Benzenoid Polycyclic Hydrocarbons with an Open-Shell Biradical Ground State

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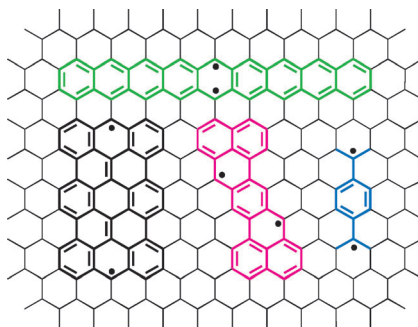**30** PUBLICATIONS   **384** CITATIONS

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FOCUS REVIEW

Open the shell! Open–shell benzenoid polycyclic hydrocarbons are of fundamentally importance to reveal the electronic structures of nanographene and to provide promising candidates for use in materials science. This review summarizes the recent advances on these open–shell biradical systems from both theoretical and experimental aspects.
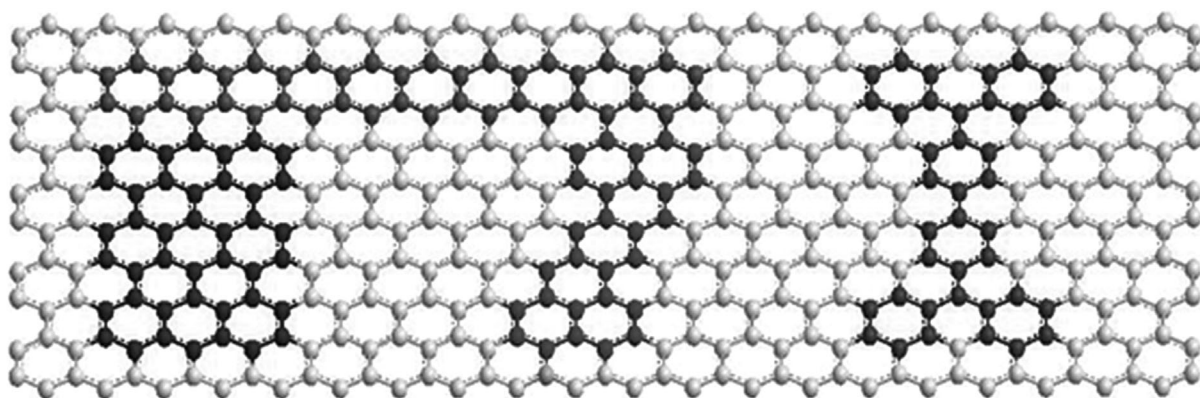
Zhe Sun, Zebing Zeng,
Jishan Wu* ⸻ ▪▪▪▪–▪▪▪▪

Benzenoid Polycyclic Hydrocarbons with an Open–Shell Biradical Ground State

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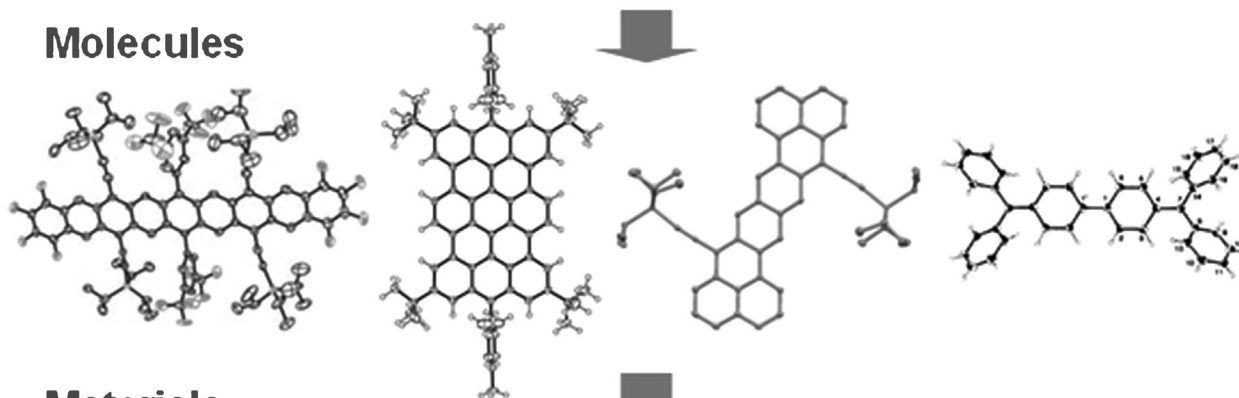**These are not the final page numbers!** ↗↗

Benzenoid Polycyclic Hydrocarbons with an Open–Shell Biradical Ground State

Zhe Sun,[a] Zebing Zeng,[a] and Jishan Wu*[a, b]

Open-shell Nanographenes
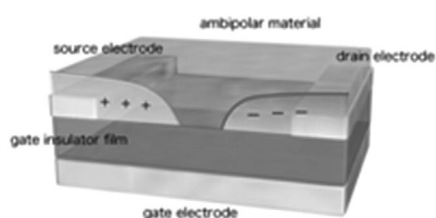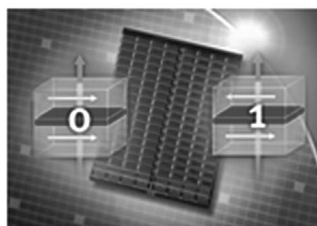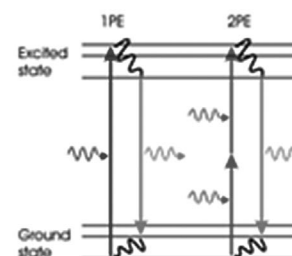
Molecules

Materials

Ambipolar OFET

Spintronics

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Abstract: This Focus Review describes the recent progress, from both theoretical and experimental perspectives, on four types of benzenoid polycyclic hydrocarbons with an open–shell biradical ground state: 1) acenes, 2) periacenes and anthenes, 3) zethrenes, and 4) extended *p*-quinodimethane derivatives. These interesting molecules have provided excellent platforms to investigate the electronic structures of nanographenes and represent promising candidates for the next generation of molecule-based materials in the field of electronics, spintronics, and nonlinear optics. The focus of this article will be put on the structural significance, the physical properties relevant to the open–shell electronic configurations, and potential applications.

