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Pro-aromatic and anti-aromatic π-conjugated molecules: an irresistible wish to be diradicals

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Aromaticity is an important concept to understand the stability and physical properties of π-conjugated molecules. Recent studies on pro-aromatic and anti-aromatic molecules revealed their irresistible tendency to become diradicals in the ground state. Diradical character thus becomes another very important concept and it is fundamentally correlated to the physical (optical, electronic and magnetic) properties and chemical reactivity of most of the organic optoelectronic materials. Molecules with distinctive diradical character show unique properties which are very different from those of traditional closed-shell π-conjugated systems, and thus they have many potential applications in organic electronics, spintronics, non-linear optics and energy storage. This critical review first introduces the fundamental electronic structure of Kekulé diradicals within the concepts of anti-aromaticity and pro-aromaticity in the context of Hückel aromaticity and diradical character. Then recent research studies on various stable/persistent diradicaloids based on pro-aromatic and anti-aromatic compounds are summarized and discussed with regard to their synthetic chemistry, physical properties, structure–property relationships and potential material applications. A summary and personal perspective is given at the end.

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1. Introduction

Diradicals are often associated with intermediate or highly reactive species in chemical reactions. Diradicals and polyradicals, given the presence of unpaired electrons, have been thought of as building blocks for magnetically active materials on the basis of the transition between low and high spin states.[1] Their design, however, has suffered from intrinsic difficulties and a particular concern is the low-to-high spin energy gap (ΔE_{LH}) which should be small in order to facilitate magnetic switching. In non-Kekulé diradicals/polyradicals the unpaired electrons cannot be bonded and therefore result in high spin triplet/multiplet ground electronic states (Fig. 1a, TMMT), providing rather large singlet/low-spin to triplet/high-spin ($\Delta E_{\mathrm{ST}}/\Delta E_{\mathrm{LH}}$) gaps. In contrast, Kekulé diradicals might display the reverse

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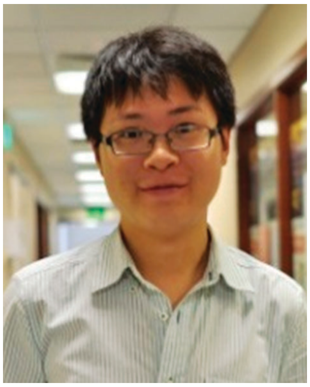

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Xueliang Shi was born in Jiangsu province, P. R. China, in 1988. He received his bachelor's degree in applied chemistry from Soochow University and he joined the National University of Singapore as a PhD student in 2011. He is currently working on the synthesis of anti-aromatic molecules based on quinoidal thienoacenes and heteroacenecs under the supervision of Dr Chunyan Chi.

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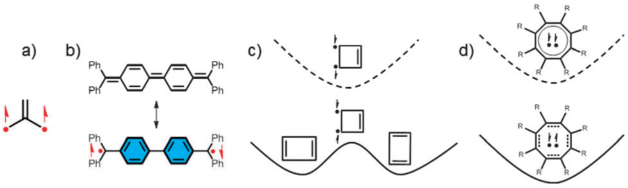
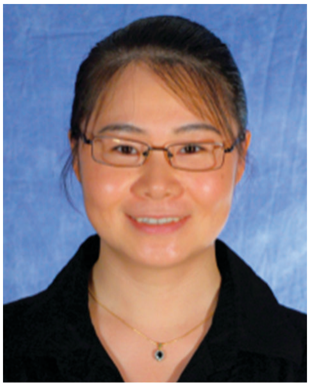


Fig. 1 (a) Trimethylenemethane (TMMT), (b) Tschitschibabin's hydrocarbon, (c) cyclobutadiene ground electronic state singlet and excited state triplet, (d) substituted cyclooctatetraene.

situation, with a singlet open-shell ground state and a high spin triplet diradical excited state lying at a rather low energy. The singular electronic structure of Kekulé diradicals allows this situation which violates Hund's rule referring to the ground electronic state maximum multiplicity.[2] We propose to deal with two main Kekulé diradicals: (i) anti-aromatic cores and (ii) pro-aromatic structures.

Anti-aromatic molecules are defined in terms of the existence of $4n$ π-electrons disposed in a planar cyclic arrangement. The prototypical example is cyclobutadiene (CBD, $n = 1$ in $4n$, Fig. 1c). In the square geometry, the instability of the CBD closed-shell electronic wavefunction makes the molecule to get stabilized as a diradical. This diradical has a singlet ground electronic state with the triplet state above ($\approx$10 kcal mol^{-1}).[3] However, the closed-shell CBD finds the most stable configuration by Jahn–Teller distortion to form a rectangular structure with the square diradical being the transition state between the



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Chunyan Chi was born in Harbin, China, in 1975. She received a bachelor degree from Qiqihar University in 1998 and a master degree from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, in 2001. She then conducted her PhD research in the Max-Planck Institute for Polymer Research under the supervision of Professor Gerhard Wegner and postdoctorate research with Professor Guillermo C. Bazan in the University of California at Santa Barbara. She is now an assistant professor in the Department of Chemistry, National University of Singapore. Her research interests mainly focus on novel acene- and heteroacene-based molecules and functional materials.

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Juan Casado

Juan Casado is Associate Professor of Physical Chemistry at the University of Málaga (Spain) with Full Professor habilitation since 2013. He received his PhD in Chemistry (1999, University of Málaga) in the field of Raman spectroscopy of oligothiophenes. In 2000, he moved to the University of Minnesota (USA) pursuing research in Organic Electrochemistry and Spectroelectrochemistry. In the period 2004–2006 he was a visiting scientist at the Steacie Institute for Molecular Sciences at the NRC in Ottawa (Canada). His actual interests are focused on conjugated molecules displaying diradicaloid properties, mixed valence behavior, ultrafast transient absorption features, non-linear optics, and vibrational circular Raman and infrared spectroscopy.

Jishan Wu

Jishan Wu received BSc degree from Wuhan University (1997), MSc degree from Changchun Institute of Applied Chemistry, CAS (2000), and PhD degree from Max-Planck Institute for Polymer Research (with Klaus Müllen, 2004). He conducted postdoc study with Sir J. Fraser Stoddart in UCLA and then joined the Department of Chemistry of NUS in 2007 as an assistant professor. He was promoted to an associate professor (2012) and recently was appointed as the Dean's Chair Professor (2014). His major interests include novel aromatic and supramolecular systems and materials. He has published more than 150 peer-reviewed articles and received more than 10 awards.

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two possible rectangular resonance isomers. Steric hindrance by substitution of CBD with bulky groups impedes the rectangular deformation and allows the stabilization of the diradical square geometry.[4] Cyclooctatetraene (COT, $n = 2$ in $4n$) and any planar [$4n$]annulene at the most symmetrical geometry can be regarded as alternant hydrocarbon diradicals.[5] Like CBD, steric congestion at the peripheral positions can stabilize the diradicaloid structures (Fig. 1d). A similar statement can be applied to pentalene, a well-known anti-aromatic molecule derived from COT by bonding the most distal 1,5-atoms.[6]

In the pro-aromatic concept for the formation of diradicals, the driving force for such solution is the aromaticity gaining of consecutive non-aromatic rings, a net energy minimization that can eventually surpass the energy required to break a double bond thus giving way to the generation of a diradical. The use of quinoidal cores is the most convenient route for this end. This is nicely exemplified by the pioneering studies at the beginning of the last century by Tschitschibabin[7] (Fig. 1b) and Thiele[8] from which most of the work on this has been inspired thereof. These quinoidal platforms are strongly stabilized by π-electron conjugation along the C=C/C–C alternant path hence representing a configuration with all π-electrons bonded and consequently with singlet closed-shell ground electronic states. The key point is that by accumulating an increasing number of these units in oligomeric arrangements, one expects that at a given number of monomeric units, the condition for the formation of the diradical is fulfilled and thus the diradical is generated. In chemical terms, in these Kekulé diradicals, there is always a contributing canonical form which pairs the two "unpaired" electrons in a full closed-shell quinoidal structure by which they always disclose, in their most symmetrical situations, singlet diradical ground electronic states. In physical terms, the preferable stabilization of the singlet over the triplet is the result of double or dynamic spin polarization (DSP).[9] DSP responds to the additional stabilizing contributions that the singlet state receives by multi-configurational mixing with other singlets, an effect that is restricted in the triplet.

In most of the known Kekulé diradicals, the two unpaired electrons are placed in two non-bonding nearly degenerate singly occupied molecular orbitals (SOMO disjoint orbitals). The energies of the singlet and triplet states in these diradicals are shown in Fig. 2. In non-Kekulé diradicals, $J_{\text{triplet}} = J_{\text{singlet}}$ (J: electronic repulsion between the two electrons) and the ground electronic state is always a triplet. In Kekulé diradicals, however, due to configurational mixing in the singlets, $J_{\text{triplet}} > J_{\text{singlet}}$, and because the magnetic exchange K is always small (disjoint character), $E_{\text{triplet}} > E_{\text{singlet}}$ and the diradical ground electronic state is a singlet (Fig. 2). DSP is contained in the condition $J_{\text{triplet}} > J_{\text{singlet}}$. From this analysis, we easily deduced that $\Delta E_{\text{ST}} = -2K$ and because K is always small, ΔE_{ST} is also small which is an intrinsic feature of Kekulé diradicals. DSP highlights the ability of the unpaired electrons to π-conjugate within the closed-shell electronic structure of the bridge. The understanding of the physics of these Kekulé diradicals in terms of DSP opens the way to address many other properties of these open-shell molecules in the context of the more general well established effect of spin polarization, for example, how alkyl substitution can tune the diradical electronic structure.

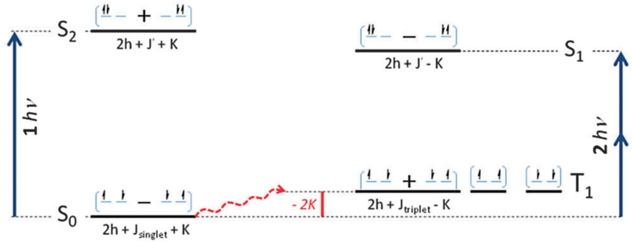

Fig. 2 Four energy levels diagram (see the T_1 constituted by three degenerated triplet states) of a Kekulé homosymmetric diradical. Note that, for instance, [↿ ⇂ _ ⇂ ↿] represents the antisymmetric combination of the product of the monoelectronic spin wavefunctions, [α(1)β(2)−α(2)β(1)], for electrons 1 and 2 of the diradical, and so on.

