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## Zethrenes, Extended *p*-Quinodimethanes, and Periacenes with a Singlet Biradical Ground State

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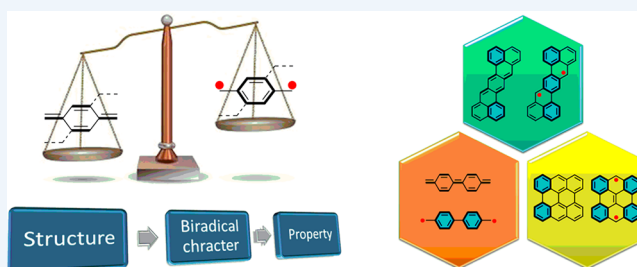
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**CONSPECTUS:** Researchers have studied polycyclic aromatic hydrocarbons (PAHs) for more than 100 years, and most PAHs in the neutral state reported so far have a closed-shell electronic configuration in the ground state. However, recent studies have revealed that specific types of polycyclic hydrocarbons (PHs) could have a singlet biradical ground state and exhibit unique electronic, optical, and magnetic activities. With the appropriate stabilization, these new compounds could prove useful as molecular materials for organic electronics, nonlinear optics, organic spintronics, organic photovoltaics, and energy storage devices. However, before researchers can use these materials to design new devices, they need better methods to synthesize these molecules and a better understanding of the fundamental relationship between the structure and biradical character of these compounds and their physical properties. Their biradical character makes these compounds difficult to synthesize. These compounds are also challenging to physically characterize and require the use of various experimental techniques and theoretic methods to comprehensively describe their unique properties.

In this Account, we will discuss the chemistry and physics of three types of PHs with a significant singlet biradical character, primarily developed in our group. These structures are zethrenes, Z-shaped quinoidal hydrocarbons; hydrocarbons that include a proaromatic extended *p*-quinodimethane unit; and periacenes, acenes fused in a *peri*-arrangement. We used a variety of synthetic methods to prepare these compounds and stabilized them using both thermodynamic and kinetic approaches. We probed their ground-state structures by electronic absorption, NMR, ESR, SQUID, Raman spectroscopy, and X-ray crystallography and also performed density functional theory calculations. We investigated the physical properties of these PHs using various experimental methods such as one-photon absorption, two-photon absorption, transient absorption spectroscopy, electrochemistry, and spectroelectrochemistry.

These systematic studies revealed that aromaticity played a very important role in determining their singlet biradical character, which is critically related to both their physical properties and their chemical reactivity. In particular, we found that Clar's aromatic sextet rule, which is useful for the closed-shell PAHs, can also predict the relative biradical character of benzenoid PH-based singlet biradicaloids. Other factors, such as structural flexibility of the biradical and quinoid resonance forms and the participation of the substitution in the  $\pi$ -conjugation, also influence the biradical character. These molecular materials demonstrate a number of unique properties such as near-infrared absorption, redox amphotericity, large two-photon absorption cross section, short excited state lifetime, stimuli-responsive magnetic activity, and singlet fission, which suggests promise for future applications.



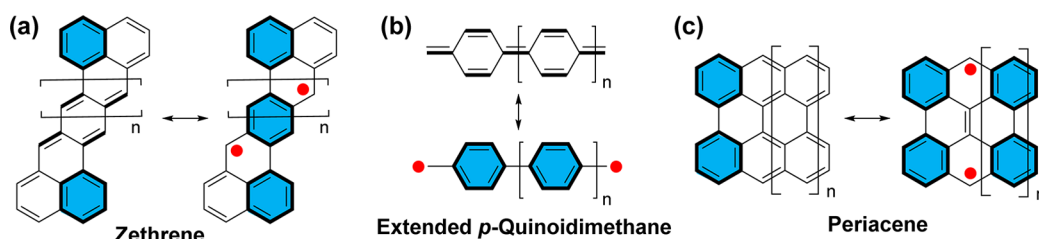
### ■ INTRODUCTION

The synthetic chemistry of polycyclic aromatic hydrocarbons (PAHs) can be dated back to Scholl's time in the early 20th century.<sup>1</sup> Later after that, Clar developed various synthetic methods and synthesized a large number of PAHs.<sup>2</sup> The hot discussion on the aromaticity of annulenes in 1950–1970s also promoted the development of PAHs.<sup>3</sup> The discovery of conducting polymers and the subsequent development of optoelectronic devices based on organic semiconductors largely stimulated the production of PAHs with diverse structures and functionalities.<sup>4</sup> Modern synthetic methods and analytical techniques now allowed us to access PAHs with unprecedented size and geometry.<sup>5,6</sup> The last 10 years witnessed explosive

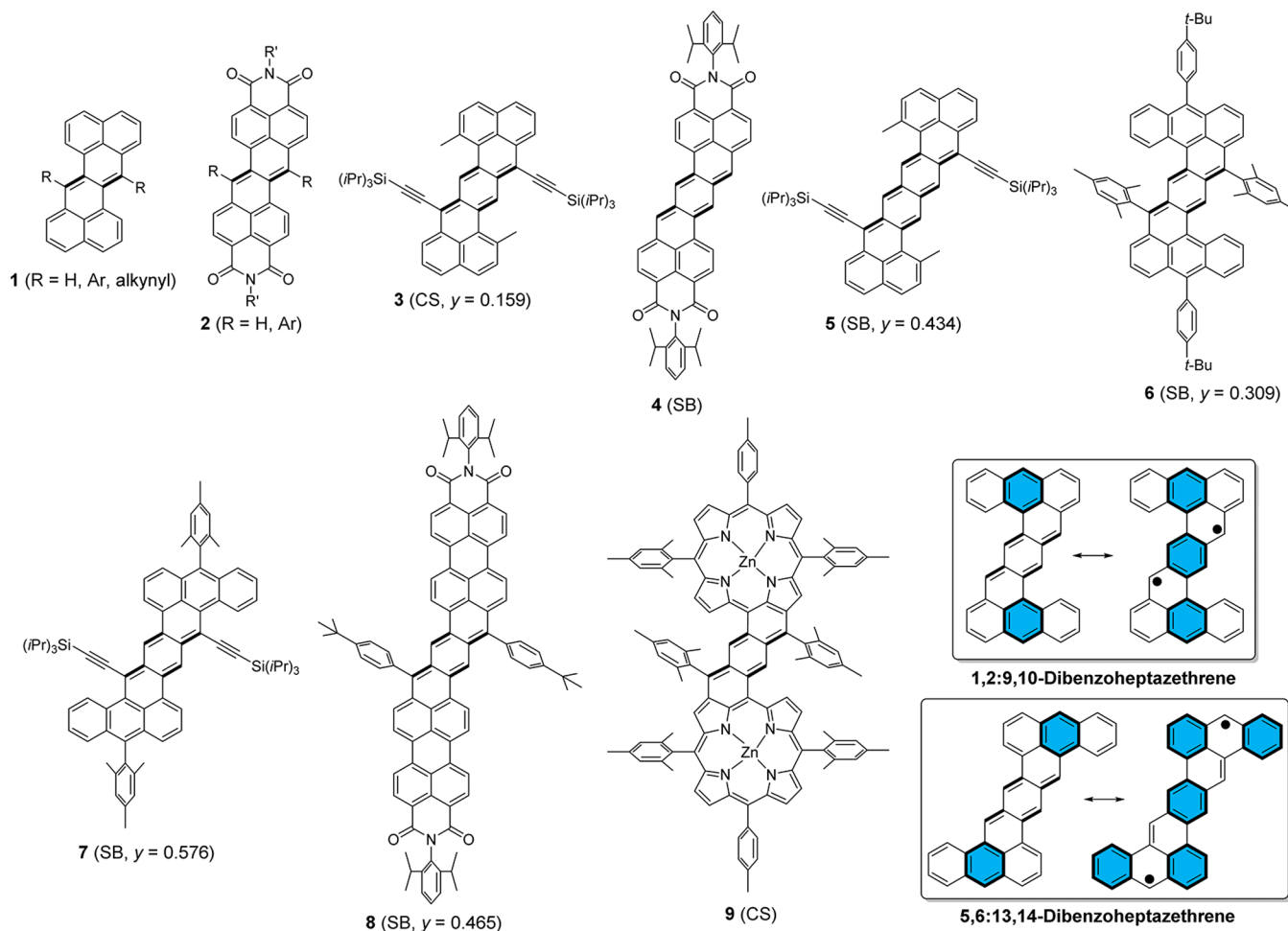
studies on graphene, which can be regarded as an infinite PAH sheet.