Keywords: aromaticity · biradical · ground state configuration · graphene · polycycles

Introduction

Graphene, a two-dimensional sheet of sp^2-hybridized carbon packing into a honeycomb lattice, has attracted enormous attention since its first isolation in 2004.[1] This enthusiasm lies not only in its intrinsic electronic and magnetic properties but also in its great potential as a next-generation carbon material.[2] The circumference of an arbitrarily shaped nanographene can be classified into two distinct edge structures, namely the zigzag edge and the armchair edge, corresponding to *trans*- and *cis*-polyacetylenes, respectively. Cutting of graphene along the two-edge directions will generate graphene nanoribbons (GNRs) with zigzag and armchair edges (Figure 1). It has been suggested that
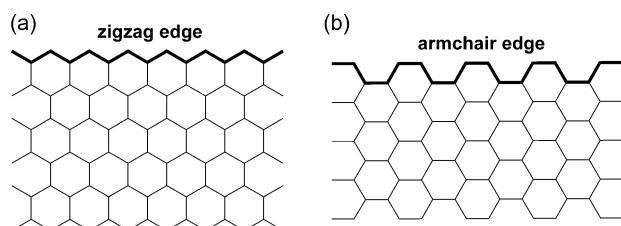

Figure 1. Chemical structures of (a) zigzag-edged and (b) armchair-edged GNRs.

zigzag-edged GNRs possess a non-bonding state localized at the zigzag edges, in addition to bonding and anti-bonding states. This state is also described as an "edge state", which is absent in armchair-edged GNRs, and is believed to result in enhanced magnetism.[3] This edge state is observable by various experimental methods, such as scanning tunneling microscopy/spectroscopy (STM/STS).[4] However, direct evidence of the edge magnetism in graphene is still lacking.

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A better insight into the electronic structure of nanographene can be provided by establishing structurally well-defined graphene fragments or benzenoid polycyclic hydrocarbons. For example, the preparation and study of hexa-*peri*-hexabenzocoronene and extended all-benzenoid polycyclic aromatic hydrocarbons (PAHs) have provided information of armchair-edged GNRs at the molecular level.[5] Similarly, graphene fragments with zigzag edges and a reliably controlled size offer an opportunity to elucidate the spin-polarized nature of zigzag-edged GNRs. Currently, a number of benzenoid polycyclic hydrocarbons with open–shell biradical characters are synthetically accessible and are effectively stabilized by means of kinetic blocking and/or thermodynamic stabilization (e.g., by delocalization of spins and substitution with electron-withdrawing groups). The open–shell characters are systematically studied by spectroscopic investigations (NMR, ESR, UV/Vis/NIR, Raman, etc.), X-ray crystallography, and superconducting quantum interfering device (SQUID) measurements, assisted by density functional theory (DFT) calculations. The developments in this field have not only rendered a glimpse of the peculiar electronic structure of zigzag-edged GNRs but also paved the way for the bottom-up production of molecule-based materials for electronics and spintronics. In this Focus Review, four types of benzenoid polycyclic hydrocarbons with an open–shell biradical ground state are discussed in terms of theoretical calculations and experimental advances. Other open–shell polycyclic hydrocarbon systems, such as those with five-membered rings and with non-Kekulé structures, are not covered.

1. Acenes

Acenes **1** can either be viewed as PAHs from the linear annelation of benzene rings or one-dimensional fragments of graphene.[6] The open–shell character of acenes, in particular the higher order acenes, has long been appealing to both theoretical and synthetic chemists. The open–shell feature of acenes can be symbolized by the chemical structure of acenes (as exemplified by pentacene **2** in Figure 2) in either a closed–shell Kekulé form with only one aromatic sextet ring, or a biradical/tetraradical form with two or three aromatic sextet rings. The extra aromatic rings can help to com-
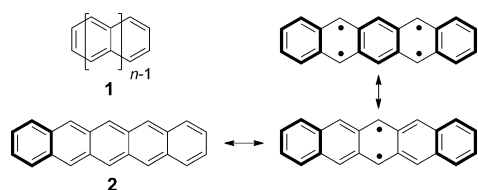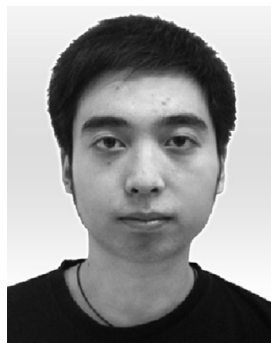
Figure 2. Chemical structure of acenes **1** and representative resonance structures of pentacene **2**.

Zhe Sun was born in Shandong province, P. R. China, in 1987. He received his Bachelor's degree in Chemistry from Sichuan University and he joined the National University of Singapore as a Ph.D. student in 2009. He is currently working on the design and synthesis of novel open–shell polycyclic hydrocarbons under the supervision of Dr. Jishan Wu.

Dr. Zebing Zeng was born in Hunan province, P. R. China, in 1981. He received a Bachelor's degree from Hunan University of Technology in 2004, a Master's degree from Nankai University in 2007, and a Ph.D. degree from the Department of Chemistry, National University of Singapore in 2012 under the supervision of Dr. Jishan Wu. His research was focused on novel chromophores based on closed–shell and open–shell polycyclic aromatic hydrocarbons.

Dr. Jishan Wu was born in Hubei province, P. R. China, in 1975. He received a Bachelor's degree in Chemistry from Wuhan University (1997) and a Master's degree in Polymer Science from Changchun Institute of Applied Chemistry, CAS (2000). He did his Ph.D. research at the Max-Planck Institute for Polymer Research under the supervision of Professor Klaus Müllen (2000-2004) and, after graduation, he worked as a project leader in the same group. He moved to the University of California at Los Angeles in 2005 and worked with Professor Sir J. Fraser Stoddart on supramolecular chemistry. Dr. Wu joined the Department of Chemistry of the National University of Singapore in 2007 as an assistant professor and was promoted to an associate professor in 2012. So far, he has published more than 110 peer-reviewed articles and book chapters with a Hirsch index of 30. He received a number of awards including the NUS Young Investigator Award (2007), the Singapore National Young Scientist Award (2010), the BASF–Singapore National Institute of Chemistry Award in Materials Science (2012), the NUS Young Researcher Award (2012), Invited Lecturer of Asian Excellence from the Japanese Society of Polymer Science (2012), Asian Core Program Lectureship Award from Japan (2010) and Hongkong (2012), and Distinguished Lectureship Award from The Chemical Society of Japan (2013).