The two lowest energy lying singlet diradical and triplet states, from which the ΔE_{ST} above is established, correspond to electronic configurations with the two electrons placed in the non-bonding orbitals. The next two excited states of the Kekulé diradical correspond to two singlets consisting in the excitation of one of these two electrons on the other, giving rise to ionic-like singlet excited states (S_1 and S_2 in Fig. 2). The S_1 ionic singlet has the same symmetry as S_0 (both correspond to the same symmetry combinations) whereas the S_2 has a different symmetry than S_0. This is important as for their optical properties: the $S_0 \rightarrow S_1/S_0 \rightarrow S_2$ optical excitations are forbidden/allowed by one-photon absorption and allowed/forbidden by two-photon absorption (TPA) but both have strong oscillator strengths given the ionic-like character. In general, the optical properties of Kekulé diradicals display these general characteristics, strong one-photon absorption in the Vis-NIR spectral region and large TPA by NIR excitation.[10]

It is clear that the singlet–triplet gap, ΔE_{ST}, becomes a fingerprint of the degree of diradical character (y), a value that has been combined with other figures, such as the energy differences and transition properties between three singlet states within the two-site diradical model, as demonstrated by Nakano *et al.*[10b,11] The rather small ΔE_{ST} gap entails them with magnetic activity (ESR non-silent spectrum) as the triplet can be populated at room temperature (Fig. 2). The ground state can be experimentally identified by variable temperature (VT) electronic absorption spectroscopy and NMR/ESR/SQUID (superconducting quantum interference device) measurements. Raman spectroscopy is also unique in giving a molecular level fingerprint of the singlet open-shell structure as DSP subtly tunes the singlet/triplet molecular structure of the diradical. In addition, it permits one to follow the quinoidal (closed-shell) to aromatic (open-shell) conversion along a homogeneous series of increasing size oligomers. In addition, broken-symmetry density functional theory (DFT) calculations provide important insights into the molecular geometry, energies, spin density distribution, diradical character, *etc.* The photophysical properties can be further investigated by transient absorption (TA) and TPA spectroscopy. The electronic properties can be also studied by electrochemistry.

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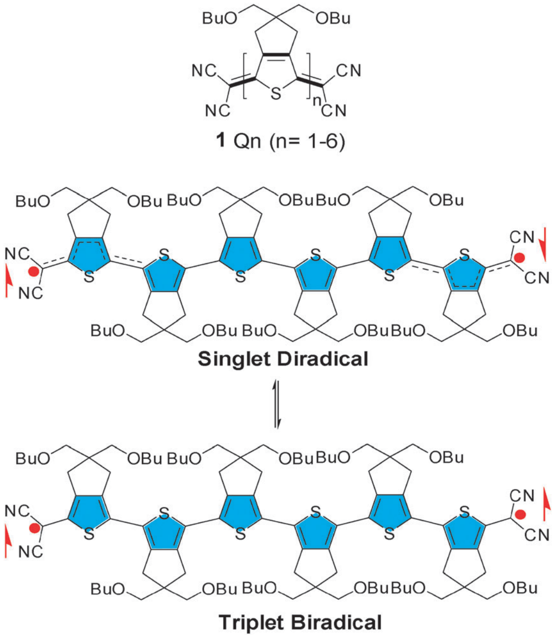
In this context, this critical review will summarize recent progress in the pro-aromatic and anti-aromatic conjugated molecules showing a distinctive diradical character in the ground state, which include (1) quinoidal oligothiophenes, (2) quinoidal polycyclic hydrocarbons and their analogues containing heteroatoms, (3) anti-aromatic indenofluorenes and their analogues, (4) quinoidal heteroacenes, and (5) other porphyrinoid-based diradicaloids. The discussion will cover their synthetic chemistry, characterization, physical properties, fundamental structure–diradical character relationships, and potential material applications.

2. Quinoidal oligothiophenes

The first report on quinoidal oligothiophenes[12] is dated back to the seventies of the last century in the context of the search for thiophene-based derivatives of tetracyanoquinodimethane (TCNQ) followed in the eighties by the work of Ogura, Tanaka, Otsubo and Fukazawa *et al.*[13] Oda prepared the first quinoidal oligothiophene in analogy to Tschitschibabin's hydrocarbon.[14] The first reference to the existence of a Kekulé diradical on thienoquinoids was by Higuchi *et al.* from their studies on tetracyano quinoidal tetrathiophenes with different substitution patterns in order to account for the resulting mixture of *cis*/*trans* isomers.[15] It was in 2005 that Takimiya *et al.* published the first homogeneous series of tetracyanoquinodimethane quinoidal oligothiophenes **1** (Q*n*, *n* = 1–6) from a dimer (Q2) to a hexamer (Q6) (Fig. 3).[16] The ESR spectra of the Q5 and Q6 constitute the first reports on the irrefutable existence of a magnetically active species of diradical character populated at room temperature. Ponce Ortiz *et al.* in 2007 established the diradical singlet ground electronic state nature of these quinoidal oligomers on the basis of the Raman spectra as well as the presence of a low energy lying triplet excited state on 1–4 kcal mol^{-1} for the longer oligomers responsible for the ESR activity.[17] In Q4 the quinoidal closed-shell structure becomes unstable and the aromatic diradical state is formed. Thiophenes, due to their rather low aromaticity, are excellent platforms for π-conjugation and therefore for the transmission of the DSP effect from external radicaloid centers; thus even in Q6 with a very large distance between the two outermost dicyanomethylene groups polarization/π-conjugation of the radicals within the thiophene core is effective and the diradical singlet persists as the ground electronic state. A very similar effect has been described in quinoidal twelve-unit oligothiophene dications showing a diradical singlet ground electronic state mimicking a polaron-pair structure with a very low lying triplet (≈1 kcal mol^{-1}).[18] Quinoidal tetrathiophenes **2–4** with different substitution patterns, such as Q4, disclose diradical fingerprints with tuned ΔE_{ST} gaps due to the stabilization of the singlet diradical ground electronic state by spin polarization with the substituting groups (Fig. 4).[19] The thienoacene derivative **5** in Fig. 4 shows an increased ΔE_{ST} gap due to the planarity of the bridge and more effective DSP.[20]



1 Qn (n= 1-6)

Fig. 3 Chemical structures of the tetracyano-substituted quinoidal oligothiophenes, Q*n*, from Takimiya *et al.* Structures of the singlet diradical and triplet from the Raman spectra.

The more recent syntheses of these quinoidal oligothiophenes follow Takahashi's method described in 1984 and consist of the use of the dihalide oligothiophene derivatives (usually dibromo derivative) which are reacted with the *in situ* generated malonitrile anion (malonitrile/NaH) in the presence of a catalyst (Pd) followed by dehydrogenation of the product to yield the corresponding tetracyanomethylene oligothiophene dianion.[21] The last step to the quinoidals is the oxidation of the dianion by Br_2/H_2O (Pappenfus), air (Takimiya) or with potassium ferricyanide/KOH to give the benzoquinone derivatives. The choice of the oxidation method is a key step based on the dicyano-thiophene captodative effect which stabilizes the radicals *versus* the dianions, thus favoring single one-electron oxidations that generate the bis-radical species that collapse into the quinoidal form or into the open-shell neutral diradical.

Shorter tetracyanoquinodimethane oligothiophenes, trimers and some tetramers some of which are displayed in Fig. 4, with different substitution patterns, have been used in organic field-effect transistors (OFETs) (mainly as ambipolar organic semiconductors) and complementary circuits.[22] Quinoidal oligothiophenes are characterized by strong one-photon absorption bands ranging from 500 nm (*i.e.*, Q2) up to 1000 nm (*i.e.*, Q6). The presence of strong absorption in the NIR has led to the preparation of this kind of derivatives for photovoltaic applications. The small optical gap is also accompanied by small electrochemical gaps and amphoteric redox behavior at the origin of the ambipolar hole and electron transport in OFET devices. Quinoidal mixed or co-oligomer tetracyanoquinodimethane compounds (*e.g.* **6** in Fig. 4) have also been prepared by combining them with benzene and naphthalene quinoidal units, and all the planar fused derivatives disclose well defined closed-shell behavior.[23] Apart from the tetracyano-substitution, functionalization with benzoquinone groups has been reported (**7–9** in Fig. 4) to be another interesting way of attaining Kekulé diradical structures.[24] In this case, the inclusion of the benzoquinoid

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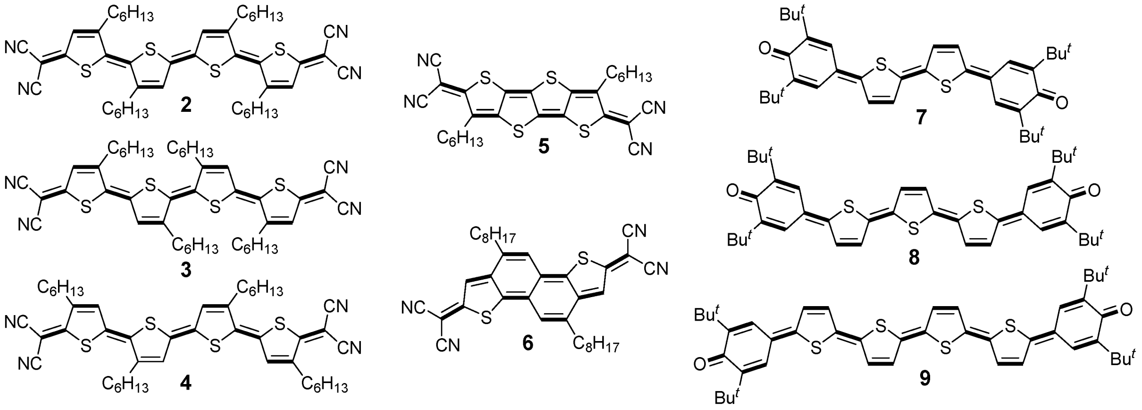

Fig. 4 Chemical structures of other tetracyano-substituted quinoidal oligothiophenes.

groups largely facilitates the aperture of the closed-shell form which is attained with bithiophene derivatives. In 1989, dibenzoquinone quinoidal oligothiophenes with three and four thiophenes were reported (Fig. 4); however, their diradical character and properties were never addressed and they still remain as compounds of potential interest in the field that might require re-synthesis.[25] Recently, quinoidal thienoacene quinoidal cores have been prepared which will be described in the next section in the context of anti-aromatic pro-diradical species.

3. Quinoidal polycyclic hydrocarbons

Compared with quinoidal oligothiophenes, quinoidal oligo-*para*-phenylenes are supposed to display larger diradical character due to the larger aromatic resonance energy in the benzene ring than that in the thiophene ring. Therefore, high reactivity is expected and how to stabilize these reactive species is a critical issue. Alternatively, incorporation of a pro-aromatic unit such as *p*-quinodimethane (*p*-QDM) into a polycyclic aromatic hydrocarbon (PAH) framework is an efficient way to attain stable compounds with distinctive diradical character. Similar to the quinoidal oligothiophenes, the fundamental driving force to the diradical resonance form is the recovery of the aromaticity of the non-aromatic quinoidal rings. In general, the more the resonance energy can be gained, the larger the character is expected. Moreover, quinoidal polycyclic hydrocarbons (PHs) with a singlet diradical ground state display unique electronic, optical and magnetic properties and have many potential applications in materials science.[26] In this section, we will summarize the synthesis, characterization, physical properties and the fundamental structure–property relationship of several types of quinoidal PHs: (1) extended *para*-quinodimethanes, (2) bisphenalenyls, (3) zethrenes, and (4) quinoidal rylenes.

