between the tert-butylphenyl groups and mesityl groups are measured as 19.04° and 32.15° for CA 2 and CA 3, respectively. The C–C bond lengths at the peri-positions (a, b) of CA 2 and CA 3 are the shortest (≈1.35 Å) in contrast to the other C–C bonds of the CA motif, and hence both of them show the strongest double bond character. The unusual lengthening of the d bond (1.44 Å) is attributed to the steric effect of the bulk phenyl substituents at the zigzag edge periphery. 

Next, the magnetic properties of open-shell compounds BPT 1, BPT 2 and CA 1 were investigated by electron paramagnetic resonance (EPR) and superconducting quantum interfering device (SQUID) measurements (Figure 2). The solid samples of BPT 1, BPT 2 and CA 1 showed intense EPR signals at room temperature (Figure 2 inset). The broad unresolved signals of BPT 1, BPT 2 and CA 1 gave g values of 2.0026, 2.0031 and 2.0029, respectively. The line widths were 9.45, 9.03 and 7.98 G for BPT 1, BPT 2 and CA 1, respectively. Furthermore, temperature-dependent SQUID measurements (in the range of 4–300 K) were conducted with the powder samples of BPT 1, BPT 2 and CA 1. The samples were cooled down to 4 K without external magnetic field then the data was collected during heating to 300 K under an applied magnetic field of 1 T. Plots of the product of molar magnetic susceptibility (\(\chi_m T\)) with the temperature (T) revealed a continuous increase after 150–200 K.

For a further investigation, the data of \(\chi_m T\) vs. T were fitted by using Bleaney–Bowers equation (Eq. (1)): 

\[
\chi_M T = \frac{N_A \mu_B^2 g^2}{k_B} \left( \frac{2 \exp \left( \frac{2J}{k_B T} \right)}{1 + 3 \exp \left( \frac{2J}{k_B T} \right)} \right)
\]

in which \(N_A\) is the Avogadro number, \(\mu_B\) is the Bohr magneton, \(g = 2.0\) is the g-factor, \(k_B\) is the Boltzmann constant, and \(J\) is the total angular momentum quantum number. Accordingly, the singlet-triplet energy gap (\(\Delta E_{ST} = -2J/k_B T\)) were found to be \(-2.01, -1.75\) and \(-3.59\) kcal mol\(^{-1}\) for BPT 1, BPT 2 and CA 1, respectively. All these experimental results confirm that BPT 1, BPT 2 and CA 1 exhibit well-defined open-shell properties.
1, BPT 2 and CA 1 display a single open-shell ground state. Variable-temperature $^1$H NMR measurements show no significant signal broadening caused by an increasing population of the paramagnetic triplet state at higher temperatures (Figures S13, S22, S29). Slowed-down motion of the quinoid ring in BPT 1 and CA 1 probably causes the line broadening and upfield shift that are observed at lower temperatures for protons adjacent to this moiety (Figures S14, S29).

To gain further insights into the electronic structures of BPT 1, BPT 2 and CA 1, Hartree–Fock (HF) and DFT calculations were performed. The biradical index ($y_0$) that reflects the degree of biradical feature, was calculated by symmetry-broken UHF/6-31G* method based on natural orbital (NO) occupations.[31] Owing to the gain of additional Clar’s sextets[4, 38] and thereby the increase in aromatic stabilization energies (Scheme S5), the open-shell characters are decreased from 4-PA to BPTs/CA s. In the case of CA 1, the CA core is laterally n-extended with a quinoid ring (Scheme S6) and, hence, the energy-gap ($\Delta E$) is lowered (1.3 eV) compared to that of CA 2-4 ($\Delta E_1 \approx 1.8$ eV).[36] Thus, the evolution of moderate biradical feature in CA 1 is justified. Additionally, the singly occupied molecular orbitals (SOMOs $\alpha$ and $\beta$) and anisotropy of the induced current-density (ACID)[49] maps of BPT 1, BPT 2, and CA 1 calculated at UB3LYP/6-31G(dp) level indicate that the electron densities are distributed over their aromatic core, whereas the electron densities are more localized over the zigzag periphery in 4-PA (Figure S50–S52). Therefore, it is supported that, upon benzanellation of the bay position of 4-PA, the electron density would extend to the newly fused benzene moieties. The calculated singlet biradical indices ($y_0$) are 0.55, 0.61 and 0.46, for BPT 1, BPT 2 and CA 1, respectively, which are noticeably smaller than 4-PA ($y_0 = 0.72$). Moreover, the BPT and CA core of these molecules possess clock-wise electronic current flow, thus indicating their global aromaticity.