pensate the energy loss from π-bond cleavage and enhance the open–shell contribution to the ground state.[7] Recent theoretical advances on the electronic structure of higher acenes were reviewed systematically by Bettinger.[8] A large controversy was raised from the ground-state multiplicities of larger oligoacenes. Initially, the triplet ground state was concluded for oligoacenes from nonacene onwards by Angliker et al. by extrapolation of experimental singlet–triplet differences from benzene to hexacene.[9] Later, it was proposed by Houk et al. that oligoacenes larger than nonacene would behave as two parallel polyacetylene ribbons with a triplet ground state and a vanishing band gap, on a basis of B3LYP calculations.[10] When the calculation is extended to acenes of infinite length, a one-dimensional conductor with a zero band gap was expected.[11] However, these results were challenged by Bendikov et al. in 2004, who found that the wave function at the RB3LYP/6-31G(d) level of theory became unstable for oligoacenes larger than hexacene, while re-optimization using the unrestricted broken symmetry B3LYP method (UB3LYP) led to a singlet state with biradical character, as a consequence of the disjoint nature of ground states of oligoacenes. The authors also pointed out that oligoacenes and probably polyacene derivatives should exhibit a nonzero band gap.[12] This work has changed the view of chemists on the multiplicity of higher order acenes, but raised another question: what will happen if the acene length keeps growing? A sophisticated study was performed by Hachmann et al. using complete active space (CASSCF) calculations in the framework of a density matrix renomalization group (DMRG) algorithm, and it was found that acenes larger than dodecacene would exhibit singlet polyradical character having one unpaired spin every five to six rings.[13] This conclusion was further supported by Jiang and Dai by using a spin polarized DFT method on oligoacenes up to 40-acene,[14] and an open–shell polyradical character in the ground state was also confirmed by Qu et al. in a valence bond study.[15]

The abundant theoretical results have left many unanswered questions to synthetic chemists. However, experimental results on higher order acenes are still rare so far due to the multistep synthetic sequences required and the intrinsic instability of higher order acenes, which tend towards dimerization/polymerization and oxidation.[16] Fueled by the fast development of synthetic methodologies, functionalized acenes up to nonacene have already been synthesized and isolated in their crystalline form. From a theoretical point of view, heptacene lies at a critical point from which a singlet biradical ground state may appear. However, so far, all the obtained heptacene derivatives favor a closed–shell ground state judging from the sharp NMR resonances.[17] This observation makes the synthesis of acenes longer than heptacene increasingly important to examine the calculated results. One effective method to synthesize unsubstituted octacene and nonacene was developed in Bettinger's group, using photo-irradiation of acene precursors under conditions of matrix isolation.[18] This method provided a spectroscopic glimpse of higher acenes with absorption be-

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havior (418 nm for nonacene and 377 nm for octacene), which further supports an antiferromagnetic (AFM) ground state. The substituted octacene is still not attainable by conventional synthetic chemistry. However, nonacene derivatives were successfully prepared independently in the groups of Miller and Anthony (Figure 3a). Miller's nonacenes **3a–b** were protected by arylthio groups, which by calculation would eliminate the total spin when located at terminal rings, and hence lead to a closed–shell species. Indeed, the sharp NMR resonances seem to further support this conclusion.[19] But later, Chen and Miller himself suggested an open–shell singlet biradical ground state for this nonacene by unrestricted broken spin-symmetry density functional theory (UBS-DFT) at B3LYP/6-31G*, irrespective of the positions of the substituents.[20] On the other hand, Anthony's nonacene derivatives **4a–c** were intensively protected by trialkylsilylethynyl and bis(trifluoromethyl)phenyl groups on the zigzag edges and fluorine atoms on the outer rings, and the structures of these nonacenes were unambiguously confirmed by single-crystal analysis. The nonacene featured a prominent S_0–S_1 transition at 1014 nm with an energy gap of 1.2 eV based on the absorption onset, while no fluorescence was observed in the visible region. Interestingly, the nonacene samples appear to be NMR silent, and an ESR signal was observed with $g = 2.0060$. Although the origin of the signal is unclear, there is a possibility that it could be an intrinsic characteristic of open–shell nonacene.[21] In summary, despite of the optimized theoretical calculations on higher order acenes and polyacenes which lead to an open–shell ground state, definite evidence is still lacking. We believe that the answer will be given in the future by further investigations on nonacene and by the development of new synthetic methods for even longer acenes.

2. Periacenes and Anthenes

Periacenes and anthenes are rectangular-shaped graphene fragments possessing both zigzag and armchair edges (Figure 4). Due to the existence of both edge structures, periacenes and anthenes have provided suitable models for the study of the electronic structures of graphene. Bisanthene **7** falls into the intersection of periacenes and anthenes. Extension of the conjugation laterally along the zigzag edges of bisanthene will lead to periacenes, such as peritetracene **5** and peripentacene **6**, while fusion of more anthryls vertically along the armchair edges will generate anthenes, such as teranthene **8** and quarteranthene **9** (Figure 4). The chemical structure of both periacenes and anthenes can be drawn as either a closed–shell Kekulé form or an open–shell biradical/tetraradical form. In both cases, more aromatic sextet rings appear in the open–shell form than in the closed–shell form. In other words, the aromatic stabilization energy can help to balance the destabilization by π-bond cleavage and thus increase the open–shell character. The biradical character will increase with the increase in molecular size, as a result of the cumulative increase of the aromatic sextet