3.1 Extended *para*-quinodimethanes

p-QDM is a fundamental pro-aromatic unit and was proposed as an intermediate in the pyrolysis of *p*-xylene.[27] However, it has never been separated due to its extremely high reactivity, which is closely related to its intrinsic diradical character. That is, the non-aromatic quinoidal ring has a high tendency to become an aromatic sextet ring (the ring highlighted with a blue background) (Fig. 5). Its π-extended analogues 2,6-naphthoquinodimethane (NQDM)[2] and 2,6-anthraquinodimethane (AQDM) were not isolated either, both of which are predicted to be a singlet diradicaloid due to the formation of one aromatic naphthalene/anthracene ring (also highlighted in blue color) in the diradical form (Fig. 5). One efficient strategy to stabilize these highly reactive species is to substitute the terminal methylene sites by strong electron-withdrawing cyano groups, and the formed compounds 7,7,8,8-tetracyanoquinodimethane (TCNQ),[28] 9,9,10,10-tetracyano-2,6-naphthoquinodimethane (TNAP),[29] and 11,11,12,12-tetracyano-2,6-anthraquinodimethane (TANT)[30] are stable under ambient conditions due to kinetic blocking and spin delocalization (Fig. 5). Despite the fact that these tetracyano-substituted molecules gain one aromatic benzene/naphthalene/anthracene ring in their respective diradical resonance forms, they remain as typical closed-shell quinoidal structures in the ground state. That means, the gained aromatic resonance energy is not sufficient to compensate the energy required to break a π bond.

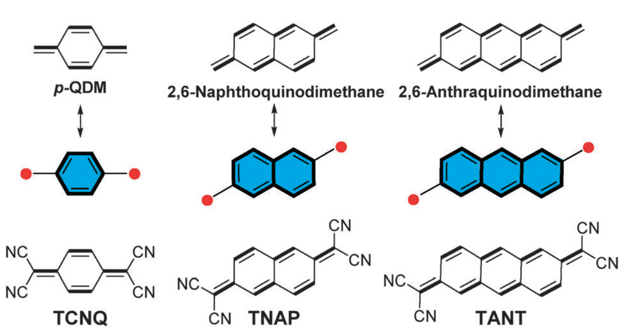

Fig. 5 Structures of *p*-QDM, NQDM, ADQM and their tetracyano-derivatives.

The linearly extended tetracyanodiphenoquinodimethane (TCNDQ, Fig. 6) end capped by four cyano groups exhibited very high reactivity and tended to polymerize in solution, indicating its much larger diradical character due to the recovery of two aromatic sextet rings in the diradical form.[31] However, once the central biphenyl unit is linked by two additional ethyl or ethenyl groups, the obtained compounds TCNTP and TCNP[32] become

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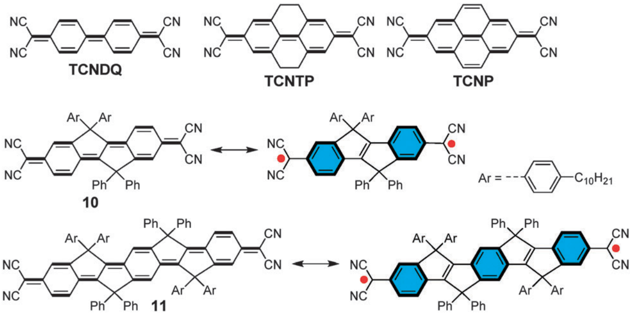

Fig. 6 Tetracyano-substituted extended *para*-quinodimethane derivatives.

stable, with a typical closed-shell quinoidal structure in the ground state (Fig. 6). Such a change of the ground electronic state and reactivity can be explained by more effective π-conjugation (or spin-polarization) of the two terminal spins with the π-bridge in the planarized TCNTP and TCNP. In TCNDQ, the steric repulsion between the two phenyl rings drives the molecule out of plane and it thus has a higher tendency to become a diradical. Another problem associated with the synthesis of the extended *p*-QDMs is their poor solubility as observed in TCNTP and TCNP. A good solution of this problem was reported by Nakamura *et al.*, who developed a series of soluble and stable tetracyano-substituted oligo-(*para*-phenylene vinylenes) such as **10** and **11** (Fig. 6).[33] Different from TCNDQ, the fused pentalene moiety with aryl substituents was inserted between each quinoidal benzene ring, providing sufficient solubility and effective conjugation. Both compounds are air- and thermo-stable compounds with a deep color. It was found that **10** is a closed-shell quinoidal compound, while **11** turned out to be a singlet diradicaloid in the ground state. Compound **11** displayed temperature-dependent broadening of its ^{1}H NMR spectrum in solution and a well-resolved ESR spectrum in the solid state. Compound **11** has a very narrow HOMO–LUMO energy gap (1.02 eV) estimated by cyclic voltammetry and UV-Vis-NIR spectroscopy. In contrast, the closed-shell compound **10** exhibited sharp NMR signals and a relatively large energy gap (1.58 eV). For **11**, the singlet–triplet energy gap (ΔE_{S-T}) was estimated as -2.12 kcal mol^{-1} based on SQUID measurements, which agrees well with density functional theory calculations. Compound **11** showed a fine ESR spectrum with a spin–spin distance estimated as 14.6 Å, consistent with the distance between the two terminal spin centers. Compared to **10** with a distinctive quinoidal absorption band with a maximum at 627 nm, compound **11** absorbed NIR light with a maximum at 850 nm. This example illustrated that in a planar conjugated system, the diradical character will increase with the increase of the number of pro-aromatic units, simply because more aromatic sextet rings can be drawn in the diradical form. Moreover, the change of the electronic ground state from a closed-shell quinoid to an open-shell singlet diradical results in very different optical, electronic and magnetic properties.

Another way to improve the stability of extended *p*-QDMs is to substitute the terminal methylene sites by phenyl groups. The well-known examples are Thiele's hydrocarbon[8] and Tschitschibabin's hydrocarbon[7,34] (Fig. 7), as already stated.

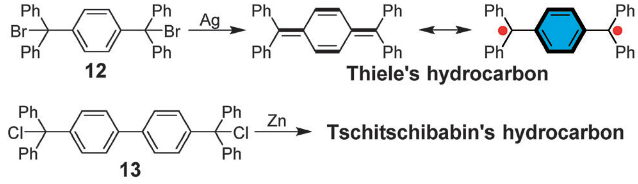

Fig. 7 Synthesis and structures of Thiele's hydrocarbon and Tschitschibabin's hydrocarbon.

In 1904, Thiele's hydrocarbon was first synthesized as an orange-yellow solid by treatment of the dibromide **12** in benzene with the silver metal (Fig. 7). It has been examined by a variety of physical methods, and X-ray crystallographic analysis showed that the four phenyl substituents and the terminal methylene groups adopt a twisted conformation. The steric factor increases the kinetic stability of Thiele's hydrocarbon in comparison to its parent *p*-QDM, and the relatively stable compound was separated and characterized at low temperature. Later, Tschitschibabin's hydrocarbon was synthesized by treatment of the dichloride precursor **13** with zinc (Fig. 7). The X-ray crystallographic data and ESR analysis suggested that it has a large diradical character. Both Thiele's hydrocarbon and Tschitschibabin's hydrocarbon are inherently reactive (*e.g.* reacting with oxygen) due to the intrinsic diradical character arising from the recovery of the aromaticity of the central benzenoid ring.

To obtain extended *p*-QDMs with better stability, Wu's group developed a "benzannulation" strategy. That is, four aromatic benzene rings were annulated onto the central biphenyl unit of Tschitschibabin's hydrocarbon to generate the tetrabenzo-Tschitschibabin's hydrocarbon **14a** (Fig. 8).[35] The synthesis took advantage of a four-fold Suzuki coupling reaction between the tetrabromide **16** and 4-*tert*-butylphenylboronic acid and the obtained compound **14a** was stable in both solution and solid state. X-ray crystallographic analysis showed that the bond lengths for the *exo*-methylene bonds (1.342 Å) and the bond between the two anthracene units (1.349 Å) are quite close to those of typical double bonds in closed-shell quinoidal molecules. A highly twisted butterfly-like geometry in the crystalline form was observed due to large steric repulsion between the two anthracene units and the four phenyl groups. Besides crystallographic data, the observation of sharp NMR peaks and silence in the ESR spectrum all pointed to a closed-shell quinoidal structure for compound **14a**. Such a difference from Tschitschibabin's hydrocarbon can be simply explained by the fact that two more aromatic sextet rings can be drawn in the closed-shell form. Interestingly, its diradical form **14b** as a meta-stable compound can be generated *via* another synthetic approach (Fig. 8). Attempted oxidative cyclodehydrogenation of **14a** by using common cyclization conditions such as DDQ/CH_3SO_3H or $FeCl_3$ gave an unexpected product diol **17** and reduction of **17** with $SnCl_2$ afforded the diradical **14b** quantitatively. Interestingly, the *in situ* generated diradical **14b** showed a slow mono-exponential decay to the quinoidal ground state **14a**, with a half-life of *ca.* 495 min. A large energy barrier (up to 22.7 kcal mol^{-1} at room temperature) arising from a sterically hindered transition state from the

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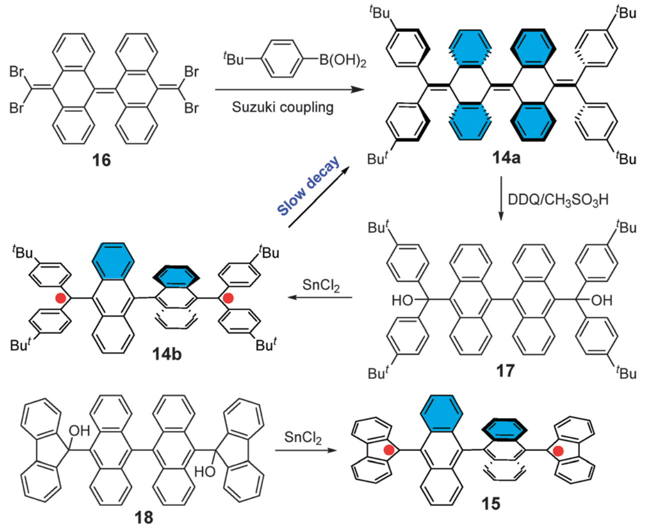

Fig. 8 Synthesis and structures of tetrabenzo-Tschitschibabin's hydrocarbons.

orthogonal diradical form (excited state) to a butterfly-like quinoidal form (ground state) is responsible for such an unusual finding.