During the synthesis of various PAHs, difficulties were found for some compounds due to their high reactivity, for example, parent acenes longer than pentacene,<sup>7</sup> heptazethrene,<sup>8</sup> octazethrene,<sup>9</sup> and so forth. The fundamental reason now can be ascribed to their intrinsic biradical character. To date, most reported PAHs in the neutral state have shown a closed-shell configuration in the ground state. However, recent studies revealed that certain types of polycyclic hydrocarbons (PHs) could have a singlet biradical ground state, for example, acenes

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**Figure 1.** Resonance structures of zethrenes, extended *p*-quinoidimethane, and periacenes.



**Figure 2.** Chemical structures of the reported stable zethrenes and the resonance structures of the two dibenzo-heptazethrene isomers. SB, singlet biradical; CS, closed-shell;  $y$ , singlet biradical character index.

longer than heptacene,<sup>10</sup> and some zigzag edged graphene nanoribbons (GNRs)<sup>11</sup> were theoretically predicted to have a singlet biradical and even polyradical ground state. The major driving force is that the molecule possesses more aromatic sextet rings in the biradical or polyradical resonance forms, and the gained resonance energy can compensate the energy required to break a double bond. Experimentally, this was nicely supported by Kubo and co-workers' teranthrene<sup>12</sup> and quarteranthrene compounds.<sup>13</sup> Recent research also showed that incorporation of a proaromatic unit such as *p*-quinodimethane (*p*-QDM) into an aromatic PH framework could lead to a new type of quinoidal PH showing a singlet biradical ground state due to the recovery of the aromaticity of the proaromatic unit in the biradical resonance form.<sup>14–17</sup> The contribution of the biradical resonance form to the ground-state structure can be quantified by singlet biradical character index ( $y$ ), which can be

theoretically calculated using the natural orbital occupancy number (NOON)<sup>18</sup> of the LUMO using the spin-unrestricted Hartree–Fock method.<sup>19</sup> The  $y$  is formally expressed as  $y = 1 - (2T/(1 + T^2))$ , where  $T$  can be represented by using the occupation numbers ( $n$ ) of UHF natural orbitals:  $T = (n_{\text{HOMO}} - n_{\text{LUMO}})/2$ . A compound with  $y = 0$  indicates a pure closed-shell structure, while a compound with  $y = 1$  implies a pure diradical structure. In reality, most PAHs have a  $y$  value between 0 and 1.

PHs with significant biradical character usually exhibit unique optical, electronic and magnetic properties. The compounds usually have a small energy gap and show amphoteric redox behavior; thus, they can find applications in near-infrared (NIR) dyes, ambipolar organic field effect transistors (OFETs),<sup>20</sup> and energy storage devices.<sup>21</sup> Compounds with a small and moderate biradical character were predicated to show

large second hyperpolarizability and two-photon absorption (TPA) cross sections,<sup>22,23</sup> which opened the opportunities for nonlinear optic (NLO) applications (e.g., optical limiting). Recent studies also showed that chromophores with a small singlet biradical character could exhibit unique singlet fission phenomenon and have potential applications for next generation organic photovoltaic devices.<sup>24</sup> The unique magnetic activity upon external stimuli (e.g., heat, light, electric field, magnetic field, etc.) qualifies them as multifunctional responsive materials and as spin injection/transporting materials in spintronic devices.<sup>25</sup>

Synthesis of PHs with a singlet biradical ground state is challenging due to their intrinsic high reactivity. Therefore, both thermodynamic stabilization (by delocalization and substitution with electron-withdrawing groups such as triisopropylsilylethynyl (TIPSE)<sup>26,27</sup> and imide<sup>28</sup>) and kinetic stabilization (by substitution of the reactive sites with bulky groups) are essential to obtain stable materials. The characterizations are also challenging, and the collaborative works between chemists and physicists in recent years now can provide reliable methods. Experimentally, the ground state can be identified by electronic absorption spectroscopy, variable temperature (VT) NMR/ESR/superconducting quantum interference device (SQUID), X-ray crystallographic analysis, and Raman spectroscopy. In addition, broken-symmetry density functional theory (DFT) calculations (UCAM-B3LYP or UB3LYP) provide important insights on the molecular geometry, energies, spin density distribution, biradical character, and so forth. The photophysical properties can be further investigated by transient absorption (TA) and TPA spectroscopy. The electronic properties can be studied by electrochemical method, and the charged states can be further investigated by spectroelectrochemical measurements or chemical oxidation/reduction.

To do tailored material design, it is important to understand the fundamental structure–biradical character–physical property relationship. In the past 5 years, our group paid particular attention to three types of PHs with significant singlet biradical characters: (a) Z-shaped hydrocarbons known as zethrenes, (b) extended *p*-quinodimethanes, and (c) *peri*-fused acenes called periacenes (Figure 1). The first two types of molecules can be regarded as proaromatic quinoidal PHs, and the biradical resonance forms are stabilized by the recovery of the aromaticity of the proaromatic unit. The periacenes can be categorized as zigzag edged GNRs, and the driving force for the stabilization of biradical form is similar, that is, the gain of additional aromatic sextet rings (highlighted in blue color). This Account will first go through the challenging chemistry and physical characterizations of these compounds, then summarize the fundamental findings and principles, and finally give a perspective view on the future design and material applications. The excellent works by Kubo, Haley, and Tobe et al. have been discussed in previous review articles and will not be discussed here.<sup>29–32</sup>

## ZETHRENES

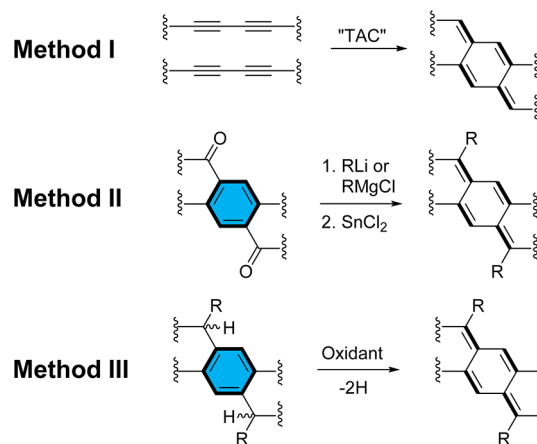
The name zethrene (**1**) comes from its Z-shape, and it was first reported by Clar et al. in 1955 (Figure 2).<sup>33,34</sup> It can be regarded as a PH in which two naphthalene units are fixed by a *trans*-1,3-butadiene unit (Figure 1, *n* = 0). Extension of the butadiene unit gives higher order analogues such as heptazethrene (*n* = 1) and octazethrene (*n* = 2), in which two naphthalene units are bridged by a *p*-QDM and 2,6-

naphthoquinodimethane unit, respectively. For the smallest member, zethrene, the aromaticity could by no means be recovered from closed-shell to biradical resonance form due to the lack of benzenoid spacer. As a result, all of the zethrene derivatives reported so far adopted a regular closed-shell configuration. The stability of the parent zethrene can be improved by either bay substitution with aryl/alkynyl (**1**) or *peri*-substitution by electron-withdrawing dicarboximide groups (**2**) or by both (Figure 2).<sup>35–38</sup> The attempted syntheses of the parent heptazethrene<sup>8</sup> and octazethrene<sup>9</sup> were not successful due to their high tendency to polymerize and addition with oxygen. Kinetic blocking of the most reactive sites by TIPSE or aryl groups and thermodynamic stabilization by *peri*-substitution with dicarboximide groups have been used to obtain stable heptazethrene derivatives **3** and **4**, and octazethrene derivative **5** (Figure 2).<sup>39,40</sup> Our detailed studies showed that **3** is a typical closed-shell PH while **4** and **5** both have a singlet biradical ground state. To further understand the role of the aromatic sextet ring on singlet biradical character, two dibenzoheptazethrene isomers were synthesized, with the most reactive sites blocked by aryl or TIPSE groups (**6** and **7**).<sup>41</sup> Looking into the number of the aromatic sextet rings in the biradical resonance forms, one can see that there are maximum three for the first isomer while there are five for the second isomer (Figure 2). Then a question is raised: which isomer should possess greater biradical character? More extended heptazethrene analogues such as the *p*-QDM bridged perylene monoimide dimer **8**<sup>42</sup> and the porphyrin dimer **9**<sup>43</sup> were also synthesized for deeper understanding of the factors that determine the biradical character and also to access soluble and stable near-infrared (NIR) dyes. The electronic ground state of molecules shown in Figure 2 can be assigned to either closed-shell (CS) or singlet biradical (SB) based on the energy levels calculated for each state and the experimental behavior of these compounds.