3a R = H, **3b** R = ⋯⟨2,6-dimethylphenyl⟩

4a R = *i*Pr
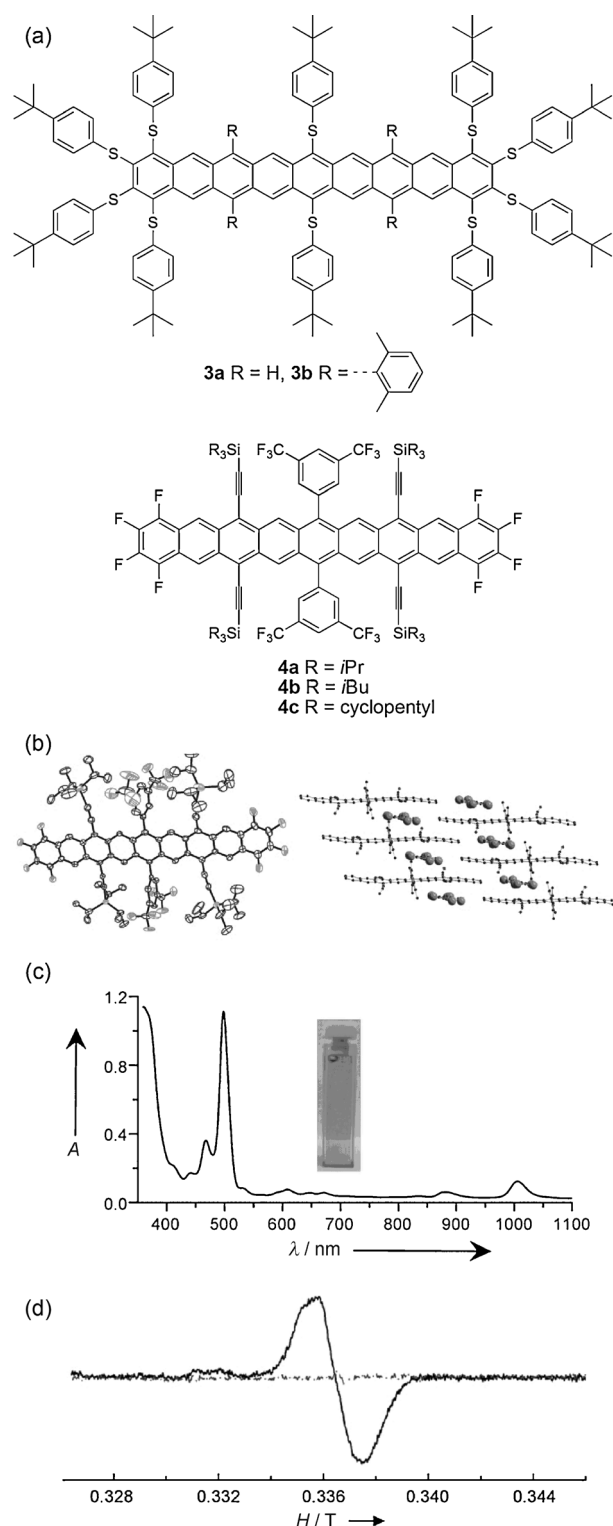**4b** R = *i*Bu
4c R = cyclopentyl

Figure 3. (a) Chemical structures of nonacene derivatives **3a–b** and **4a–c**. (b) Crystal structure and packing mode of **4a**. (c) UV absorption spectrum of **4c** in toluene. (d) ESR spectrum of **4b** in 2-methyltetrahydrofuran. Adapted with permission from ref. [21]. Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

rings. When the size of periacenes is expanded to a certain extent, a tetraradical character should be taken into consid-
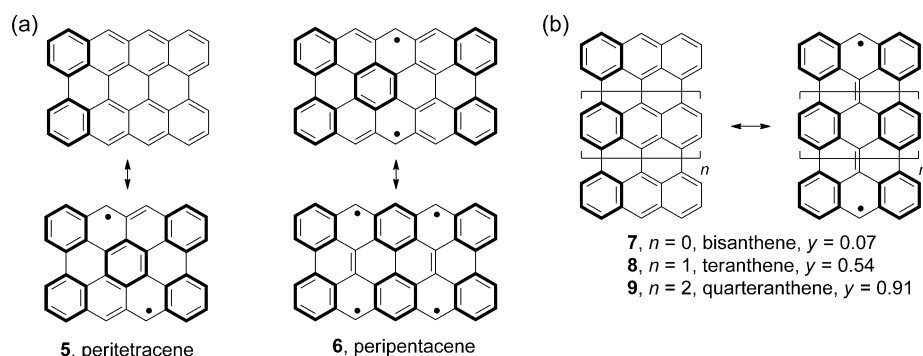
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Figure 4. (a) Resonance structures of peritetracene **5** and peripentacene **6**. (b) Resonance structures of anthenes.

7, $n = 0$, bisanthene, $y = 0.07$
8, $n = 1$, teranthene, $y = 0.54$
9, $n = 2$, quarteranthene, $y = 0.91$

eration (Figure 4). By using DFT calculations, Jiang et al. also predicted a crossover from the nonmagnetic phase to the antiferromagnetic phase for both periacenes and anthenes from bisanthene onwards, which further supported the open–shell characters for these interesting graphene fragments.[22]

Experimentally, the synthesis of periacenes is very challenging. So far, no stable periacene other than bisanthene has been prepared. The major obstacle for the preparation of periacenes is their low stability, especially at the exposed zigzag edges. Even the closed–shell bisanthene is an unstable material.[23] One strategy developed in our group to stabilize the bisanthene is to introduce imide groups or other substituents to the zigzag edges, which led to a series of stable bisanthenes.[24] Efforts were also made to apply this concept to the synthesis of higher periacenes. For example, in order to prepare peritetracene functionalized by imide groups, intermediates **10** and **11** were prepared (Figure 5). However, the subsequent coupling turned out to be a failure.[25] On the way to substituted peripentacenes, **12** and **13** were prepared, but the nucleophilic addition of **13** with excess Grignard reagent only led to the 1,4-Michael addition product instead of the 1,2-addition adduct because of the
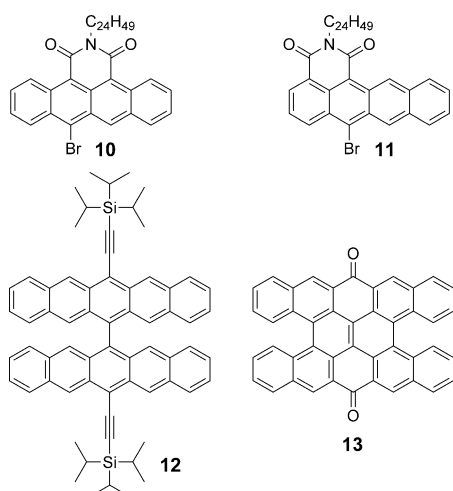
α,β-unsaturated ketone structure in **13**, as revealed by crystallographic analysis.[26,27] Although continuous attempts are being made, the preparation of open–shell periacenes is still an unfulfilled dream.