Capping of the terminal methylene sites by two fluorenyl units generated another new tetrabenzo-Tschitschibabin's hydrocarbon **15**, which can be synthesized by reduction of the corresponding diol precursor **18** with SnCl$_2$ (Fig. 8). Different from the closed-shell **14a**, compound **15** turned out to be a stable diradical with a weak intramolecular spin–spin interaction, which was supported by VT ESR and SQUID measurements. The efficient delocalization of the spin through the two fluorenyl units may account for the observed more stable diradical ground state.

Related to this work are the extended bisanthrylquinone **19** and the fused bisanthenequinone **20** reported by Wu's group (Fig. 9).[36] Both compounds were synthesized by the same strategy, *i.e.*, nucleophilic addition of 2,6-di-*tert*-butyl-phenoltrimethylsilane magnesiumbromide to the bisanthrylquinone **21** or bisanthenequinone **22**, followed by desilylation and dehydration. The unfused quinone **19** was predicted to have a butterfly-like quinoidal structure in the ground state although there is a large steric hindrance between the anthracene units. The fused bisanthenequinone also displayed a closed-shell ground state and exhibited largely red-shifted absorption and amphoteric redox behavior due to more efficient π-conjugation.

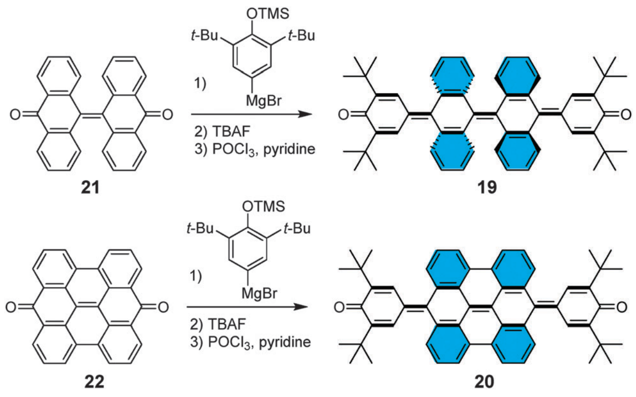

Fig. 9 Synthesis of extended bisanthryl and bisanthenequinones.

3.2 Bisphenalenyls

An alternative approach to access stable *p*-QDM based systems is to embed a quinoidal moiety such as *p*-QDM, NQDM and AQDM into the framework of an aromatic PAH to attain an enhanced structural rigidity and more efficient spin delocalization. In addition, kinetic stabilization by blocking the most reactive sites with bulky substituents can further improve the stability. The representative examples are the family of bisphenalenyls developed by Nakasuji and Kubo *et al.* Connection of two phenalenyl moieties by a pro-aromatic unit such as *p*-QDM and its extended analogue (NQDM and AQDM) produced a series of bisphenalenyl molecules containing two five-membered rings (Fig. 10). In fact, the phenalenyl monoradical was reported as the smallest, persistent open-shell PAH, and molecules containing this structural motif demonstrated exciting potential for molecular electronic devices and magnetic materials due to their diverse electronic spin structures.[37] However, it is not an easy task to prepare stable phenalenyl monoradicals due to their inherent instability. The obtained bisphenalenyls **23–25** are stable hydrocarbons due to efficient spin delocalization. Compounds **23a–d**[38] consist of a simple *p*-QDM unit, while compounds **24a–b**[39] and **25a–b**[40] contain extended NQDM and AQDM spacers, respectively. In all cases, the observed line broadening in the NMR spectra at elevated temperature and gradual sharpening at lower temperature indicated a singlet diradical ground state. These bisphenalenyl based diradicaloids displayed unique physicochemical properties[41] such as small HOMO–LUMO energy gaps, large TPA cross sections and ambipolar charge transporting behaviour. These findings provided insights into the design of new materials for organic electronics, nonlinear optics and spintronics.

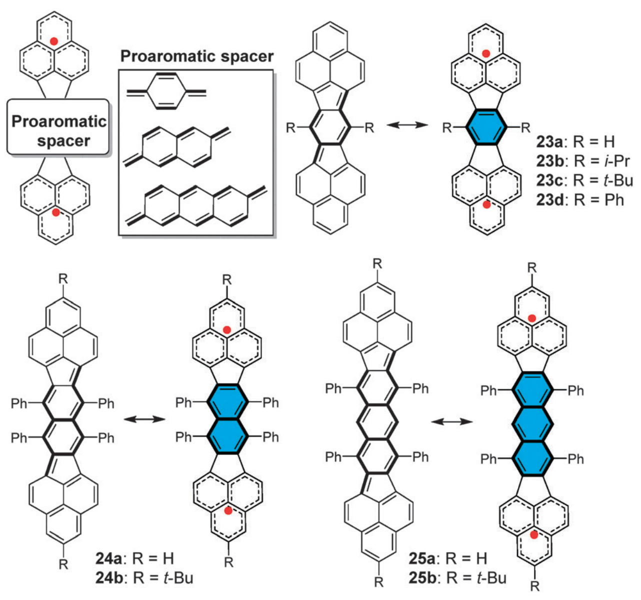

Fig. 10 Structures of bisphenalenyls reported by Nakasuji and Kubo *et al.*

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Notably, extending the spacer increased the diradical character because more resonance energy was attained in the diradical form for the largely extended quinodimethanes. In addition, strong intermolecular interactions with a distance shorter than the normal π–π distance were observed in all cases, which can be accounted for the strong multi-centre spin–spin interactions between the phenalenyl units. For instance, **24d** exhibits a slipped stacking arrangement with an average intermolecular distance of 3.137 Å, substantially shorter than the van der Waals contact of carbon atoms (3.4 Å). In addition, with the extension of the spacer, it was found that the intermolecular spin–spin interaction is strengthened while the intramolecular spin–spin interaction is weakened due to more localized spin distribution at the two ends. Other linkers such as thiophene were also reported as an effective part of bisphenalenyl systems with singlet diradical electronic state.[42] Similar to bisphenalenyls, the thienodiphenalene discloses amphoteric redox ability, low energy absorption band as well as dimeric pairs between molecules.

3.3 Zethrenes

Zethrene can be regarded as a result of a ''head-to-head'' fusion of two phenalenyl moieties into a Z-shaped molecular structure. The high order zethrenes, where two phenalenyls are linked by a pro-aromatic quinodimethane unit (*e.g.* *p*-QDM, NQDM, AQDM), are named as heptazethrene, octazethrene and so on, based on the number of fused rings (Fig. 11). Different from the bisphenalenyls discussed above which always contain two five-membered rings inside the conjugated framework, zethrenes possess only six-membered rings. So far, all the reported zethrene derivatives are featured with a closed-shell quinoidal ground state, because the number of aromatic sextet rings in the closed-shell and diradical forms is the same (Fig. 11). However, the higher homologues can be regarded as pro-aromatic PHs and an additional aromatic benzene/naphthalene/anthracene ring can be drawn in the diradical form. As a result, they are potentially singlet diradicaloids (Fig. 11).[43] The parent zethrene is a relatively stable hydrocarbon,[44] and substitution at the reactive 7,14-positions can further enhance the stability.[45] The parent higher order zethrenes are highly reactive,[46] and only recently, their stable derivatives were obtained by Wu's group. Since the first synthesis of zethrene by Clar in 1955,[44] various synthetic methods and stabilizing strategies have been developed to access zethrene-based materials.[45] For example, by introducing electron-withdrawing dicarboximide groups, stable zethrenebis(dicarboximide) **27** was synthesized by one-pot Stille coupling reaction between **26** and bis(tributylstannyl)acetylene (1 : 1 ratio) followed by simultaneous transannular cyclization reaction.[47] Compound **27** showed a closed-shell structure in the ground state with a relatively low band gap compared to the parent zethrene. The fixed butadiene unit in the middle showed high reactivity to electrophilic addition.

Using a similar concept, the first relatively stable heptazethrene derivative, the heptazethrene diimide **29**, was prepared from the corresponding diacetylene intermediate **28** (Fig. 11).[48] In contrast to the zethrene diimide **27**, the heptazethrene diimide **29** has a rather small energy gap (1.0 eV) and displayed NMR broadening at room temperature and line sharpening at low temperatures, indicating a singlet diradical ground state. Broken symmetry DFT calculations also predicted that the energy of the singlet diradical form of **29** was 5.8 and 7.5 kcal mol^{-1} lower than that of the closed-shell quinoidal form and triplet biradical form. Kinetic blocking of the most reactive sites in heptazethrene and octazethrene by triisopropylsilyl ethynylene (TIPS) groups led to two stable heptazethrene and octazethrene derivatives **31a** and **31b** (Fig. 11).[49] The synthesis took advantage of nucleophilic addition of TIPS Grignard reagents to the corresponding diketone precursors **30** followed by reduction with $SnCl_2$. Interestingly, the TIPS-substituted heptazethrene **31a** displayed a typical closed-shell structure in the ground state, which is very different from the heptazethrene diimide **29**. The fundamental reason could be ascribed to its relatively large energy gap (1.47 eV), which makes the HOMO–LUMO admixing in the ground state less efficient. However, the higher octazethrene derivative **31b** exhibited all the features of a singlet diradicaloid, with the appearance of weak absorption bands in the lower energy NIR region which could be correlated to a low-lying excited singlet state dominated by a doubly excited electronic configuration (H,H → L,L). For compound **31b**, the electronic state was confirmed as a singlet diradical by systematic experimental studies including VT NMR, ESR, SQUID, FT-Raman spectroscopy and X-ray

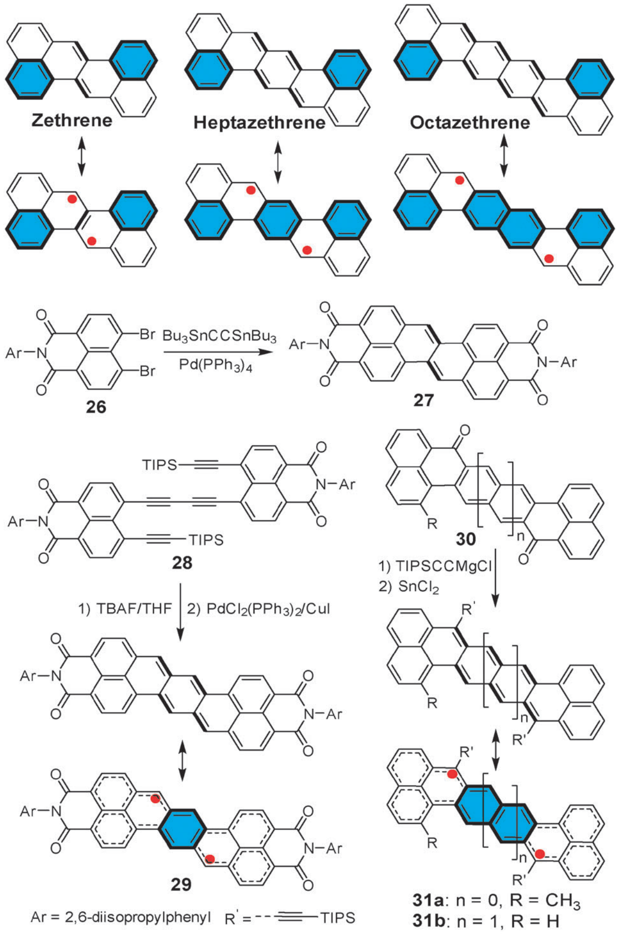

Fig. 11 Structures of zethrenes and representative synthesis of some zethrene derivatives.