## Synthesis

Different synthetic methods have been developed for zethrenes and their analogues (Scheme 1). The first method is intramolecular “transannular cyclization” (TAC), which involves simultaneous cyclization of an octadehydronaphthoanulene intermediate to give the heptazethrene derivative such as **4**. However, this approach encountered inevitable flaws such as low reaction yield and the prohibition of bay region substitution. The second method is a two-step sequence

**Scheme 1.** Typical Synthetic Methods for the Zethrene Derivatives





involving a nucleophilic addition of the corresponding diketone precursor with organolithium or Grignard reagents, followed by reduction with  $\text{SnCl}_2$  (Scheme 1). This method was used to synthesize compounds **3**, **5**, and **7** in good yields, and substitution at the bay positions is also allowed. However, it is not suitable for precursors carrying with active groups such as imide, ester, ketone, and aldehyde. The third method is the oxidative dehydrogenation of a dihydro-precursor which is often obtained by intramolecular cyclization of the corresponding diol promoted by  $\text{BF}_3 \cdot \text{OEt}_2$ . This method has better tolerance with active functional groups, and the conversion efficiency is usually good. However, the choice of oxidant is quite tricky and is largely dependent on the precursors. For example, air could serve as the oxidant to afford the porphyrin dimer **9**, but stronger oxidant DDQ is needed to form compounds **6** and **8**. It is also crucial to use appropriate amounts of oxidant and to control the reaction temperature and time to prevent overoxidation.

### Ground-State Geometric and Electronic Structures

The first diagnostic tool for PHs with a singlet biradical ground state is their electronic absorption spectrum. For example, **3** shows a typical *p*-band similar to most closed-shell PAHs, while **4**, **5**, **7**, and **8** display an obviously different pattern, with the emergence of weak absorption bands in the lower energy region (Figure 3). The origin of these bands is the presence of a low-

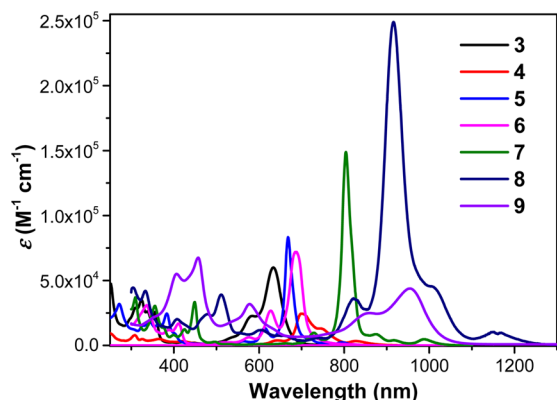


Figure 3. UV-vis-NIR absorption spectra of **3**–**9** in solutions.

lying excited singlet state dominated by a doubly excited electronic configuration ( $\text{H,H} \rightarrow \text{L,L}$ ).<sup>44</sup> In addition, the absorption spectra of the singlet and triplet are different from each other and the shift of the singlet–triplet equilibrium can be observed in the temperature dependent absorption spectrum.

The second diagnostic tool for PH-based singlet biradicaloids is their magnetic activity. PHs with prominent singlet biradical character usually possess a small singlet–triplet energy gap ( $\Delta E_{\text{S-T}}$ ), making the paramagnetic triplet species thermally accessible. These paramagnetic species are detectable by NMR, ESR and SQUID as they could broaden the NMR spectrum and produce ESR signal. Moreover, the  $\Delta E_{\text{S-T}}$  value can be quantitatively determined by VT ESR or SQUID measurements. For example, in the  $\chi T$ – $T$  plot of **5**, an increase of magnetic susceptibility happened above 220 K, and the fitting of data using the Bleaney–Bowers equation based on the singlet–triplet model gave an exchange interaction energy  $2J/k_{\text{B}}$  (i.e.,  $\Delta E_{\text{S-T}}$ ) of  $-1946$  K (Figure 4). Similar behavior was

observed for **7** and **8**, and the  $\Delta E_{\text{S-T}}$  values were determined by SQUID as  $-3.80$  and  $-2.97$  kcal/mol, respectively.

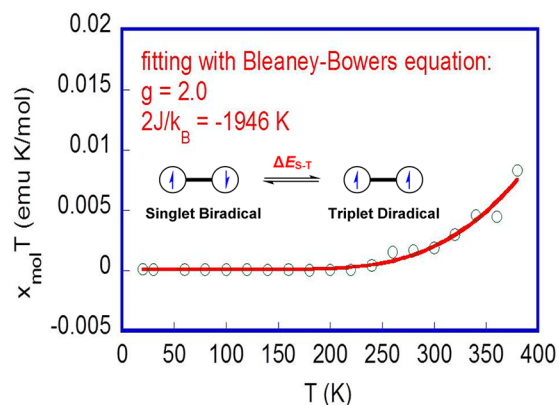


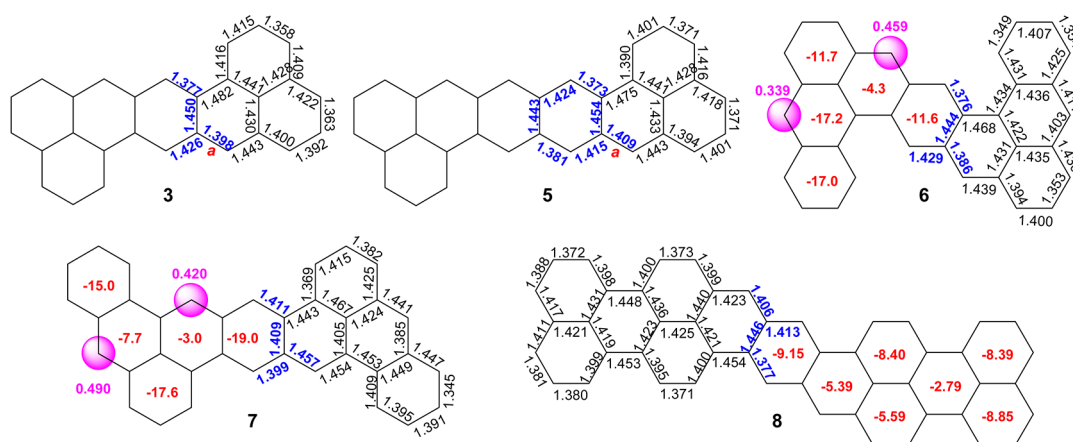
Figure 4.  $\chi T$ – $T$  plot based on the SQUID data of **5**. The fitting curve was drawn using the Bleaney–Bowers equation. The inset shows the singlet–triplet equilibrium.

X-ray crystallographic analysis provides important information on the ground-state geometric structure. For example, the *exo*-methylene bond (labeled as “*a*” bond) of the *p*-QDM unit in **3** is shorter than that of the 2,6-naphthodimethane unit in **5**, indicating a larger biradical character for **5** (Figure 5). Similarly, the bond lengths of the central benzene ring in **7** are almost uniform while an obvious alternation exists in **6**, indicating a more stabilized biradical structure and thus a larger biradical character for **7**. In addition, both **3** and **5** form 1D infinite chains via a close  $\pi$ – $\pi$  interaction (weak spin–spin interaction), indicating their potential applications in ambipolar OFETs.

Raman spectroscopy is a very powerful tool to probe the “quinoidal” or “benzenoid” character of zethrenes such as **3**–**5**,<sup>45</sup> which is correlated to their different biradical character. In addition, the population from the singlet to triplet can be observed by the VT Raman measurements for **5**.

Broken-symmetry DFT calculations at the UCAM-B3LYP/6-31G(d,p) level provide insights on the ground-state configuration,  $\Delta E_{\text{S-T}}$ , biradical index, spin density distribution, and other parameters. For example, the calculated biradical character index  $\gamma$  (Figure 2) gives the most straightforward evaluation for the biradical character and could serve as guidance for molecular design. The calculated NICS(1)<sub>zz</sub> values and spin density on specific positions (Figure 5) reveal the aromaticity for specific ring and the most possible positions for radical to reside, which help us to better understand the contribution of each resonance form.