The UV/Vis-NIR and fluorescence spectroscopies of BPTs and CA s were performed (BPT 1, BPT 2, CA 2 and CA 3 in CH$_2$Cl$_2$; CA 1 and CA 4 in C$_6$H$_5$Cl). As shown in Figure 3a, BPT 1 displayed broad absorption at NIR region, which are centered at 809 nm ($\varepsilon = 24700 \text{ m}^{-1} \text{ cm}^{-1}$) and 920 nm ($\varepsilon = 10800 \text{ m}^{-1} \text{ cm}^{-1}$), whereas BPT 2 revealed intense absorption with a maximum at 788 nm ($\varepsilon = 59500 \text{ m}^{-1} \text{ cm}^{-1}$). CA 1 showed broad NIR absorption band with a maximum at 816 nm ($\varepsilon = 17900 \text{ m}^{-1} \text{ cm}^{-1}$). The NIR absorptions (750–1100 nm) of BPT 1, BPT 2 and CA 1 can be attributed to their open-shell biradical characters at the ground state.[19, 35] The time-dependent UV/Vis-NIR measurements of BPT 1, BPT 2, and CA 1 were conducted under ambient conditions to investigate their kinetic stabilities. During the measurement, the solutions of BPT 1, BPT 2 and CA 1 were exposed to ambient air and sun light conditions (Figure S1–S3). There was no significant change of the intensities of the absorption spectra of BPT 1, BPT 2 and CA 1 with the time. All these results support the air stability of BPT 1, BPT 2 and CA 1. In contrast, compounds CA 2, CA 3 and CA 4 displayed sharp absorptions at 630 nm ($\varepsilon = 71300 \text{ m}^{-1} \text{ cm}^{-1}$), 635 nm ($\varepsilon = 79000 \text{ m}^{-1} \text{ cm}^{-1}$) and 648 nm ($\varepsilon = 58100 \text{ m}^{-1} \text{ cm}^{-1}$), respectively, which are more like the typical p-band of a closed-shell polycyclic aromatic hydrocarbon (PAH).[46] The optical energy-gaps ($E_{opt}$) of BPT 1, BPT 2 and CA 1 were estimated to be 1.09, 1.50 and 1.26 eV, respectively, based on their lowest energy absorption onset,[46] which are significantly narrow.[46] In contrast, the $E_{opt}$ of CA 2, CA 3, and CA 4 were determined to be 1.91, 1.90 and 1.80 eV, respectively. Moreover, CA 2, CA 3 and CA 4 exhibited intense emissions (Figure 3b) at 639, 643, and 674 nm, respectively. The relatively smaller stocks shifts of 9, 8 and 26 nm for CA 2, CA 3 and CA 4, respectively, are implied to their structural rigidity[47] and weak π–π stacking capability of the CA cores due to the presence of bulky groups at the zigzag edge peripheries. Note worthy, moderate fluorescence quantum yields ($\Phi_f$) of 17–29% were estimated for CA 2, CA 3 and CA 4 (Table 1) in dilute solutions using rhodamine 6 g as reference; whereas compounds BPT 1, BPT 2 and CA 1 did not show emissions in this range, which is consistent with the previously reported open-shell polycyclic hydrocarbons.[31, 27]

The electrochemical properties of BPTs and CA s (Figure 4) were investigated by cyclic voltammetry (CV) in dry DCM, in which Ag/AgCl was used as the reference electrode. Due to the presence of (CO-CCl)$_3$ moiety, BPT 1 and CA 1 are highly electron deficient and display three reduction ($E_{red}$) waves (reversible and quasi-reversible) between −0.45 and −1.40 V, while BPT 2 is moderately electron deficient and shows two reduction waves at −0.85 V ($E_{red}$) and −1.30 V ($E_{red}$). In addition, two oxidation waves (reversible and quasi-reversible) are observed for BPT 1, BPT 2 and CA 1 ($E_{ox}$) between 0.45 and 1.45 V. The electrochemical energy-gaps ($E_{E_g}$) of BPT 1, BPT 2 and CA 1 are determined as 1.13, 1.47 and 1.33 eV, respectively, which are in accordance with their $E_{opt}$. The closed-shell CA...
Table 1. Electrochemical and optical data of BPTs and CAs.