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crystallographic analysis, assisted by DFT calculations. In comparison with **31a**, the singlet diradical **31b** had a more aromatic-like π-bridge from FT-Raman spectroscopy and X-ray crystallographic analysis. A large diradical character ($y = 0.56$) was experimentally determined for **31b**. Similarly, such a difference can be explained by the larger resonance energy gained in **31b** than in **31a**. It is also worth noting that the spins are evenly distributed in the zethrene-based diradicaloids, which is different from Nakatsuji and Kubo's bisphenalenyls in which the spins are mainly localized in the two phenalenyl units.

A more extended heptazethrene diimide **33** was also synthesized by the oxidative dehydrogenation of a dihydro-precursor **32** with DDQ (Fig. 12).[50] Looking into the structure, this new molecule can be regarded as a *p*-QDM bridged perylene monoimide dimer. As expected, compound **33** adopted a singlet diradical ground state with a smaller energy gap ($E_g = 0.80$ eV) and singlet–triplet energy gap ($\Delta E_{S-T} = -2.97$ kcal mol^{-1} based on SQUID) compared to **29**. However, by replacing the peryleneimide with porphyrin, the obtained *p*-QDM bridged porphyrin dimer **34** displayed only a closed-shell quinoidal structure in the ground state, presumably because resonance to the diradical destroys the aromaticity of the two porphyrin macrocycles.[51] To validate the concept that more aromatic sextet rings promote singlet diradical character, two dibenzoheptazethrene isomers **35** and **36** were synthesized, with the most reactive sites blocked by aryl or TIPS groups (Fig. 11).[52] For compounds **35** and **36**, the maximum number of aromatic sextets that can be drawn is three and five, respectively. As a result, compound **36** showed larger diradical character (0.576 *vs.* 0.309), lower energy gap (1.20 eV *vs.* 1.46 eV) and larger TPA cross section ($\sigma^{(2)}_{\max}$: 2800 GM at 1600 nm *vs.* 530 GM at 1400 nm) in comparison to **35**. Such findings indicated that Clar's aromatic sextet rule can be further extended to open-shell benzenoid PHs to predict their relative diradical character.

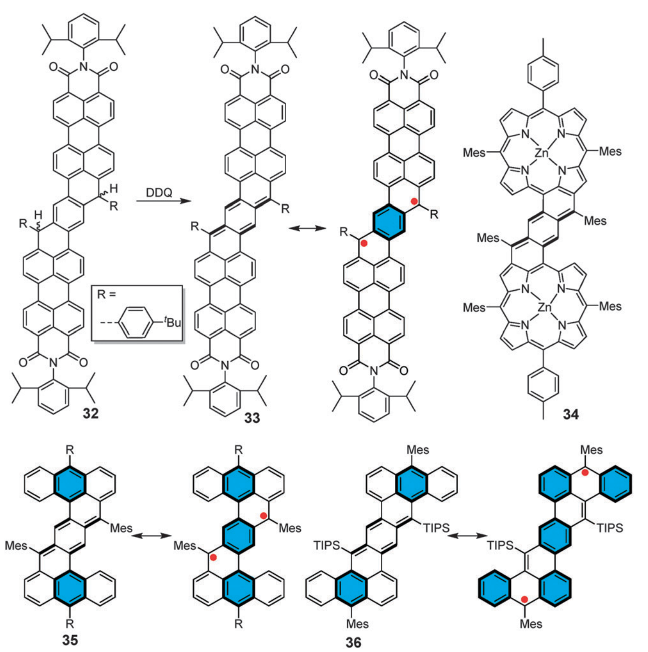

Fig. 12 Chemistry and resonance structures of π-extended heptazethrenes.

3.4 Quinoidal rylenes

In recent years, organic semiconductors with a quinoidal character have demonstrated good potentials for ambipolar and n-type OFETs.[53] So far, most of them have a closed-shell quinoidal structure in the ground state. Synthesis of more extended quinoidal compounds with a distinctive diradical character has become a big challenge. Recently, Wu's group developed a series of quinoidal rylene based stable diradicaloids by using *N*-annulated perylene (NP) as the basic building block (Fig. 13). Firstly, a family of quinoidal tetracyano-oligo(*N*-annulated perylene)quinodimethanes **38a–f**, from monomers to hexamers, were prepared and found to display very interesting properties.[54] The NP unit in this series can be regarded as a dibenzannulated quinoidal biphenyl, and the stability and solubility are ensured by *CN*- and *N*-alkyl substitution, respectively. These oligomers were synthesized by Takahashi coupling of corresponding dibromo–NP oligomers **37a–f** with malononitrile/NaH and subsequent oxidative dehydrogenation with *p*-chloranil or air. The longest hexamer pushes the extended *p*-QDMs to the limit consisting of 12 *para*-linked benzenoid rings, but oligomers longer than hexamer are unstable and cannot be purified by routine column chromatography. While the electronic structure for the monomer **38a** was described as a typical closed-shell quinoid, the open-shell solution was gradually more stable for longer oligomers from singlet diradicals (**38b–d**) to weakly coupled biradicals (**38e–f**). Thus, their ground state is chain-length dependent, and the diradical character displays a continuous increase to saturation at the tetramer **38d**. Two driving forces were proposed for such transformation: (i) additional resonance energy is gained by the recovery of the aromatic perylene units in the diradical form, and (ii) large steric repulsion between the perylene units in the quinoidal form tends to release the strain in the flexible diradical structure. The spin-state evolution was systematically investigated by VT NMR, ESR, SQUID, Raman and UV-vis-NIR electronic absorption measurements, assisted by broken-symmetry DFT calculations. For example, in the Raman spectra, the vibrational bands for the ($C{=}C$) (benzenoid rings and the *exo*-$C{=}C(CN)_2$) were shifted to lower frequency from the monomer to tetramer due to the increased diradical character with the extension of chain length. After tetramer, the spectra remain the same as the diradical character reached saturation. The unique electronic nature of these oligomers is also responsive for the optical, electrochemical, and magnetic properties, such as chain-length dependent one/two photon absorption, energy band gap and magnetic activities.

One way to validate the important role of steric repulsion in the electronic state of the above mentioned system is to fuse the non-planar oligomers **38b–f** into planar oligomers. However, direct intramolecular cyclization of **38b** gave a complicated mixture. Alternatively, the dibromo-quaterrylene (fused dimer) and hexarylene (fused trimer) **39a–b** were first prepared from the corresponding unfused dibromo–NP dimer and trimer with DDQ/Sc(OTf)$_3$ (Fig. 13).[55] The highly branched aliphatic ether substituents (R$_3$) must be used to ensure sufficient solubility for both the large π intermediates and target compounds.

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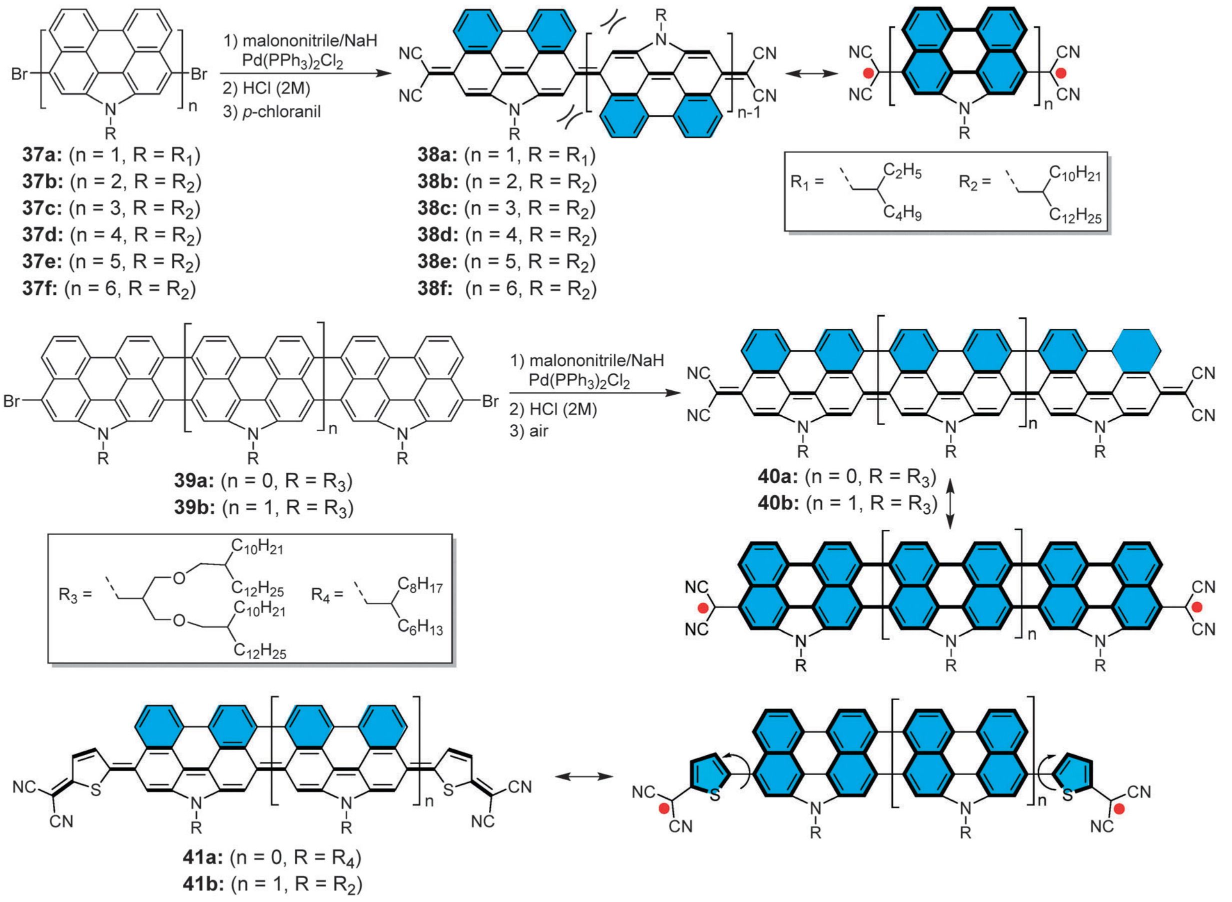

Fig. 13 Synthesis and structures of quinoidal rylenes.