The insight of how substitution and extension of conjugation make impact on the biradical character can be gained simply by comparison among **3**–**9**. For example, the biradical character of **5** is much larger than that of **3**, suggesting that the central naphthalene moiety could provide larger aromatic stabilization than the benzene moiety. With the same heptazethrene core, the larger biradical character of **4** in comparison to **3** can be explained by a more significant stabilization effect toward the biradical structure provided by the imide than the TIPSE group, due to its strong participation in the overall molecular  $\pi$ -conjugation. The difference in the biradical character between **6** and **7** highlights the importance of the number of aromatic sextet rings in the biradical resonance forms. As **5** with more

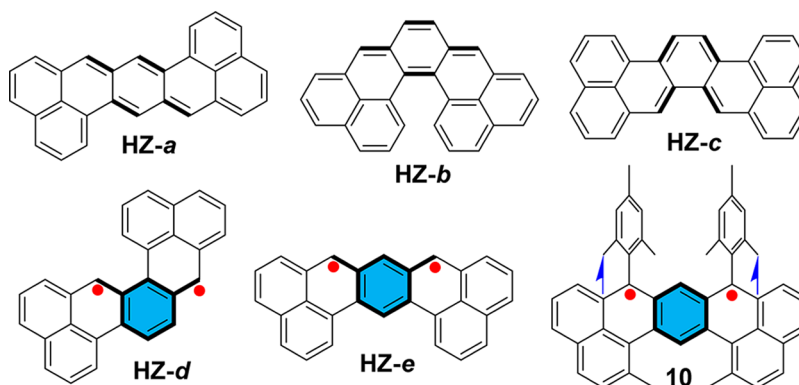


**Figure 5.** Mean values of bond lengths (Å) in the X-ray crystallographic structures of **3** and **5–8**, and calculated  $\text{NICS}(1)_{zz}$  values (red numbers in the rings) and spin densities at the specific positions (pink color) for some compounds.

**Table 1.** Optical and Electrochemical Data of Compounds **3–9**<sup>a</sup>

compd	$\lambda_{\text{abs}}$ (nm)	$\epsilon_{\text{max}}$ ( $\text{M}^{-1}\text{cm}^{-1}$ )	$\tau$ (ps)	$\sigma_{\text{max}}^{(2)}$ (GM)	HOMO (eV)	LUMO (eV)	$E_{\text{g}}^{\text{EC}}$ (eV)	$E_{\text{g}}^{\text{opt}}$ (eV)
3	584, 634	60 000	3400	920 (1250 nm)	−4.87	−3.41	1.46	1.82
4	641, 701, 747, 827	24 382			−5.22	−4.23	0.99	1.16
5	613, 668, 719, 795	83 300	1600	1200 (1250 nm)	−4.73	−3.60	1.13	1.50
6	819, 687, 628	72 000	670	530 (1400 nm)	−4.54	−3.20	1.34	1.46
7	989, 919, 879, 804, 727	148 900	330	2800 (1600 nm)	−4.57	−3.55	1.02	1.20
8	820, 915, 1008, 1157	248 900	27	1300 (1800 nm)	−4.81	−4.01	0.80	0.99
9	405, 457 579, 851, 955	45 400 (955 nm)	25	2080 (1800 nm)	−4.70	−3.84	0.86	1.08

<sup>a</sup> $\lambda_{\text{abs}}$ , absorption maxima;  $\epsilon_{\text{max}}$ , molar extinction coefficient measured at absorption maximum;  $\tau$ , the singlet excited-state lifetime obtained from TA;  $\sigma_{\text{max}}^{(2)}$ , the maximum TPA cross section (values in brackets are excitation wavelengths); HOMO and LUMO energy levels were calculated from the onset potentials of the first oxidative and reductive redox wave, respectively;  $E_{\text{g}}^{\text{EC}}$ , electrochemical energy gap derived from LUMO–HOMO;  $E_{\text{g}}^{\text{opt}}$ , optical energy gap.



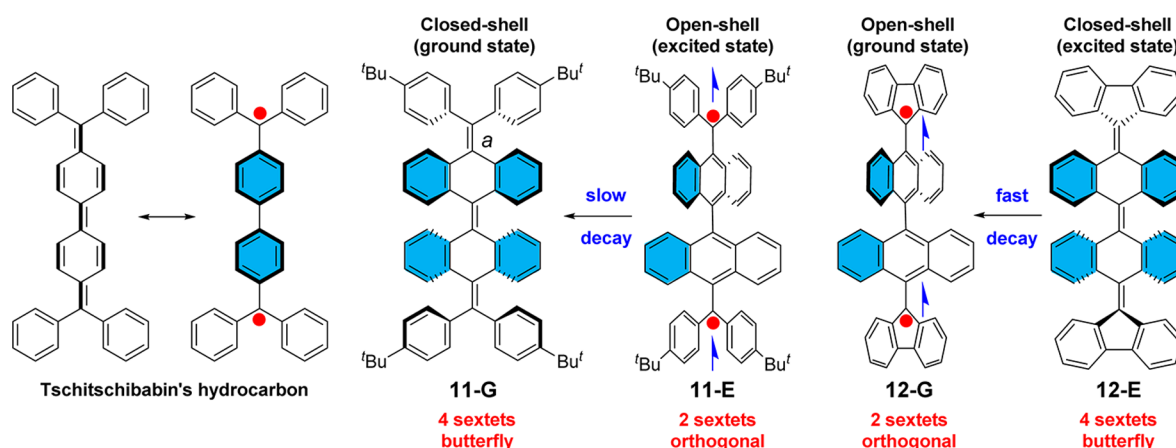
**Figure 6.** Representative five isomers of heptazethrene (HZ-a–HZ-e) and mesityl blocked 1,14:11:12-dibenzopentacene triplet diradical **10**.

sextets would enjoy a more stabilized biradical form than **6** by aromatic stabilization, it possesses a larger biradical character. This result actually leads to an extension of Clar's aromatic sextet rule to singlet biradicaloids, that is to say, for benzenoid polycyclic hydrocarbons with the same chemical composition, the molecule with more aromatic sextet rings in the biradical resonance forms exhibits greater singlet biradical character. The *p*-QDM bridged perylene dimer **8** can be regarded as an extended heptazethrene diimide and has a singlet biradical ground state. In contrast, the *p*-QDM bridged porphyrin dimer **9** favors a closed-shell quinoidal structure presumably because resonance to the biradical destroys the aromaticity of the two porphyrin macrocycles.

### Optical and Electrochemical Properties

The extended zethrenes have small energy gaps and show intense absorption in the NIR region (Figure 3 and Table 1). They are usually not fluorescent or weakly fluorescent due to short excited-state lifetimes as determined by TA measurements (Table 1). Recent theoretical and empirical results have pointed out that a moderate biradical character is responsible for the enhanced two-photon absorption ability.<sup>22,23</sup> Indeed, larger TPA cross sections were observed for **5** and **7** compared to **4** and **6** with smaller biradical characters (Table 1).

Multiple-stage amphoteric redox behavior was observed by cyclic voltammetry for all compounds due to their small HOMO–LUMO energy gap. The oxidation/reduction process can be achieved by chemical oxidation/reduction or by



**Figure 7.** Resonance structures of Tschitschibabin's hydrocarbon and ground-state and excited-state structures of **11** and **12**.

electrolysis and followed by UV–vis–NIR and ESR measurements.<sup>45</sup> The stability of the charged species can be ascribed to their (pseudo)aromaticity. The observed multiple redox waves implies their applications as active electrode materials for lithium ion batteries or supercapacitors.

#### Heptazethrene Isomers with Different Ground States

The heptazethrene can be regarded as a structure in which two phenalene units are fused with one benzene ring. Based on the fusion mode, five possible isomers can be drawn (Figure 6). In the first three isomers (HZ-*a*–HZ-*c*), the two naphthalene units are linked with *p*-QDM or *o*-QDM moiety and both closed-shell quinoidal and open-shell biradical forms can be drawn. However, in the last two isomers (HZ-*d*–HZ-*e*), the two naphthalene units are bridged by a *m*-xylylene moiety and they can only be drawn in an open-shell diradical form. As a result, they are predicted to be highly reactive triplet diradicals. Synthesis of such high-spin system is very challenging and very recently, we synthesized a kinetically blocked HZ-*e* derivative (**10**), which is persistent at  $-78\text{ }^{\circ}\text{C}$  under nitrogen protection.<sup>46</sup> The triplet diradicals were generated by oxidation of the corresponding dianion and was measured by low temperature ESR and ESTN.