|       | \(J_{\text{abs}}\) [nm] | \(E_{\text{red}}^{\text{i}}\) [V] | \(E_{\text{red}}^{\text{c}}\) [V] | \(E_{\text{ox}}^{\text{i}}\) [V] | \(E_{\text{ox}}^{\text{c}}\) [V] | HOMO [eV] | LUMO [eV] | \(E_{\text{HOMO}}^{\text{opt}}/E_{\text{LUMO}}^{\text{opt}}\) [eV] |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-------------|-------------|------------------------|
| BPT 1 | 333, 381, 488, 809, 920 (br) | -0.55 | -1.00 | -1.29 | 0.58 | 1.10 | -4.98 | -3.85 | 1.09/1.13 |
| BPT 2 | 410, 568, 788 | -0.85 | -1.30 | - | 0.62 | 1.14 | -5.02 | -3.55 | 1.50/1.47 |
| CA 1  | 412, 655, 816 (br) | -0.48 | -0.99 | -1.31 | 0.85 | 1.36 | -5.25 | -3.92 | 1.26/1.33 |
| CA 2  | 403, 581, 630 | -1.07 | -1.47 | - | 0.76 | 1.34 | -5.16 | -3.33 | 1.91/1.83 |
| CA 3  | 405, 586, 635 | -1.09 | -1.47 | - | 0.75 | 1.31 | -5.15 | -3.31 | 1.90/1.84 |
| CA 4  | 439, 601, 648 | -0.87 | -1.31 | - | 0.89 | 1.40 | -5.29 | -3.53 | 1.80/1.76 |

[a] \(E_{\text{red}}^{\text{i}}\) and \(E_{\text{red}}^{\text{c}}\) are half-wave potentials of the reductive and oxidative waves (vs. Ag/AgCl), respectively. The HOMO/LUMO are determined by the equation: HOMO/LUMO = (\(-4.4 + E_{\text{HOMO}}^{\text{opt}}\)) eV.

4-PA (\(y_0 = 0.72\)) biradicaloid was converted into stable open-shell BPT 1 and BPT 2 (BPT 1, \(y_0 = 0.55\); BPT 2, \(y_0 = 0.61\)) upon respective one-side Diels–Alder reaction. A step-wise Diels–Alder reaction was carried out with 4-PA and, hence, achieving the open-shell CA 1 (\(y_0 = 0.46\)) with asymmetric edge-substitutions. Notably, BPT 1, BPT 2 and CA 1 biradicaloids possessed narrow energy gaps (\(\approx 1.1–1.5\) eV) and exhibited remarkable stability under ambient conditions. On the other hand, the two-fold Diels–Alder reaction of 4-PA with suitable dienophiles gave closed-shell CA 2, CA 3 and CA 4. Our synthetic strategy reported herein shed light on the development of open-shell zigzag-edged NGs with tailor-made magnetic properties with high stability, which can be useful for the advancement of carbon-based nanomaterials with superior quantum performance capability.\(^{20,21}\)

Experimental Section

Synthesis of PA 1

Compound PA 1 was synthesized by following the previous report.\(^{20}\)