Subsequent Takahashi coupling reaction of dibromide precursors **39a–b** with malononitrile followed by simultaneous oxidation provided tetracyano-quaterrylenequinodimethane **40a** and hexarylenequinodimethane **40b**. In contrast to **38b**, the planarized **40a** displayed a closed-shell quinoidal structure in the ground state due to the efficient intramolecular antiferromagnetic coupling between the two spins *via* the previously mentioned DSP mechanism. However, molecule **40b** turned out to be a singlet diradical in the ground state with a small diradical character (y = 0.064), while the non-fused trimer **38c** exhibited more distinctive diradical character (y = 0.99) and a smaller singlet–triplet energy gap (-0.107 kcal mol^{-1} in **38c** *vs.* -4.21 kcal mol^{-1} in **40b**). In this case, the major driving force would be the accumulated resonance energy *via* formation of six aromatic naphthalene units in the diradical form. Based on this, we believe that by carefully controlling the aromaticity and steric hindrance in a conjugated system it is possible to design singlet diradicaloids with tunable diradical character and physical properties. To validate this, quinoidal rylenes **41a–b** were synthesized in which one additional thiophene unit was incorporated between the rylene and the dicyanomethylene site in **37a** and **40a** (Fig. 13).[56] The resulting compounds exhibited distinct diradical characters and small singlet–triplet energy gaps (-4.71 and -0.16 kcal mol^{-1}, for **41a** and **41b**, respectively). Such an evolution can be explained by the recovery of two additional aromatic thiophene rings in the diradical resonance forms together with the conformational flexibility around the thiophene–rylene connections. In addition to the tunable ground states, all the above discussed quinoidal rylenes showed tunable non-linear optical response. For example, **40b** with largely extended conjugation and moderate diradical character showed a very large TPA cross-section value ($\sigma^{(2)}_{\max}$ = 3300 GM at 2000 nm), but the chromophores with a large diradical character (*e.g.* **38c–f**) and less effective conjugation displayed smaller TPA cross-section values (*e.g.*, $\sigma^{(2)}_{\max}$ = 770 GM and 710 GM at 1700 nm for **38c** and **38d**, respectively). This observation is in agreement with the theoretical prediction that singlet diradicaloids with small and moderate diradical character would display enhanced second hyperpolarizability, which is the origin of the third-order nonlinear optical properties.[57]

4. *para*-Quinodimethane analogues containing hetero atoms

So far, we mainly discussed the polycyclic hydrocarbon based diradicaloids containing a pro-aromatic quinodimethane moiety. Such a concept can be extended to some heteroatom containing quinoidal π-conjugated systems. *p*-Disilaquinodimethane **43** was first reported by Sekiguchi *et al.* (Fig. 14).[58] It was synthesized by reductive dehalogenation of bis(bromosilyl)benzene **42** by KC_8

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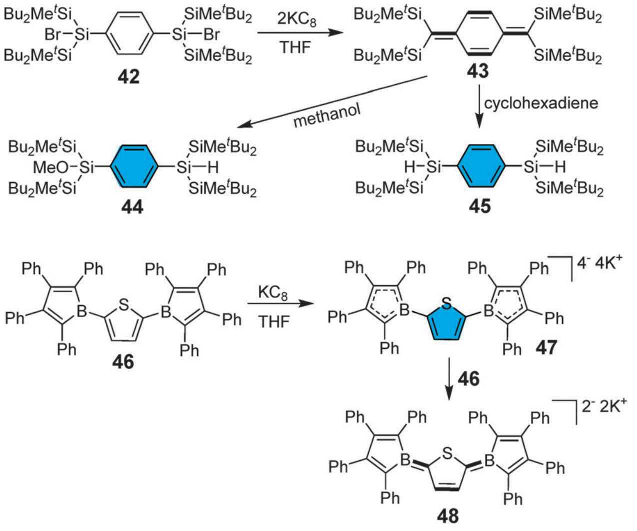

Fig. 14 Synthesis and chemical reactivity of disilaquinodimethane and bis(borole)quinodimethane.

in dry THF at 78 °C, and found to be an air-sensitive purple compound. X-ray diffraction and solid-state NMR studies revealed its quinodimethane-like structure. But the disilyl compound **43** was readily reactive toward methanol or cyclohexadiene to give the 1,6-adduct **44** or hydrogen-abstraction product **45** in quantitative yield, suggesting the significant contribution of the singlet diradical resonance form to the ground electronic state.

Bis(borole) dianion **48** represented a rare example of *p*-QDM analogues containing strongly Lewis acidic borolyl groups across the pro-aromatic thiophene spacer (Fig. 14).[59] Because of the difficulties in the clean preparation of the desired dianion, an aromatic tetraanion **47** was produced firstly by full reduction of **46** with excess KC_8, and then a comproportionation reaction between **47** and the neutral bis(borole) **46** was conducted to form the desired dianion product **48**. From the view point of molecular structure, **48** can be viewed as a negative bipolaron, while it can be also drawn as a diradical resonance structure with two spins seated at the two boron centers. This compound displayed a strong absorption band in the vis-NIR region (from 600 to 1300 nm), with a maximum at 800 nm. The closed-shell quinoidal structure of this bis(borole) was confirmed by the characteristic NMR spectroscopy and crystallographic analysis of its dianion analogue after two-electron reduction reaction of **46** with decamethylcobaltocene, which revealed large bond length alternation in the thiophene ring similar to the reported quinoidal thiophene derivatives.

Arylamine radical cations that can be feasibly generated by electrochemical and/or chemical oxidation are well-known for their instability. However, the dication (or diradical dication) of bis(arylamine) with a *para*-biphenyl spacer may display improved stability and unique properties due to the contribution of both diradical dication resonance form and the quinoidal dication form to the ground state (Fig. 15). A relatively stable bis(arylamine) dication **50** was obtained by the reaction of two equivalents of methylene-linked triphenylamine monomer **49** with 0.5 equivalent of $Ag[Al(OR_F)_4]$ by Wang's group (Fig. 15).[60] Alternatively, this dication was also prepared by reacting monoradical cation **51** and natural amine **49** (1 : 1 ratio) upon addition of 5 mol% $Ag[Al(OR_F)_4]$. X-ray crystallographic structure of **50** revealed planar geometries about the nitrogen centers, and bond length analysis suggested some diradical contribution to the ground electronic state. The UV-vis absorption spectrum of the dication **50** gave a low energy band with a maximum at 841 nm, and the ^1H NMR spectra showed line broadening at room temperature. However, there was no observed triplet species in SQUID measurements likely due to the rather small population of triplet biradicals. Thus, the dication **50** can be described as a resonance hybrid of quinoidal form and diradical structure. The singlet diradical nature was also supported by theoretical calculations, and the diradical character index was predicted as 0.77 by defining with the occupancy of the lowest unoccupied natural orbital (LUNO) at the UBHandHLYP/6-31G* level. Later, a new class of tetraphenylbenzidine dications **53a–c** were investigated by oxidation of corresponding biphenyl-bridged

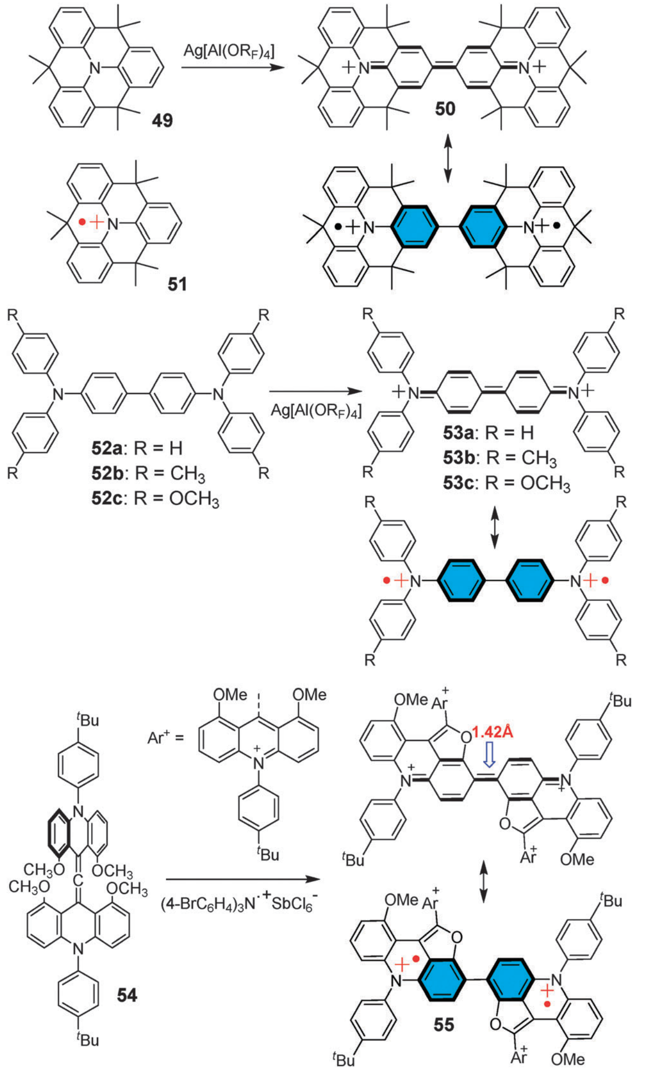

Fig. 15 Synthesis and resonance structures of arylamine based diradical dications.

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bis(triphenylamine) **52a–c**.[61] Interestingly, both **53a** and **53b** did not exhibit ESR and SQUID signals, while **53c** had all features of a singlet diradical. An increasing population of triplet biradical species was detected for **53c** at above 320 K and 200 K in powder ESR and SQUID measurements, respectively. The diradical character of **53c** is consistent with low-energy lying absorption in the NIR region with a maximum at 878 nm, which is significantly red-shifted compared with that of **53a** and **53b** (at 742 and 800 nm, respectively). A prominent diradical character for **53c** was also reflected by the fact that the bond length in the central part lies between double bond and single bond values. However, the homologues **53a** and **53b** showed a typical quinoidal bond length in their single crystal structure. Thus, both **53a** and **53b** feature a closed-shell quinoidal structure. This series of oxidized dications provided substituent dependent diradical character, that is, the electron-donating group at the *para*-position of the aryl group on the amine moiety increased the diradical contribution.