Alternatively, extension of conjugation along the armchair edge of bisanthene results in higher order anthenes. Owing to their higher stability they are less challenging to make compared to periacenes. Anthene is a class of PAHs with significant biradical contribution to the ground state, and the biradical character increases with more anthryl units fused. According to the calculation at the CASSCF(2,2)6-31G level, the singlet biradical character (y) values are estimated to be 0.07 for bisanthene, 0.54 for teranthene, and 0.91 for quarteranthene (Figure 4).[28] Because the unpaired electrons are fixed to the *meso*-positions of anthenes, the effect of delocalization is minimized and the discussion with regard to the biradical character can be focused on the aromatic stabilization effect. Therefore, anthenes represent excellent models to study how the formation of aromatic sextet rings affects biradical/polyradical characters in PAHs with Kekulé-type structures and to investigate the spin-polarized state in zigzag-edged GNRs. Inspiringly, bisanthene to quarteranthene derivatives have been prepared and isolated in the crystalline form in Kubo's group, thus allowing a detailed examination of their molecular structure, chemical behavior, and physical properties (Figure 6a).[28–30] Due to solubility and stability problems, *tert*-butyl substituents were introduced to the periphery of the anthenes and aryl groups were introduced to the *meso*-positions to block the reactive sites. The physical measurements including ESR and NMR spectroscopies for bisanthene derivatives **14** suggested the absence of appreciable open–shell species, while the spin-polarized state may be present, as suggested by the high chemical reactivity towards oxygen. For teranthene and quarteranthene derivatives, a moderate to large biradical character and an edge localization of unpaired electrons were confirmed by a combination of physical measurements and DFT calculations. Both teranthene and quarteranthene derivatives **15** and **16** are NMR silent at room temperature, and for **15** the peaks become sharp upon cooling. By contrast, the NMR baseline of **16** remained flat even when the temperature was lowered to 183 K. The absence of NMR signals for **16** is due to a large population of thermally accessible triplet biradical species. The NMR results can also be explained by SQUID measurements, which showed a small singlet–triplet gap for both compounds (1920 K for **15** and 347 K for **16a**). Single crystals suitable for X-ray analysis of both **15** and **16a** revealed a high planarity and symmetry for the anthene core (Figure 6b). Moreover, as shown in the resonance structures, the contribution from the biradical res-

Figure 5. Structures of intermediates for the synthesis of periacenes.

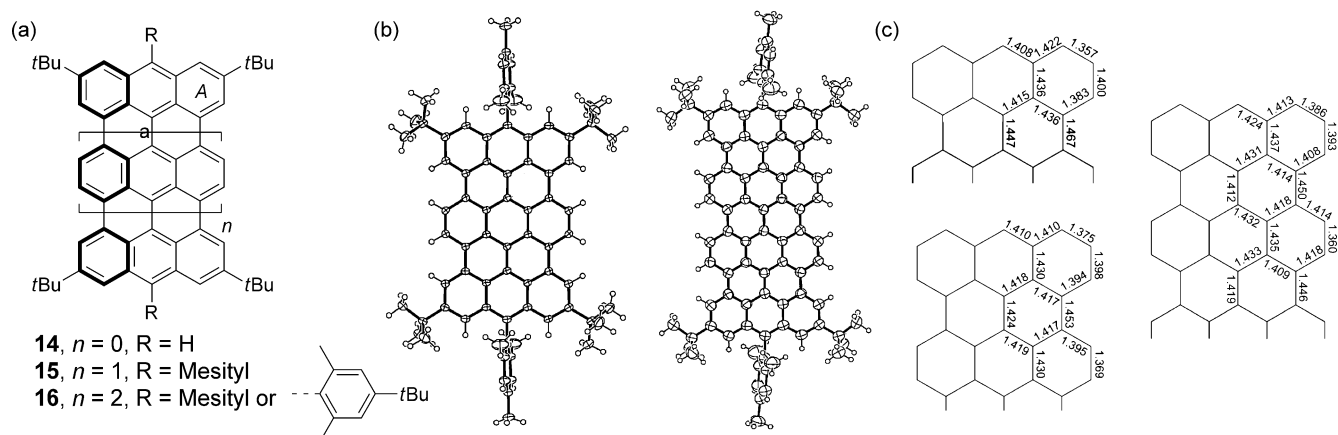↖↖ **These are not the final page numbers!**

Figure 6. (a) Structures of bisanthene, teranthene, and quarteranthene derivatives. (b) Crystal structures of **15** and **16**. (c) Bond length of anthenes from single-crystal analysis. Adapted with permission from ref. [28]. and ref. [30]. Copyright 2013 American Chemical Society and 2010 American Chemical Society.

onance shortens the bond *a* due to the enhanced double bond character. From the bond lengths information provided by the X-ray crystallography analysis, the bond length of bond *a* is much shorter in quarteranthene (1.412 Å) than in teranthene (1.424 Å) and bisanthene (1.447 Å). Furthermore, the harmonic oscillator model of aromaticity (HOMA) values of ring A is highest for quarteranthene and lowest for bisanthene, thus indicating that quarteranthene has more benzenoid character at the peripheral rings and, hence, a larger biradical character (Figure 6c). Another interesting property for quarteranthene is the absorption behavior. At room temperature, the absorption band located at 920 nm derives from a mixture of triplet and singlet species, while at lower temperature (183 K), a bathochromic shift to 970 nm was observed corresponding to the singlet ground state. However, the shape of the two spectra is quite similar due to their similar distribution of unpaired electrons at the zigzag edges. The investigations on the anthene series have therefore paved the way for understanding the intrinsic properties of zigzag-edged GNRs and the fabrication of nanographene-based optical and magnetic devices.

3. Zethrenes

A remarkable open–shell biradical character was also predicted for zethrene **17**, a Z-shaped polycyclic hydrocarbon with fixed double bonds (Figure 7). The structure of zethrene can be viewed as a dibenzotetracene or a "head-to-head" fusion of two phenalenyl moieties. When the two phenalenyl units are separated by benzene or naphthalene, the longitudinal homologues of zethrene named heptazethrene **18** and octazethrene **19** will be obtained (Figure 7). On the basis of the occupancy numbers of spin-unrestricted Hartree–Fock natural orbitals (UNOs), the biradical character *y* value was calculated to be 0.407 for zethrene, 0.537 for heptazethrene, and 0.628 for octazethrene.[31] This trend can be explained by the resonance structures from a closed–shell
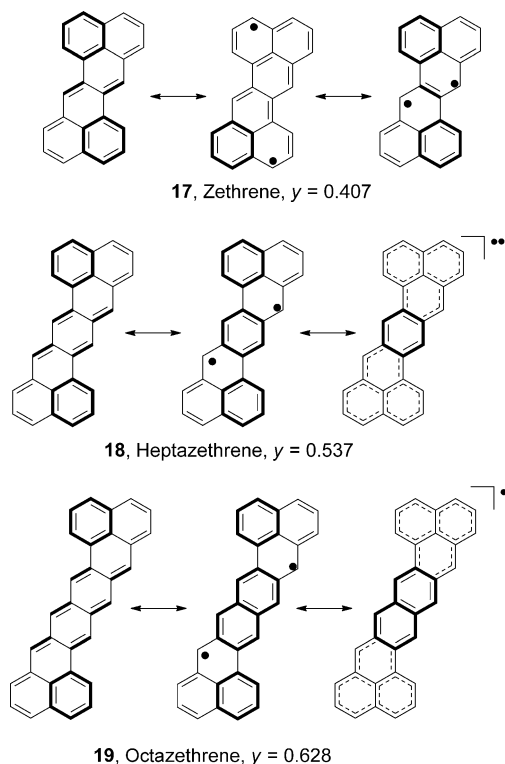

Figure 7. Resonance structures of zethrene, heptazethrene, and octazethrene.