#### ■ EXTENDED *p*-QDMs

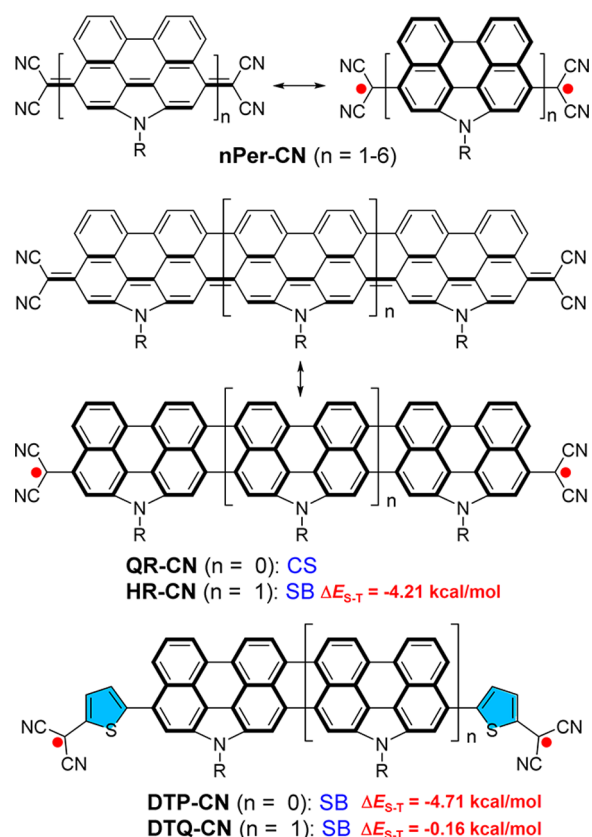
The extended *p*-QDM is another interesting  $\pi$ -scaffold with significant biradical character (Figure 1). To gain stability, the terminal methylene sites (radical centers) are usually protected by substituents such as phenyl or cyano (CN) groups. One well-known example in this family is the Tschitschibabin hydrocarbon (Figure 7), which is very reactive due to its large biradical character.<sup>47</sup> To obtain materials with better stability, our strategy is by benzannulation of the central biphenyl unit to generate the tetrabenzo-Tschitschibabin hydrocarbons **11** and **12** (Figure 7).<sup>48</sup> Their ground states are determined by a competing effect from three different aspects: First, the aromaticity. With this regard, both **11** and **12** will favor a closed-shell structure as two aromatic sextet rings are sacrificed in the biradical form. Second, the molecular geometry. The closed-shell forms of **11** and **12** adopt a butterfly-like geometry with a larger steric hindrance which is less favorable than the orthogonal biradical structure. Lastly, the terminal substitution. The fluorenyl moiety in **12** offers better thermodynamic stability than di-*tert*-butylphenyl substituents in **11** due to more efficient delocalization of the spin. Through a systematic analysis by NMR, ESR, absorption spectra, SQUID, FT Raman,

and X-ray crystallographic analysis assisted by DFT calculations, it was found that **11** has a closed-shell quinoidal structure while **12** can be regarded as a weakly coupled diradical in the ground state. Interestingly, the excited state of **11** (the biradical form, **11-E**) was chemically accessible and it showed an unusually slow decay ( $t_{1/2} = 495\text{ min}$ ) to the ground state (**11-G**), which can be explained by the large energy barrier (95 kJ/mol) for the transition from the orthogonal biradical form to a butterfly-like quinoidal form. On the other hand, for compound **12**, the quinoidal form **12-E** quickly converted into the biradical form **12-G** during the synthesis.

Similarly, a series of tetracyano-olgio(*N*-annulated perylene)-quinodimethanes *n*Per-CN ( $n = 1\text{--}6$ ) were synthesized mainly by Takahashi coupling reaction of the corresponding dibromo-oligomers followed by oxidative dehydrogenation (Figure 8).<sup>49</sup> This new series of compounds can be regarded as more extended benzannulated *p*-QDMs, and the stability and solubility are guaranteed by CN- and *N*-alkyl substitution, respectively. Interestingly, with extension of the chain length, the ground states gradually change from closed-shell (Per-CN) to singlet biradical (2Per-CN–4Per-CN) then to weakly coupled diradicals (5Per-CN–6Per-CN) (Table 2). Two driving forces are responsible for this transformation. One is the recovery of aromaticity of the quinoidal perylene unit in the biradical form, and the longer the oligomer, the more aromatization stability will be obtained. Another driving force is the strain release from the rigid quinoidal structure to the more flexible biradical structure. With an increase of the chain length, the biradical character increases to nearly 1 for higher oligomers such as pentamer and hexamer, and the spins are mainly distributed to the terminal perylene units, resulting in two separated radicals. Z-Scan measurements also showed that the oligomers with a moderate biradical character (e.g., 2Per-CN) showed higher TPA cross sections than those with large biradical characters (e.g., 4Per-CN to 6Per-CN, Table 2), which is in agreement with theoretical prediction.

To minimize the influence of strain release, planarized tetracyano-quaterylenequinodimethane (QR-CN) and hexarylenequinodimethane (HR-CN) were prepared from the corresponding dibromo-rylenes (Figure 8).<sup>50</sup> In contrast to the case of 2Per-CN with a large biradical character, the rigidified QR-CN has a closed-shell quinoidal structure in the ground state due to the efficient intramolecular antiferromagnetic coupling between the two spins via a double spin polarization mechanism. The HR-CN has a singlet biradical





**Figure 8.** Structures of tetracyano-*N*-annulated perylene quinodimethanes *n*PerCNs, QR-CN, HR-CN, DTP-CN, and DTQ-CN.

**Table 2.** Ground States, TPA Cross Sections, Electrochemical Energy Gap, and Singlet-Triplet Gap Data for *n*Per-CN, QR-CN, HR-CN, DTP-CN, and DTQ-CN.

compd	ground state	$\sigma_{\max}^{(2)}$ (GM)	$E_g^{EC}$ (eV)	$\Delta E_{S-T}$ (kcal/mol)
Per-CN	CS <sup>a</sup>	1300 (1200 nm)		
2Per-CN	SB <sup>b</sup>	1060 (1700 nm)	0.61	−0.342
3Per-CN	SB	770 (1700 nm)	0.53	−0.107
4Per-CN	SB	710 (1700 nm)	0.52	0.064
5Per-CN	DR <sup>c</sup>	730 (1700 nm)	0.57	0.556
6Per-CN	DR	710 (1700 nm)	0.53	0.883
QR-CN	CS	1400 (1800 nm)	0.80	
HR-CN	SB	3300 (2000 nm)		−4.21
DTP-CN	SB	1000 (1700 nm)	0.83	−4.71
DTQ-CN	SB	1700 (2400 nm)	0.37	−0.16

<sup>a</sup>CS: closed-shell. <sup>b</sup>SB: singlet biradical. <sup>c</sup>DR: weakly coupled diradical.

ground state due to the accumulated resonance energy via formation of six aromatic naphthalene units in the biradical form. However, compared with 3Per-CN, it has a smaller biradical character and larger singlet–triplet energy gap (Table 2). Both QR-CN and HR-CN showed very strong one-photon absorption and large two-photon cross sections in the NIR regions.

Very recently, we found that incorporation of one thiophene unit between the rylene and the dicyanomethylene site in Per-CN and QR-CN readily turns on their biradical states (Figure 8).<sup>51</sup> The resulting compounds DTP-CN and DTQ-CN both have a singlet biradical ground state with small singlet–triplet

energy gaps (Table 2). Such an evolution can be explained by the recovery of two additional aromatic thiophene rings in the biradical resonance forming together with the conformational flexibility around the thiophene–rylene connections.

## ■ PERIACENES

Periacenes are rectangular graphene fragments encompassing both zigzag and armchair edges (Figure 1) and a singlet biradical ground state has been predicted for peritetracene and above.<sup>11</sup> Even the smallest member of this family, bisanthene, is very reactive species. Our group has developed different approaches to stabilize the bisanthene (Scheme 2), for example, by substitution with dicarboximide (**13**)<sup>52</sup> and by substitution of the *meso*-positions with aryl or alkyne groups (**14**).<sup>53</sup> The unique diene character at the bay region allows further modification by double Diels–Alder addition reactions, and more extended bisanthene **15**<sup>54</sup> and an *n*-type semiconductor dicyno-ovalenediimide **16**<sup>55</sup> were prepared this way. The extended bisanthenequinone **17**<sup>56</sup> is a closed-shell quinoid rather than a singlet biradical. To date, the synthesis of periacenes longer than bisanthene is still not successful although some attempts have been done by us and by Müllen's group (Scheme 2). Our route toward substituted peripentacene was based on 6,6'-dipentacenylquinone **18**.<sup>57</sup> Oxidative photocyclization of **18** gave partially cyclized product **19**, and subsequent reaction with aryl Grignard reagents gave unexpected Michael addition products **20** and **21**.<sup>58</sup> Compound **21** cannot undergo further nucleophilic addition or reduction reactions.