Yamamoto *et al.* found an interesting demethylation and dimerization of allenic compound **54** upon addition of the oxidant $(4\text{-BrC}_6H_4)_3N^{\bullet+}SbCl_6^-$, leading to an unexpected tetracation **55** as a dark purple solid (Fig. 15).[62] Although there was a small amount of monoradical impurity inside the **55** salt, its single crystal suitable for crystallographic analysis was obtained. The central bond length was measured as 1.42 Å (as labelled in the molecular structure), and was longer than a typical double bond (~1.34 Å), but slightly shorter than the typical biphenyl single bond (1.48 Å), suggesting significant contribution of the diradical dication form to the ground state. The diradical character of **55** was estimated to be 0.605 by theoretical examination at the UBHandHLYP/6-31G(d) level, leading to significant positive contributions to the second hyperpolarizability γ. Consistent with the theoretical prediction, this diradical tetracation exhibited strong TPA response with a maximum TPA cross section up to 3600 GM at 1200 nm. Like compound **53c**, the driving force for the formation of a singlet diradical ground state is the gain of two aromatic sextet rings in the diradical form, and they both can be regarded as analogues of Tschitschibabin's hydrocarbon.

The carbon-centered radical is usually unstable unless appropriately substituted by phenyl groups or strong electron-withdrawing groups (*e.g.* CN). An alternative way would be the incorporation of the carbon-centered radical into a π-conjugated heteroatom ring such as imidazole and pyridine. Zimmermann *et al.* first prepared the air-persistent quinoidal bisimidazole benzene **56** by bromine oxidation of the corresponding sodium salt (Fig. 16).[63] Interestingly, the quinoidal **56** isomerized on heating to the benzenoid diradical **57**, which reversed to the original quinoidal form on cooling.[64] At room temperature, compound **56** showed that about 0.1% of the molecules in a solution are paramagnetic, and the population of **57** increased with increasing temperature as revealed by the combined studies of UV and ESR measurements.[65] Such obvious evidence points to the contribution of diradical character in a pro-aromatic molecule. Abe *et al.* provide a direct proof for the contribution of the diradical form in bisimidazole derivatives by the detection of an imidazole dimer **59** confirmed by X-ray crystallographic analysis.[66] The two newly formed C–N bonds in the dimer suggest that unpaired electrons distribute on both carbon and nitrogen atoms with cyclic delocalization. The dimer could be transformed into monomer **58** upon irradiation with 360 nm light, giving rise to photochromic behaviour with color change from colorless to blue-purple. In addition, the fluorine atoms on the central benzene ring could destabilize the quinoidal form and stabilize the diradical form. The larger population of triplet biradicals (0.4%) has arisen from the lower singlet–triplet energy gap.

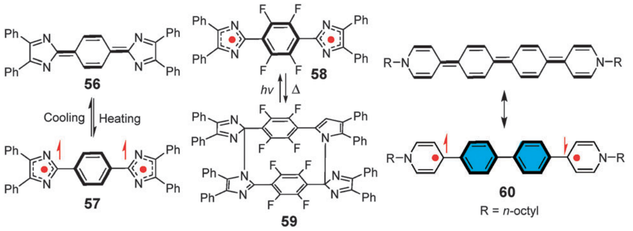

Fig. 16 Chemical and resonance structures of quinoidal bisimidazoles and reduced extended viologen.

The reduced viologen derivatives represent another heterocyclic *p*-QDM analogue associated with the typical Thiele's and Tschitschibabin's hydrocarbons. The reduced extended viologen **60** with a π-delocalized structure was synthesized and it showed a singlet diradical ground state (Fig. 16).[67] From X-ray crystallographic analysis, the central C=C displayed an even longer bond length (1.438 Å) compared to Tschitschibabin's hydrocarbon (1.420 Å). The broadened NMR spectrum indicated the presence of thermally accessible triplet species, but this was not observable by the ESR spectrum. The spin transformation from a singlet to a triplet during heating was also successfully followed with Raman spectroscopy.[68]

5. Anti-aromatic indenofluorenes and analogues

Indenofluorenes contain 20 π-electrons and can be regarded as a unique anti-aromatic/pro-aromatic system. Based on different fusion patterns at the central six-membered ring and at the five-membered ring, indenofluorenes have five isomers such as indeno[1,2-*a*]fluorene **61**, indeno[1,2-*b*]fluorene **62**, indeno[2,1-*a*]fluorene **63**, indeno[1,2-*c*]fluorene **64**, and indeno[2,1-*b*]fluorene **65** (Fig. 17). In all these isomers, monocyclic conjugated annulene-like structures containing either 16 (in **61**, **65**) or 12 (in **62–64**) π-electrons fused by one or two aromatic benzenoid rings can be drawn and thus they can be regarded as an anti-aromatic system. On the other hand, some of them can be regarded as a *p*-QDM (**62**, **64**) or *o*-QDM (**63**) bridged pro-aromatic system. The resonance between the closed-shell form and the open-shell diradical form implies that they are potential diradicaloids.

The derivatives of **61** are unknown, which is expected to most probably have a triplet ground state with extremely high reactivity. The initial studies of **62** were conducted by Scherf *et al.* during their attempted synthesis of conjugated ladder polymers.[69] Swager *et al.* later reported an air-sensitive

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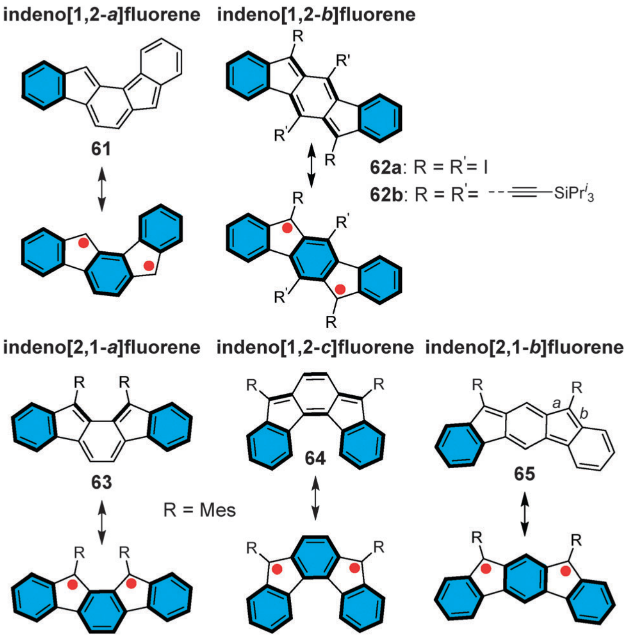

Fig. 17 Chemical and resonance structures of indenofluorene isomers.

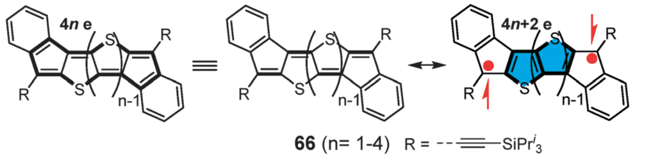

Fig. 18 Chemical structures of bisindenothienoacenes **66**.

tetraiodo-indeno[1,2-*b*]fluorene **62a**.[70] Stable derivatives such as **62b** were synthesized by reduction of the corresponding diol precursors.[71] A variety of derivatives **62** were prepared and intensively studied by Haley's and Yamashita's groups, with respect to their crystal packing, HOMO/LUMO energies and charge transport properties.[72] Similarly, stable mesityl derivatives **63**[73] and **64**[74] were also investigated regarding their molecular structures and optical and electrochemical properties. The indenofluorenes mentioned above are better described as closed-shell quinoidal compounds in the ground state due to the absence of line broadening in their NMR, silence in ESR and large bond length alternation. However, the mesityl substituted isomer **65** turned out to be a singlet diradical in the ground state.[75] No NMR resonance signal was observed for this compound at 30 °C because of the existence of thermally excited triplet species and only broad signals were detected after cooling to −93 °C. The intensity of the ESR signal decreased with decreasing temperature, and the singlet–triplet energy gap was estimated to be -4.2 kcal mol^{-1} based on temperature-dependent magnetic susceptibility measurements. X-ray crystallographic analysis provided solid evidence of the diradical character, for example, the bond lengths of bond *a* (1.437 Å) and *b* (1.431 Å) are similar and at a typical length for a singlet C–C bond. Moreover, the diradical **65** showed a very low-energy light absorption band at 850–2000 nm, which is impressive for such a small π-conjugated system. The difference in the ground state for these indenofluorene isomers can be simply explained by the number of aromatic sextet rings gained from the closed-shell form to the diradical form. All of the isomers can be drawn with three aromatic sextet rings in the diradical form, and in the closed-shell resonance form, two aromatic sextet rings can be drawn for **62–64** while only one aromatic sextet ring can be drawn for **61** and **65**. Therefore, from the closed-shell to the open-shell diradical resonance form, only one additional aromatic sextet ring is obtained for **62–64**, whereas two additional aromatic sextet rings are gained for **61** and **65**. That means **61** and **65** receive more resonance stabilization energy in the diradical form and thus show larger diradical character.

In addition to the pure hydrocarbon based indenofluorenes, bisindenothienoacenes and indolocarbazoles containing pentacyclic thiophene or pyrrole rings were recently developed. A series of stable and soluble bisindeno-[*n*]thienoacenes **66** (n = 1–4), consisting of a quinoidal thienoacene unit annulated with two indene rings, were synthesized and investigated by Haley[76] and Chi[77] independently (Fig. 18). Looking into the structures, this type of molecules can be also viewed as dibenzannulated anti-aromatic systems containing $4n$ π-electrons, or pro-aromatic systems which are in resonance with diradicals containing an aromatic thienoacene unit. Their ground state geometry and electronic structures were investigated using different experimental techniques such as X-ray crystallographic analysis, NMR, ESR and Raman spectroscopy assisted by DFT calculations. Interestingly, with the extension of the chain length, the molecules showed a gradually increasing singlet diradical character and decreasing anti-aromaticity. The longest homologue **66** (n = 4)[77] displayed a diradical character index of 0.202 and was very reactive. These compounds also displayed an inherent transformation from anti-aromatic to pseudo-aromatic/aromatic systems upon electrochemical oxidation and reduction.[77]

Although dihydro (dialkyl)-indolocarbazoles have been widely studied as a promising class of semiconductors for OFETs due to their rigid, linear, coplanar conjugated structures and high charge carrier mobility,[78] the indolocarbazoles with an anti-aromatic character are less reported. Replacing the carbon radical centers in indenofluorenes with nitrogen atoms will lead to a new family of nitrogen-centered diradicaloids. However, such molecules are rarely reported mainly due to synthetic challenges. Similar to the corresponding indeno[1,2-*b*]fluorene, the nitrogen centered indo[3,2-*b*]carbazole was demonstrated to have a quinoidal structure.[79] Recently, Wu's group developed a new class of indolo[2,3-*b*]carbazole derivatives **68** and **70** in which the aminyl radical centers are kinetically blocked by bulky *tert*-butyl groups and 4-*tert*-butylphenyl groups (Fig. 19).[80] Similar to Tobe's indenofluorene **65**, compound **68** showed a distinctive singlet diradical character. Synthesis of compound **68** was performed by treating the dihydro-precursor **67** with excess *tert*-BuOK at room temperature followed by oxidation with iodine at −78 °C, while compound **70** was obtained by dehydrogenation of **69** by PbO_2. As expected, **68** exhibited a well-defined ESR spectrum, and its ESR intensity was found to decrease with decreasing temperature, indicating a singlet diradical ground state.