Kekulé form to an open–shell biradical form. For zethrene, no additional aromatic sextet ring is formed from the closed–shell form to the open–shell form, while for heptazethrene onwards, one additional aromatic sextet ring will be gained. Therefore, higher order zethrenes are more prone to exhibit biradical characters (Figure 7).

The pursuit of zethrene compounds can be dated back to the 1950s. At that time, Clar et al. attempted to make zethrene, heptazethrene, and a series of benzozethrenes. How-

ever, most of the compounds were found unstable, and the characterizations were limited by the technology back then.[32] Recently, modern synthetic chemistry provided several methods to synthesize and stabilize zethrene compounds, and a series of stable derivatives, from zethrene to octazethrene, have been prepared (Figure 8). Stable zeth-
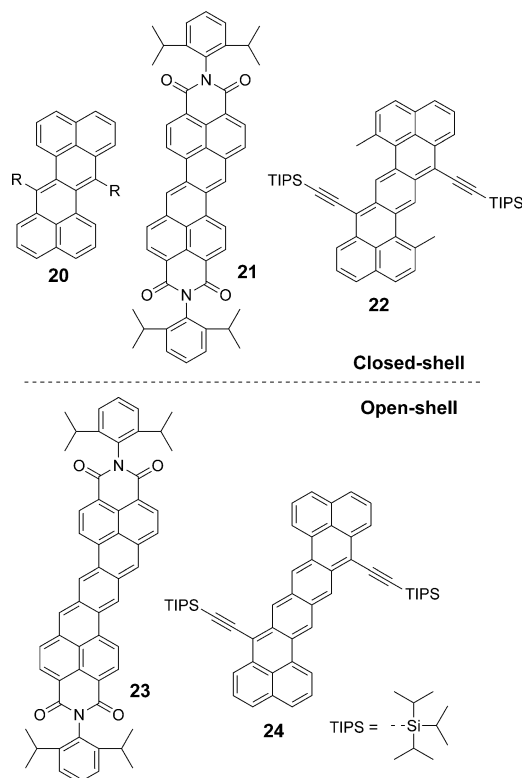

Figure 8. Chemical structures of zethrene, heptazethrene, and octazethrene derivatives.

rene derivatives **20** can be obtained by introducing substituents to the 7,14-positions (bay position), and the substituted zethrenes are synthesized through either a transannular cyclization reaction,[33] or a Pd-catalyzed dimerization reaction.[34] In order to make zethrene more stable and soluble, a zethrene diimide compound (**21**) was synthesized in our group by a transannular cyclization reaction.[35] Due to the introduction of the electron-withdrawing imide groups, **21** exhibited a smaller band gap with a lower-lying HOMO energy level. In contrast to the theoretical prediction on the biradical character, all of these zethrene derivatives display a typical closed–shell feature. It is also worth noting that the central part of zethrene has more butadiene character, as revealed from the bond length obtained by single-crystal analysis and the high reactivity towards electrophilic addition. To explore the open–shell character of the zethrene series, two heptazethrene derivatives (**22** and **23**) were synthesized in our group by means of nucleophilic addition of the corresponding diketone precursors and transannular cyclization reaction, respectively.[36,37] Interestingly, although both contain the same heptazethrene core, **22** showed the typical

closed–shell feature while **23** possessed a remarkable biradical character as evidenced by the line broadening in the ^{1}H NMR spectrum. Calculations on **23** suggested a large delocalization of spins, which even extended to the imide groups, and the band gap for **23** (0.99 eV) is much smaller than that of **22** (1.46 eV), as shown from cyclic voltammetry measurements. These results point out that the biradical character of heptazethrene may not only be related to the recovery of aromatic sextets but also to the spin delocalization and the narrowing of the band gap. The longest zethrene prepared so far is the octazethrene derivative **24** synthesized by our group in a manner similar to **22**.[37] It has been shown that **24** possesses a singlet biradical ground state, and the biradical character y index was experimentally evaluated to be 0.56 by using the following equation:

$$y = 1 - \sqrt{1 - \left(\frac{E_{S_{1u},S_{1g}} - E_{T_{1u},S_{1g}}}{E_{S_{2g},S_{1g}}} \right)}$$

where $E_{S_{1u},S_{1g}}$ and $E_{S_{2g},S_{1g}}$ correspond to the energy of the lowest energy peaks in the one- and two-photon absorption spectra, and $E_{T_{1u},S_{1g}}$ corresponds to the energy gap between the triplet and the singlet ground state.[38] This y value is comparable to the calculated one (0.628).