Synthesis of BPT 1

A Schlenk flask was charged with PA 1 (55.0 mg, 0.058 mmol), and p-chloranil (28.4 mg, 0.116 mmol) along with dry toluene (10 mL) under argon. The flask was placed in a preheated oil bath at 105 °C and magnetically stirred for 24 h. The solution brought to RT and the solvent was removed in vacuo. The crude solid was purified by silica gel column chromatography with DCM/iso-hexane mixture as eluent to afford BPT 1, along with its monochloro derivative, as dark greenish yellow solid. The minor monochloro BPT 1 impurity is inseparable and the combined yield is 40% (26 mg). \(R = 0.55\) (iso-hexane/DCM 1:1 v/v). \(^1\)H NMR (500 MHz, C\(_6\)D\(_4\)Cl\(_4\), 60 °C): \(\delta = 9.43\) (d, 10.2, 1H), 9.34 (d, 10.2, 1H), 9.08 (d, 7.6, 2H), 9.73 (t, 7.5, 2H), 7.8–7.7 (2H), 7.68 (d, 10.2, 1H), 7.96 (d, 10.2, 1H), 7.21 (d, 10.2, 2H), 7.19 (d, 10.2, 2H), 7.09 (d, 10.2, 2H), 7.06 (d, 10.2, 2H), 6.73 (2 x s, 4H), 2.37 (s, 6H), 1.87 (s, 6H), 1.79 (s, 6H), 1.47 (s, 9H), 1.46 ppm (s, 9H). \(^{13}\)C NMR (125 MHz, C\(_6\)D\(_4\)Cl\(_4\), 60 °C): \(\delta = 178.0, 149.2, 149.0, 143.0, 142.9, 141.3, 140.5, 139.8, 136–137, 132.4, 132.0, 131.8, 131.4, 131.0, 130.4, 129.0, 128.9, 128.2, 128.1, 128.0, 127.7, 127.3, 127.1, 126.6, 126.4, 125.6, 125.1, 125.0, 124.5, 123.5, 122.8, 122.3, 121.8, 34.2, 31.3, 21.0, 20.9 ppm. Detailed \(^1\)H and \(^{13}\)C signal assignments are given in Table S3. HR-M5 MALDI (m/z): calcd for C\(_{29}\)H\(_{42}\)Cl\(_2\)O\(_2\): M\(^+\), 1123.381; found, 1123.383.
Synthesis of CA 1

A solution of BPT 1 (10.5 mg, 0.009 mmol), diethyl acetylenedicarboxylate (3) (477.6 mg, 2.81 mmol), and p-chloranil (6.9 mg, 0.028 mmol) in dry toluene (4 mL) was heated at 105 °C with gentle stirring under argon. After 24 h, excess of p-chloranil (20.0 mg) was added to the reaction mixture and continued heating for 2 h. The solvent was removed in vacuo and the crude solid was purified by silica gel column chromatography with DCM as eluent to afford CA 1 (3 mg, 25 %) as dark-green solid.

Synthesis of CA 2

A Schlenk flask was charged with PA 1 (50.0 mg, 0.053 mmol), 3 (470.7 mg, 2.63 mmol), and p-chloranil (32.3 mg, 0.131 mmol) along with dry toluene (10 mL) under argon. The solution was heated at 105 °C and magnetically stirred for 20 h. The resultant dark brown solution was mixed with excess of p-chloranil (80.0 mg) and heated for another 4 h. The solvent was removed in vacuo and the solid was purified by silica gel column chromatography with DCM as eluent to afford CA 2 (21.6 mg, 32 %) as purplish green solid, Rf = 0.21 (DCM). 1H NMR (500 MHz, CDCl3, 30 °C): δ = 9.11 (d, 9.7, 2 H), 9.10 (d, 9.7, 2 H), 8.55 (d, 9.7, 2 H), 8.50 (d, 9.7, 2 H), 7.85 (3.5, 8.3, 8 H), 6.89 (s, 4 H), 4.73 and 4.72 (2 x q, 7.2, 8 H), 1.77 (s, 12 H), 1.58 and 1.59 (2 x t, 7.2, 12 H), 1.54 (s, 18 H), 2.46 (s, 6 H) ppm. 13C NMR (125 MHz, CDCl3, 30 °C): δ = 169.3, 169.2, 149.7, 139.0, 138.8, 138.2, 137.6, 137.2, 131.2, 130.2, 129.8, 129.6, 128.8, 128.4, 127.5, 127.3, 127.2, 126.0, 125.9, 125.7, 125.3, 124.1, 122.1, 122.0, 121.8, 121.6, 120.7, 120.5, 120.3, 120.8, 120.6, 120.4 ppm. Detailed 1H and 13C signal assignments are given in Table S3. HR-MS MALDI (m/z): calcd for C94H66N2O4 [M]+, 1286.502; found, 1286.498.

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