Müllen attempted an alternative “pyrene approach” (Scheme 2).<sup>59</sup> The tetracyano-pyrene intermediate **22** was prepared, and subsequent cyclization afforded the tetraketone **23**, which however cannot undergo further photocyclization. Oxidative cyclodehydrogenation of **22** in the presence of PIFA/BF<sub>3</sub> was successful, but subsequent acid-promoted acylation only gave the target peripentacenetetraketone **24** in trace. Unfortunately, **24** exhibited very poor solubility in organic solvents and no further reaction was reported. Therefore, the synthesis of periacenes beyond bisanthene is still a big challenge.

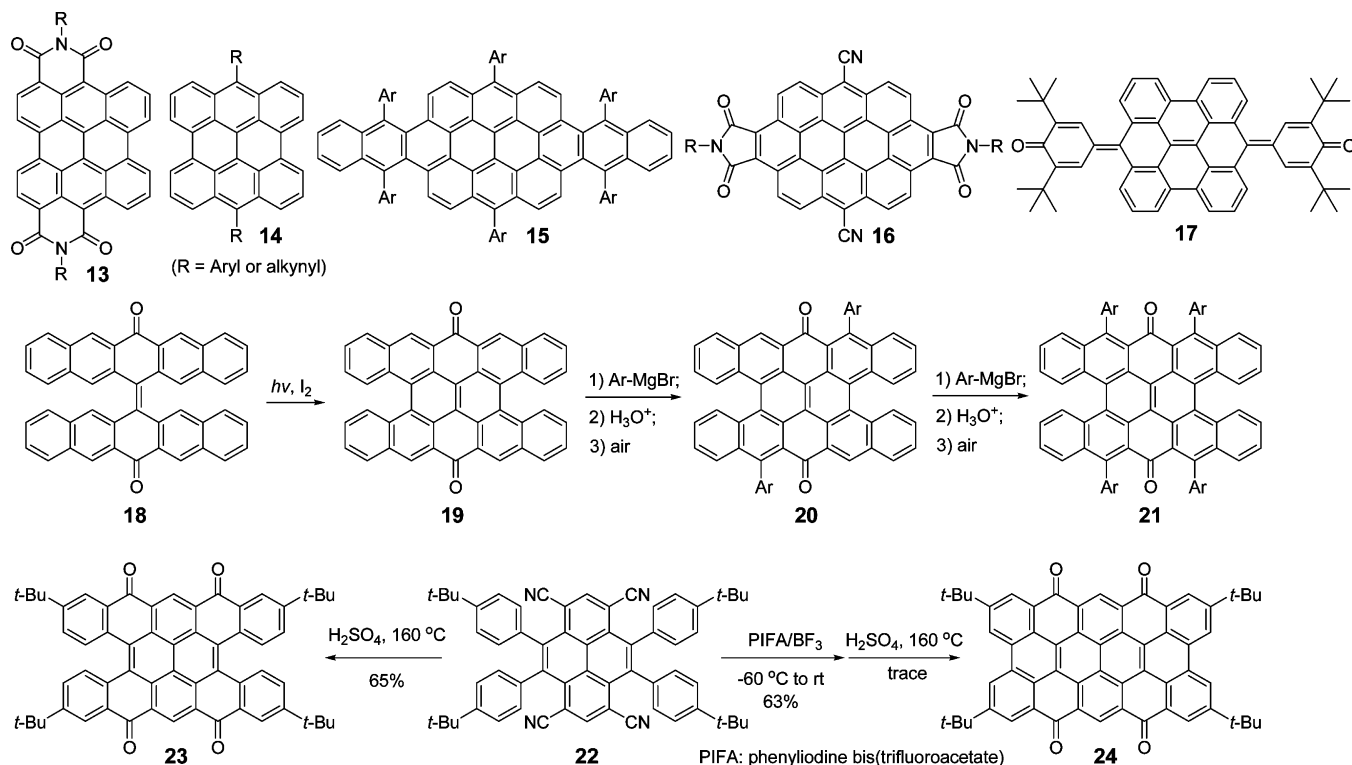
## ■ CONCLUDING REMARKS

In summary, recent studies on the PHs with a singlet biradical ground state revealed many interesting phenomena. Based on the chemistry developed by us and other groups, it is now feasible to prepare stable biradicaloids with sufficient stability similar to other closed-shell  $\pi$ -conjugated systems. The systematic experimental and theoretic studies now offered us much clearer understanding on the fundamental structure–biradical character–physical property relationship. It was found that the aromaticity is the most fundamental origin and Clar's aromatic sextet rule can be further extended to the singlet biradicaloids. In addition, steric effect and substituent effect should be also considered. The biradical character then largely determines the physical properties and chemical reactivity. The unique electronic, optical, and magnetic activity opened many opportunities for organic electronics, photonics, spintronics, and energy storage devices.

The future targets can be extended from biradical to polyradical, from low-spin to high-spin, and from pure hydrocarbon to hybrid systems. For practical application, it is important to seek a balance between biradical character, material stability, and molecular order. We believe that many



Scheme 2. Structures of Bisanthenes and Attempted Synthesis of Peripentacene Derivatives



new physics can be discovered for this unique system, and by appropriate design novel devices can be fabricated in thin films, at the nanoscale, and even at the molecule scale.

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### Notes

The authors declare no competing financial interest.

### Biographies

**Dr. Zhe Sun** was born in Shandong province, China, in 1987. He received his Bachelor's degree in Chemistry from Sichuan University in 2009 and Ph.D. degree from NUS in 2013 under the supervision of Professor Jishan Wu. He mainly worked on the design and synthesis of novel open-shell polycyclic hydrocarbons. He recently joined Professor Hiroyuki Isobe's group at Tohoku University as a research associate.

**Dr. Zebing Zeng** was born in Hunan province, China, in 1981. He received a bachelor degree from Hunan University of Technology in 2004, a Master degree from Nankai University in 2007, and a Ph.D. degree from the Department of Chemistry, NUS in 2012 under the supervision of Professor Jishan Wu. His research was focused on novel chromophores based on closed-shell and open-shell polycyclic aromatic hydrocarbons. He recently accepted a faculty position at Hunan University.

**Dr. Jishan Wu** conducted his Ph.D. research at the Max-Planck Institute for Polymer Research under the supervision of 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 Sir J. Fraser Stoddart on supramolecular chemistry. Dr. Wu joined the Department of Chemistry of NUS in 2007 as an assistant professor and was promoted to an associate professor in 2012, and recently he was

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## REFERENCES

- (1) Grzybowski, M.; Skonieczny, K.; Butenschön, H.; Gryko, D. T. Comparison of Oxidative Aromatic Coupling and the Scholl Reaction. *Angew. Chem., Int. Ed.* **2013**, *52*, 9900–9930.
- (2) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: New York, 1964; Vol. I/II.
- (3) Spitler, E. L.; Johnson, C. A.; Haley, M. M. Renaissance of Annulene Chemistry. *Chem. Rev.* **2006**, *106*, 5344–5386.
- (4) Hadziioannou, G.; Malliaras, G. G., Eds. *Semiconducting Polymers: Chemistry, Physics and Engineering*, 2nd Ed.; Wiley-VCH: New York, 2006.
- (5) Wu, J.; Pisula, W.; Müllen, K. Graphenes as Potential Materials for Electronics. *Chem. Rev.* **2007**, *107*, 718–747.
- (6) Vikki, M.; Tsefrikas, V. M.; Scott, L. T. Geodesic Polyarenes by Flash Vacuum Pyrolysis. *Chem. Rev.* **2006**, *106*, 4868–4884.