The physical properties of zethrene and higher order zethrenes were investigated with a variety of techniques, and they were found to be closely related to the biradical character. The absorption behavior, in particular, exhibited a very different band shape for closed–shell species and open–shell species. Comparisons of the absorption spectra between **21** (closed–shell) and **23** (open–shell), as well as **22** (closed–shell) and **24** (open–shell) are shown in Figure 9. In both cases, the closed–shell species displays a well-resolved p-band with an intense band at the absorption maximum and a weaker shoulder band at a shorter wavelength, corresponding to 0–0 and 0–1 electronic transitions, which is typical for many closed–shell PAHs.[39] By contrast, the open–shell species shows an intense sharp peak at the maximum, with a weak shoulder at a lower energy region. This feature is also observed in other biradicaloid species such as teranthene and quinoidal oligothiophenes,[40] which likely originates from a lower-lying excited singlet state dominated by a doubly excited electronic configuration (H, H→L, L). The magnetic properties of open–shell octazethrene **24** were studied by NMR, ESR, and SQUID measurements, and a paramagnetic species was detectable at elevated temperature due to a small singlet–triplet gap (3.87 kcal mol^{-1}). The bond length of **22** and **24** provided by single-crystal analysis offered a better insight into the structural characteristics. As shown in Figure 10, the bond length of the exo-methylene C=C bond of the central p-quinodimethane unit in **22** (1.398 Å) is shorter than that of the 2,6-naphthaquinodimethane unit in **24** (1.4088 Å), thereby indicating a more quinoidal structure for **22** and a more aromatic structure for **24**, in agreement with their ground state configurations. Both **22** and **24** are packed into a 1D infinite chain via π–π stacking,
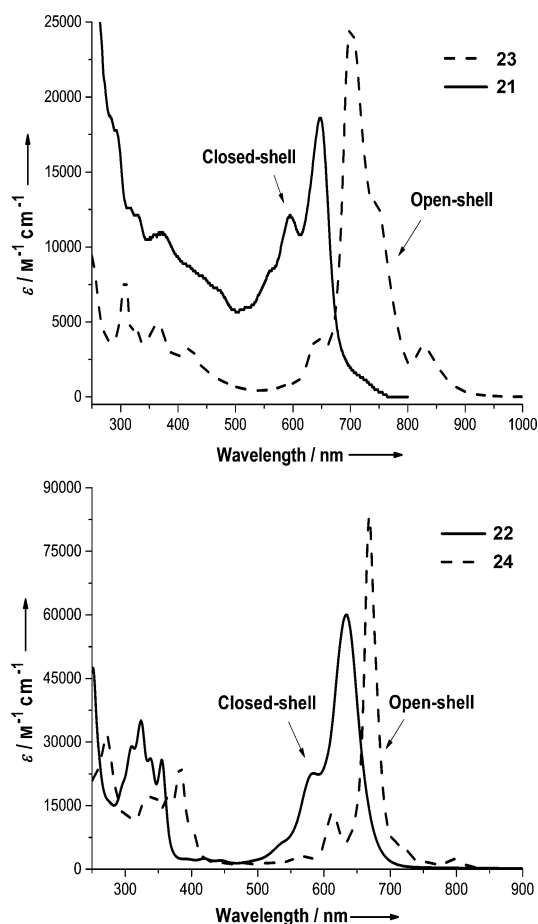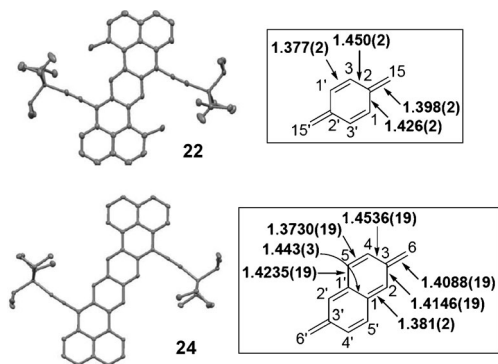
Figure 9. UV absorption spectra of **21–24**.

Figure 10. Crystal structures and bond length analysis of **22** and **24**. Adapted with permission from ref. [37]. Copyright 2012 American Chemical Society.

thus showing promise in applications such as ambipolar field effect transistors and spintronics. In addition, both compounds show large TPA cross sections (920 GM at 1250 nm for **22**, 1200 GM at 1250 nm for **24**), making them candidates for non-linear optics.

4. Extended *p*-QDM Derivatives

p-Quinoidimethane (*p*-QDM) is a fundamental building block with a structural resonance between a quinoidal form and a biradical form, and the aromaticity is recovered in the biradical form, which leads to a high reactivity. One effective way to obtain stable *p*-QDM derivatives is by terminal substitution of the methylene sites, and the simplest examples are Thiele's hydrocarbon **25** and Tschitschibabin's hydrocarbon **26** end-capped with four phenyl groups (Figure 11).[41] The ground state configuration of these *p*-QDM derivatives had been controversial until the single-
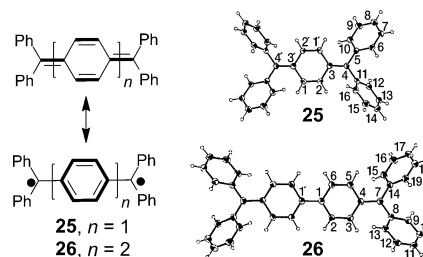

Figure 11. Resonance structures and crystal structures of Thiele's hydrocarbon **25** and Tschitschibabin's hydrocarbon **26**.

crystal analysis was conducted in 1986.[42] For Thiele's hydrocarbon, a well-defined bond alternation (1.346 Å and 1.449 Å) was observed for the *p*-QDM moiety, thus suggesting that a closed–shell quinoidal structure predominates in the ground state. On the other hand, the bond length for Tschitschibabin's hydrocarbon lies halfway between single and double bond values (1.420 Å and 1.372 Å), thus indicating significant biradical contribution to the ground state. This observation is also in agreement with the higher stability of **25** as compared to **26**.

Another challenge for the study of *p*-QDM-based open–shell systems is to prepare extended *p*-QDMs, as the increased biradical character often obscures the synthesis and isolation. A new strategy developed in our group is the benzannulation of the central biphenyl unit, and two stable tetrabenzannulated hydrocarbons **27** and **28** (Figure 12) were prepared.[43] Interestingly, this type of hydrocarbons exhibited a tunable ground state towards terminal substituents; for
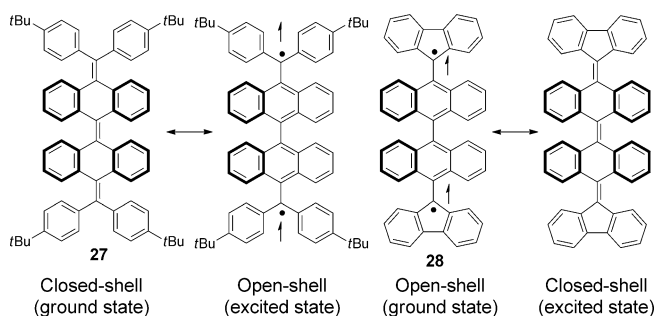

Figure 12. Structures of ground states and excited states for **27** and **28**.

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example, the 4-*tert*-butylphenyl-substituted compound **27** possesses a closed–shell ground state and a biradical excited state, while the fluorenyl-substituted compound **28** has a triplet biradical ground state and a quinoid excited state. This difference is due to the higher thermodynamic stabilization of the radicals by the fluorenyl units than by the di(*tert*-butylphenyl)methane groups. Moreover, the corresponding excited states of **27** and **28** are chemically accessible with different decay processes. For **27**, the biradical (excited state) was obtained by reduction of the diol precursor, which slowly decayed to the closed–shell form (ground state) with a half-life time of 495 min, as monitored by UV/Vis spectroscopy. By plotting $\ln(k/T)$ as a function of $1/T$ (where k is the decay rate constant and T is the temperature) in a temperature range of 298–337 K and fitting the data by Eyring equation,

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\ddagger}}{R}\cdot\frac{1}{T} + \ln\left(\frac{k_{B}}{h}\right) + \frac{\Delta S^{\ddagger}}{R}$$

the Gibbs energy of activation $\Delta G^{\ddagger}$ was determined as 95.0 ± 2.5 kJ mol^{-1}. Calculations also predicted that the molecule has an orthogonal conformation at the excited state (singlet/triplet biradical) and that the conversion from the excited biradical to the ground-state quinoidal form with a butterfly conformation requires overcoming a high energy barrier of 118 kJ mol^{-1} (Figure 13), which explains the un-
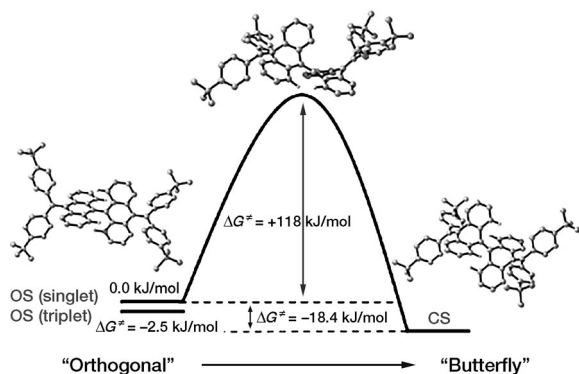

Figure 13. Calculated energy diagram for **27** and schematic representation of different conformers. Adapted with permission from ref. [43]. Copyright 2012 American Chemical Society.

usually slow decay process. On the other hand, the triplet biradical ground state of **28** was unambiguously confirmed by the strong ESR signal and the absence of an NMR signal. The singlet–triplet gap was estimated to be $2J/k_{B} = 166$ K (1.4 kJ mol^{-1}) by SQUID measurements. The synthesis of the closed–shell form of **28** was also attempted by using a Stille coupling reaction between **29** and **30**, but it was found that the intermediate quickly relaxed to the biradical ground state, which is more stable (Scheme 1). It should also be noted that **28** exhibited a large TPA cross-
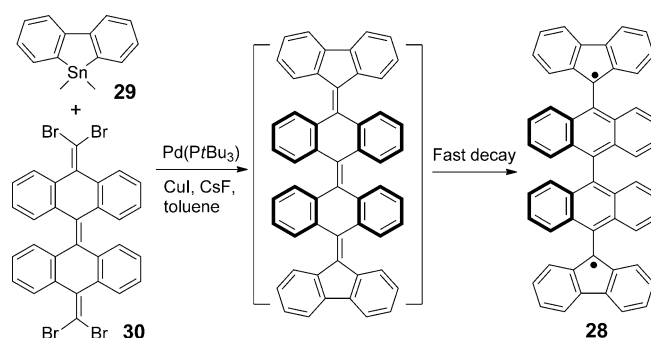
Scheme 1. Synthesis of quinoidal form of **28** and the decay process to the ground state.

section (760 GM) at 1200 nm; thus, **28** holds promise in nonlinear optics.

Inspired by the success in the preparation of **27** and **28**, a series of stable oligo(*N*-annulated perylene)quinodimethanes (**nPer-CN**, $n = 1$–6) terminated by cyano-substitution were synthesized by us very recently (Figure 14).[44] These
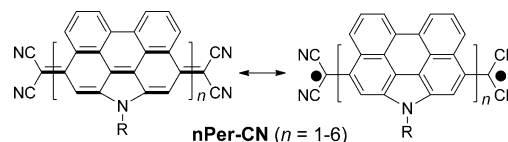

Figure 14. Resonance structures of **nPer-CN**.

oligomers exhibited an interesting chain-length dependence of their ground states, with a closed–shell quinoid for **Per-CN**, an open–shell singlet biradical for **2Per-CN–4Per-CN**, and an open–shell triplet biradical for **5Per-CN** and **6Per-CN**, as revealed by variable-temperature ESR (VT-ESR) spectroscopic measurements. The singlet–triplet gaps of all oligomers were estimated by SQUID measurements (see Table 1). The ground state of **4Per-CN** is better described as a singlet biradical based on the VT-ESR spectra and calculations despite of the negative singlet–triplet gap obtained from SQUID. The large biradical character in the higher order oligomers is caused by the steric repulsion between the neighboring perylene units and the recovery of the aromaticity of the quinoidal perylene rings in the biradical forms. Moreover, strong TPA responses were observed for

Table 1. Tabulated data of ground states, TPA cross-section $\sigma^{(2)}$ max, electrochemical energy gap E_{g}^{EC}, and singlet triplet energy gap ΔE_{S-T} for **nPer-CN**.

	Per-CN	2Per-CN	3Per-CN	4Per-CN	5Per-CN	6Per-CN
Ground state	CS[a]	SB[b]	SB	SB	TB[c]	TB
$\sigma^{(2)}$ max [GM]	1300[d]	1060[e]	770[e]	710[e]	730[e]	710[e]
E_{g}^{EC} [eV]	–	0.61	0.53	0.52	0.57	0.53
ΔE_{S-T} [kcal mol^{-1}]	–	0.342	0.107	−0.064	−0.556	−0.883

[a] CS: closed–shell. [b] SB: singlet biradical. [c] TB: triplet biradical. [d] Measured at 1200 nm. [e] Measured at 1700 nm.

open–shell **nPer-CN** (Table 1), which exceeded typical hydrocarbon TPA chromophores.

Conclusions

Four types of benzenoid polycyclic hydrocarbons with an open–shell biradical ground state have been discussed and summarized. Directed by theoretical calculations, the synthetic chemistry of these systems has made a big step forward in recent years by overcoming many obstacles such as stability issues. Investigations on open–shell molecules is of fundamental importance for revealing the nature of chemical bonding and basic chemical and physical phenomena in π-conjugated systems and nanographenes. However, the studies on their material applications are still in its infancy stage, limited mainly by the difficulty in scalable production and their insufficient stability and processability. However, we are happy to see that several small steps have been taken in this direction. Other open–shell systems, such as phenalenyls and bis(phenalenyl)s, have been shown to be promising as electrode-active materials in secondary batteries[45] and ambipolar field-effect transistors,[46] and theoretical works have pointed out the possibility for open–shell systems to be employed in spintronics[47] and solar cells.[48] Therefore, we have reasons to believe that open–shell benzenoid polycyclic hydrocarbons will find use in materials science in the future.

Acknowledgements

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