- (7) Clar, E.; Marschall, Ch. Heptacene, An Ultragreen Hydrocarbon. *Bull. Soc. Chim. Fr.* **1950**, 440.
- (8) Clar, E.; Macpherson, I. A. The Significance of Kekulé Structures for The Stability of Aromatic Systems-II. *Tetrahedron* **1962**, 18, 1411–1416.
- (9) Erünlü, R. K. Octazethren. *Liebigs Ann. Chem.* **1969**, 721, 43–47.
- (10) Bendikov, M.; Duong, H. M.; Starkey, K.; Houk, K. N.; Carter, E. A.; Wudl, F. Oligoacenes: Theoretical Prediction of Open-Shell Singlet Diradical Ground States. *J. Am. Chem. Soc.* **2004**, 126, 7416–7417.
- (11) Jiang, D.; Sumpter, B. G.; Dai, S. First Principles Study of Magnetism in Nanographenes. *J. Chem. Phys.* **2007**, 127, 124703.
- (12) Konishi, A.; Hirao, Y.; Nakano, M.; Shimizu, A.; Botek, E.; Champagne, B.; Ashiomi, D.; Sato, K.; Takui, T.; Matsumoto, K.; Kurata, H.; Kubo, T. Synthesis and Characterization of Teranthene: A Singlet Biradical Polycyclic Aromatic Hydrocarbon Having Kekulé Structures. *J. Am. Chem. Soc.* **2010**, 132, 11021–11023.
- (13) Konishi, A.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kishi, R.; Shigeta, Y.; Nakano, M.; Tokunaga, K.; Kamada, K.; Kubo, T. Synthesis and Characterization of Quarteranthene: Elucidating the Characteristics of the Edge State of Graphene Nanoribbons at the Molecular Level. *J. Am. Chem. Soc.* **2013**, 135, 1430–1437.
- (14) Ohashi, K.; Kubo, T.; Masui, T.; Yamamoto, K.; Nakasuji, K.; Takui, T.; Kai, Y.; Murata, I. 4,8,12,16-Tetra-*tert*-butyl-s-indaceno-[1,2,3-*cd*:5,6,7-*c'd'*]diphenylene: A Four-Stage Amphoteric Redox System. *J. Am. Chem. Soc.* **1998**, 120, 2018–2027.
- (15) Shimizu, A.; Kubo, T.; Uruichi, M.; Yakushi, K.; Nakano, M.; Shiomi, D.; Sato, K.; Takui, T.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Morita, Y.; Nakasuji, K. Alternating Covalent Bonding Interactions in a One-Dimensional Chain of a Phenalenyl-Based Singlet Biradical Molecule Having Kekulé Structures. *J. Am. Chem. Soc.* **2010**, 132, 14421–14428.
- (16) Chase, D. T.; Rose, B. D.; McClintock, S. P.; Zakharov, L. N.; Haley, M. M. Indeno[1,2-*b*]fluorenes: Fully Conjugated Antiaromatic Analogues of Acenes. *Angew. Chem., Int. Ed.* **2011**, 50, 1127–1130.
- (17) Shimizu, A.; Kishi, R.; Nakano, M.; Shiomi, D.; Sato, K.; Takui, T.; Hisaki, I.; Miyata, M.; Tobe, Y. Indeno[2,1-*b*]fluorene: A 20- $\pi$ -Electron Hydrocarbon with Very Low-Energy Light Absorption. *Angew. Chem., Int. Ed.* **2013**, 52, 6076–6079.
- (18) Döhnert, D.; Koutecký, J. Occupation Numbers of Natural Orbitals as a Criterion for Biradical Character. Different Kinds of Biradicals. *J. Am. Chem. Soc.* **1980**, 102, 1789–1796.
- (19) Yamaguchi, K. The Electronic Structures of Biradicals in The Unrestricted Hartree-Fock Approximation. *Chem. Phys. Lett.* **1975**, 33, 330–335.
- (20) Chikamatsu, M.; Mikami, T.; Chisaka, J.; Yoshida, Y.; Azumi, R.; Yase, K. Ambipolar Organic Field-effect Transistors Based on a Low Band Gap Semiconductor with Balanced Hole and Electron Mobilities. *Appl. Phys. Lett.* **2007**, 91, 043506.
- (21) Morita, Y.; Nishida, S.; Murata, T.; Moriguchi, M.; Ueda, A.; Satoh, M.; Arifuku, K.; Sato, K.; Takui, T. Organic Tailored Batteries Materials Using Stable Open-shell Molecules with Degenerate Frontier Orbitals. *Nat. Mater.* **2011**, 10, 947–951.
- (22) Nakano, M.; Kishi, R.; Takebe, A.; Nate, M.; Takahashi, H.; Kubo, T.; Kamada, K.; Ohta, K.; Champagne, B.; Botek, E. Second Hyperpolarizability of Zethrenes. *Comput. Lett.* **2007**, 3, 333–338.
- (23) Kamada, K.; Ohta, K.; Kubo, T.; Shimizu, A.; Morita, Y.; Nakasuji, K.; Kishi, R.; Ohta, S.; Furukawa, S. I.; Takahashi, H.; Nakano, M. Strong Two-Photon Absorption of Singlet Diradical Hydrocarbons. *Angew. Chem., Int. Ed.* **2007**, 46, 3544–3546.
- (24) Lee, J.; Jadhav, P.; Reusswig, P. D.; Yost, S. R.; Thompson, N. J.; Congreve, D. N.; Hontz, E.; Van Voorhis, T.; Baldo, M. A. Singlet Exciton Fission Photovoltaics. *Acc. Chem. Res.* **2013**, 46, 1300–1311.
- (25) Dediu, V.; Hueso, L. E.; Bergenti, I.; Tlani, C. Spin Routes in Organic Semiconductors. *Nat. Mater.* **2009**, 8, 707–716.
- (26) Anthony, J. E. Functionalized Acenes and Heteroacenes for Organic Electronics. *Chem. Rev.* **2006**, 106, 5028–5048.
- (27) Anthony, J. E. The Larger Acenes: Versatile Organic Semiconductors. *Angew. Chem., Int. Ed.* **2008**, 47, 452–483.
- (28) Weil, T.; Vosch, T.; Hofkens, J.; Peneva, K.; Müllen, K. The Rylene Colorant Family-Tailored Nanoemitters for Photonics Research and Applications. *Angew. Chem., Int. Ed.* **2010**, 49, 9068–9093.
- (29) Abe, M. Diradicals. *Chem. Rev.* **2013**, 113, 7011–7088.
- (30) Sun, Z.; Ye, Q.; Chi, C.; Wu, J. Low Band Gap Polycyclic Hydrocarbons: From Closed-shell Near Infrared Dyes and Semiconductors to Open-shell Radicals. *Chem. Soc. Rev.* **2012**, 41, 7857–7889.
- (31) Shimizu, A.; Hirao, Y.; Kubo, T.; Nakano, M.; Botek, E.; Champagne, B. Theoretical Consideration of Singlet Open-Shell Character of Polyperiacenes Using Clar's Aromatic Sextet Valence Bond Model and Quantum Chemical Calculations. *AIP Conf. Proc.* **2012**, 1504, 399–405.
- (32) Sun, Z.; Zeng, Z.; Wu, J. Benzenoid Polycyclic Hydrocarbons with an Open-Shell Biradical Ground State. *Chem.—Asian J.* **2013**, 8, 2894–2904.
- (33) Clar, E.; Lang, K. F.; Schulz-Kiesow, H. Aromatische Kohlenwasserstoffe, LXX. Mitteil. Zethren (1.12;6.7-Di-benzotetracen). *Chem. Ber.* **1955**, 88, 1520–1527.
- (34) Wu, T. C.; Chen, C. H.; Hibi, D.; Shimizu, A.; Tobe, Y.; Wu, Y. T. Synthesis, Structure, and Photophysical Properties of Dibenzo-[de,mn]naphthacenes. *Angew. Chem., Int. Ed.* **2010**, 49, 7059–7062.
- (35) Shan, L.; Liang, Z.-X.; Xu, X.-M.; Tang, Q.; Miao, Q. Revisiting Zethrene: Synthesis, Reactivity and Semiconductor Property. *Chem. Sci.* **2013**, 4, 3294–3297.
- (36) Umeda, R.; Hibi, D.; Miki, K.; Tobe, Y. Tetradehydrodinaphtho[10]annulene: A Hitherto Unknown Dehydroannulene and a Viable Precursor to Stable Zethrene Derivatives. *Org. Lett.* **2009**, 11, 4104–4106.
- (37) Sun, Z.; Huang, K.-W.; Wu, J. Soluble and Stable Zethrenebis (dicarboximide) and Its Quinone. *Org. Lett.* **2010**, 12, 4690–4693.
- (38) Sun, Z.; Wu, J. 7, 14-Diaryl-Substituted Zethrene Diimides as Stable Far-Red Dyes with Tunable Photophysical Properties. *J. Org. Chem.* **2013**, 78, 9032–9040.
- (39) Sun, Z.; Huang, K.-W.; Wu, J. Soluble and Stable Heptazethrenebis (dicarboximide) with a Singlet Open-Shell Ground State. *J. Am. Chem. Soc.* **2011**, 133, 11896–11899.
- (40) Li, Y.; Heng, W.-K.; Lee, B. S.; Aratani, N.; Zafra, J. L.; Bao, N.; Lee, R.; Sung, Y. M.; Sun, Z.; Huang, K.-W.; Webster, R. D.; López Navarrete, J. T.; Kim, D.; Osuka, A.; Casado, J.; Ding, J.; Wu, J. Kinetically Blocked Stable Heptazethrene and Octazethrene: Closed-Shell or Open-Shell in the Ground State? *J. Am. Chem. Soc.* **2012**, 134, 14913–14922.
- (41) Sun, Z.; Lee, S.; Park, K.; Zhu, X.; Zhang, W.; Zheng, B.; Hu, P.; Zeng, Z.; Das, S.; Li, Y.; Chi, C.; Li, R.; Huang, K.; Ding, J.; Kim, D.; Wu, J. Dibenzoheptazethrene Isomers with Different Biradical Characters: An Exercise of Clar's Aromatic Sextet Rule in Singlet Biradicaloids. *J. Am. Chem. Soc.* **2013**, 135, 18229–18236.
- (42) Das, S.; Lee, S.; Son, M.; Zhu, X.; Zhang, W.; Zheng, B.; Hu, P.; Zeng, Z.; Sun, Z.; Zeng, Z.; Li, R.; Huang, K.; Ding, J.; Kim, D.; Wu, J. *p*-Quinodimethane Bridged Perylene Dimers and *peri*-Condensed Quaterrylenes: The Effect of Fusion Mode on Their Ground States and Physical Properties. *Chem.—Eur. J.* **2014**, DOI: 10.1002/chem.201402831.
- (43) Zeng, W.; Ishida, M.; Lee, S.; Sung, Y.; Zeng, Z.; Ni, Y.; Chi, C.; Kim, D.-H.; Wu, J. A *p*-Quinodimethane-Bridged Porphyrin Dimer. *Chem.—Eur. J.* **2013**, 19, 16814–16824.
- (44) Motta, S. D.; Negri, F.; Fazzi, D.; Castiglioni, C.; Canesi, E. V. Biradicaloid and Polyenic Character of Quinoidal Oligothiophenes Revealed by the Presence of a Low-Lying Double-Exciton State. *J. Phys. Chem. Lett.* **2010**, 1, 3334–3339.
- (45) Zafra, J. L.; González Cano, R. C.; Delgado, C. R.; Sun, Z.; Li, Y.; López Navarrete, J. T.; Wu, J.; Casado, J. Zethrene Biradicals: How Pro-aromaticity is Expressed in the Ground Electronic State and in the Lowest Energy Singlet, Triplet, and Ionic States. *J. Chem. Phys.* **2014**, 140, 054706.
- (46) Li, Y.; Huang, K.-W.; Sun, Z.; Webster, R. D.; Zeng, Z.; Zeng, W.; Chi, C.; Furukawa, K.; Wu, J. A Kinetically Blocked 1,4:11,12-

Dibenzopentacene: A Persistent Triplet Diradical of Non-Kekulé Polycyclic Benzenoid Hydrocarbons. *Chem. Sci.* **2014**, *5*, 1908–1914.

(47) Montgomery, L. K.; Huffman, J. C.; Jurczak, E. A.; Grendze, M. P. The Molecular Structures of Thiele's and Chichibabin's Hydrocarbons. *J. Am. Chem. Soc.* **1986**, *108*, 6004–6011.

(48) Zeng, Z.; Sung, Y. M.; Bao, N.; Tan, D.; Lee, R.; Zafra, J. L.; Lee, B. S.; Ishida, M.; Ding, J.; López Navarrete, J. T.; Li, Y.; Zeng, W.; Kim, D.; Huang, K.-W.; Webster, R. D.; Casado, J.; Wu, J. Stable Tetrabenz-Chichibabin's Hydrocarbons: Tunable Ground State and Unusual Transition between Their Closed-Shell and Open-Shell Resonance Forms. *J. Am. Chem. Soc.* **2012**, *134*, 14513–14525.

(49) Zeng, Z.; Ishida, M.; Zafra, J. L.; Zhu, X.; Sung, Y. M.; Bao, N.; Webster, R. D.; Lee, B. S.; Li, R.-W.; Zeng, W.; Li, Y.; Chi, C.; López Navarrete, J. T.; Ding, J.; Casado, J.; Kim, D.; Wu, J. Pushing Extended *p*-Quinodimethanes to the Limit: Stable Tetracyano-oligo(*N*-annulated perylene)quinodimethanes with Tunable Ground States. *J. Am. Chem. Soc.* **2013**, *135*, 6363–6371.

(50) Zeng, Z.; Lee, S.; Zafra, J. L.; Ishida, M.; Zhu, X.; Sun, Z.; Ni, Y.; Webster, R. D.; Li, R.-W.; López Navarrete, J. T.; Chi, C.; Ding, J.; Casado, J.; Kim, D.; Wu, J. Tetracyanoquaterylene and Tetracyano-hexarylenequinodimethanes with Tunable Ground States and Strong Near-Infrared Absorption. *Angew. Chem., Int. Ed.* **2013**, *52*, 8561–8565.

(51) Zeng, Z.; Lee, S.; Zafra, J. L.; Ishida, M.; Bao, N.; Webster, R. D.; López Navarrete, J. T.; Ding, J.; Casado, J.; Kim, D.; Wu, J. Turning on The Biradical State of Tetracyano- Perylene and Quaterylenequinodimethanes by Incorporation of Additional Thiophene Rings. *Chem. Sci.* **2014**, *5*, 3072–3080.

(52) Yao, J.; Chi, C.; Wu, J.; Loh, K.-P. Bisanthracene Bis-(dicarboxylic imide)s as Soluble and Stable NIR Dyes. *Chem.—Eur. J.* **2009**, *15*, 9299–9302.

(53) Li, J.; Zhang, K.; Zhang, X.; Huang, K.; Chi, C.; Wu, J. Meso-substituted Bisanthenes as Soluble and Stable NIR Dyes. *J. Org. Chem.* **2010**, *75*, 856–863.

(54) Li, J.; Jiao, C.; Huang, K.; Wu, J. Lateral Extension of  $\pi$ -Conjugation Along the Bay Regions of Bisanthene via Diels-Alder Cycloaddition Reaction. *Chem.—Eur. J.* **2011**, *17*, 14672–14680.

(55) Li, J.; Chang, J.; Tan, P.; Jiang, H.; Chen, X.; Chen, Z.; Zhang, J.; Wu, J. Disc-like 7,14-Dicyano-ovalene-3,4:10,11-bis(dicarboximide) as a Solution Processible *n*-Type Semiconductor for Air Stable Field-Effect Transistors. *Chem. Sci.* **2012**, *3*, 846–850.

(56) Zhang, K.; Huang, K. W.; Li, J. L.; Luo, J.; Chi, C.; Wu, J. A Soluble and Stable Quinoidal Bisanthene with NIR Absorption and Amphoteric Redox Behavior. *Org. Lett.* **2009**, *11*, 4854–4857.

(57) Zhang, X.; Jiang, X.; Luo, J.; Chi, C.; Chen, H.; Wu, J. A Cruciform 6,6'-Dipentacenyl: Synthesis, Solid State Packing and Applications for Thin Film Transistors. *Chem.—Eur. J.* **2010**, *16*, 464–468.

(58) Zhang, X.; Li, J.; Qu, H.; Chi, C.; Wu, J. Fused Bispentacenequinone and Its Unexpected Michael Addition. *Org. Lett.* **2010**, *12*, 3946–3949.

(59) Zöphel, L.; Berger, R.; Gao, P.; Enkelmann, V.; Baumgarten, M.; Wagner, M.; Müllen, K. Toward the *peri*-Pentacene Framework. *Chem.—Eur. J.* **2013**, *19*, 17821–17826.