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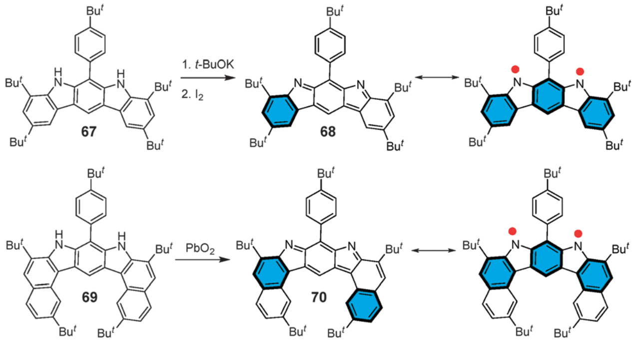

Fig. 19 Synthesis and structures of indolocarbazole derivatives.

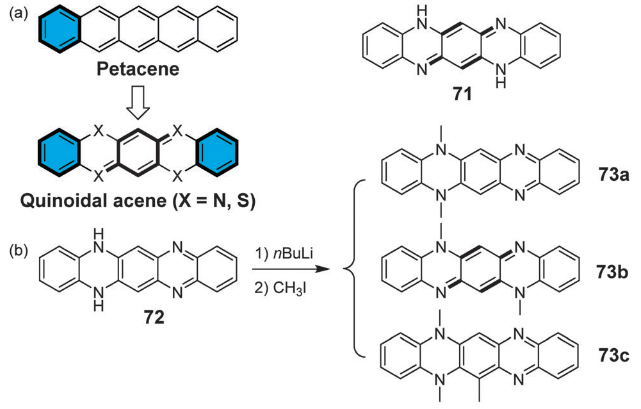

Fig. 20 Structures of quinoidal heteroacenes and tetraazapentacene derivatives.

It was persistent at room temperature under nitrogen protection, and a small singlet–triplet energy gap of −1.78 kcal mol^{-1} was estimated from VT ESR data. In contrast, compound **70** showed well-resolved sharp ^{1}H NMR peaks even upon heating up to 100 °C, and no ESR signal was detected; therefore, it is a typical closed-shell quinoidal compound in the ground state. Such difference in their electronic state can be also explained by the number of aromatic sextet rings gained from the closed-shell form to the open-shell diradical form. That is, compound **70** gained less additional aromatic sextet rings in the diradical resonance in comparison with analogue **68**. A broad absorption band from 450 nm to 760 nm with a maximum at 600 nm was observed for **68**.

6. Quinoidal heteroacenes

Acene-based molecular materials, like pentacene derivatives,[81] have been intensively investigated for their intriguing photophysical and electronic properties and potential use for organic electronics.[82] However, these oligoacenes are susceptible to oxidative and photolytic degradation, and become poorly soluble with the extension of molecular length,[83] which hamper their practical application. The heteroacenes by incorporation of a quinoidal moiety into the acene framework would be expected to be stable. Taking heteropentacene as an example, a *p*-QDM bridged molecule containing two nitrogen or sulfur atoms can be drawn with two aromatic sextet rings, but only one aromatic sextet ring can be drawn for pentacene (Fig. 20). Thus, they could show improved stability. In this context, quinoidal heteroacenes could be a new class of π-conjugated systems with unique electronic structure and potential material applications.

The nitrogen-containing dihydro-tetraazapentacene structure cannot be well represented by the structure shown as **71** (Fig. 20), which was initially proposed as a quinoid.[84] Instead, Miao *et al.* proposed a contribution from a number of resonance forms to explain the obtained *N*-alkylated and *C*-alkylated products after methylation of the dihydro-tetraazapentacene **72.**[85] X-ray crystallographic analysis revealed the structures of quinoidal heteropentacenes **73b**, benzenoid **73a** with a methyl group at the *N*-site, and **73c** with a methyl group at both the *N*-site and *C*-site. It is of interest to compare the differences between the quinoidal **73b** and the benzenoid **73a.** The molecular packing of **73b** illustrated close stacks with a π–π distance of 3.42 Å, and a chain of water molecules was formed between neighbouring stacks due to hydrogen bonding with the imine nitrogen atoms, while **73a** and **73c** had a bent structure. Both **73a** and **73b** had a relatively large HOMO–LUMO energy band gap (about 2.19 eV for **73a** and 2.16 eV for **73b**). However, molecule **73b** exhibited three absorption peaks at 551, 512, and 479 nm, red shifted by about 50 nm compared to **73a**, which displayed a peak at 498 nm with a shoulder at 520 nm. It was found that both quinoidal and benzenoid nitrogen-containing heteropentacenes were suitable for OFET operations with relatively low mobilities (1 × 10^{-4} and 5 × 10^{-4} cm^2 V^{-1} s^{-1}, respectively), possibly arising from the limitation of poor contacts in the devices.

A stable quinoidal dithiapentacene framework was developed by Chi's group.[86] The 5,12-dithiapentacenes **75a** and **75b** were synthesized by nucleophilic addition of **74** with the corresponding lithium reagents followed by reduction of the generated diols with tin(II) chloride (Fig. 21). Both dithiapentacene compounds have superior stability in solution compared with the corresponding diene-type conjugated 6,13-bis(triisopropylsilylethynylene)pentacene and 6,13-diphenylpentacene. Moreover, these two dithiapentacene derivatives exhibited increased HOMO energy levels in comparison with the corresponding pentacene analogues due to the electron-donating nature of the thioether linkage in the backbone. Large optical energy gaps of 1.88 and 2.09 eV were determined for **75a** and **75b**, respectively. X-ray crystallographic analysis showed an essentially planar backbone with a quinoidal conjugation, and illustrated a herringbone motif crystal packing. Haley *et al.* very

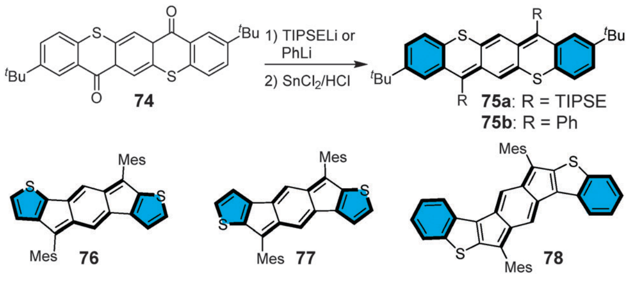

Fig. 21 Chemical structures of quinoidal dithia-acene derivatives.

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recently described quinoidal indacenodithiophene skeletons **76–78**,[87] which can be viewed as anti-aromatic systems containing 20 π-electrons in **76** and **77** and 24 π-electrons in **78**. These indacenodithiophenes realized stable HOMO and LUMO energy levels, resulting from more aromatic rings compared to their corresponding acene counterparts. X-ray crystallographic analysis revealed short intramolecular contact distances between LUMO-rich regions (thiophene units).

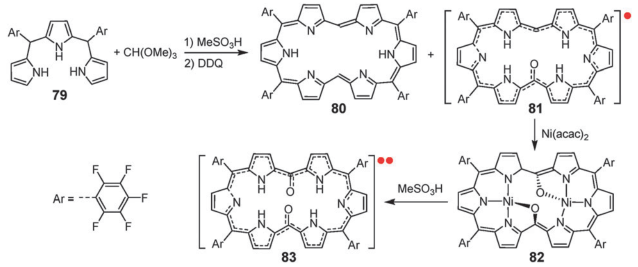

Fig. 22 Synthesis of [26]hexaphyrin and its oxygenated monoradical and diradicaloids.

7. Others

Other conjugated molecules such as expanded porphyrinoids are nice platforms to realize diverse aromaticity/anti-aromaticity as well as stable radical species.[88] Porphyrin can be regarded as a 26 π-electron aromatic system and displays a strong diatropic ring current, a sharp Soret band, and a low-energy Q band.[89] Therefore, the change of the aromaticity can be easily confirmed by comparing the ^{1}H NMR spectra and UV-vis absorption spectra. Taking advantage of a number of shared attributes with porphyrins, the expanded porphyrin framework with unique properties and functions has been attracting increasing attention. Among the various expanded porphyrins, [26]hexaphyrin **80**[90] should be a representative aromatic macrocycle that displays a strong diatropic ring current by exhibiting ^{1}H NMR signals at −4.97 and −0.37 ppm for the *meso*-protons and the inner NH protons, respectively, and in the range of 9.03–10.49 ppm for the outer β-protons. Moreover, its flat and dumbbell-shaped conformation confirmed by X-ray crystallographic analysis was favourable in achieving strong aromaticity. Accordingly, the UV-vis absorption spectrum demonstrated a Soret-like band at 549 nm. The *meso*-oxygenated hexaphyrin **81** was formed as a secondary side product with **80** after condensation and oxidation reaction of **79**, and was identified as an extremely stable monoradical species by ESR and SQUID measurements.[90] A diketoporphyrinoid **83**[91] was synthesized by metallation of **81** with Ni(acac)$_2$ followed by demetallation of the formed *meso*-/*meso*-dioxygenated **82** with methanesulfonic acid. Compound **83** was identified as a singlet diradical in the ground state and the singlet–triplet energy gap was estimated to be −2.56 kcal mol^{-1} based on temperature-dependent ESR measurements. Such a change of the ground electronic state is believed to be driven by the recovery of a strong aromatic [26]hexaphyrin-like moiety in the diradical form (Fig. 22).

Corrole can be viewed as a porphyrin-like aromatic macrocycle with 18 π-electrons, except for one direct pyrrole–pyrrole linkage (Fig. 23). The doubly linked biscorrole **87** containing an anti-aromatic COT moiety in the center was first reported by Osuka and Shinokubo *et al.* (Fig. 23).[92] The *meso*-pentafluorophenyl substituted corrole borate **84** underwent a palladium-catalysed oxidative coupling to afford the 2,2-linked corrole dimer **85**. Oxidation of **85** with DDQ provided the oxidized biscorrole **86**, as an air- and moisture-stable solid. Reduction of **86** with NaBH$_4$ gave the doubly linked biscorrole **87** quantitatively, while oxidation of **87** with DDQ yielded **86** quantitatively. The electronic absorption spectrum of **86** had characteristic absorption bands of corroles but slightly red-shifted compared with those of the corrole monomer, while compound **87** demonstrated a broad spectrum reaching the NIR region from 700 to 1600 nm. Both the oxidized and reduced biscorrole were subjected to metallation, and then the bis-zinc(II) complex **86·2Zn** and bis-cobalt(III) complex **87·2Co** were generated, which showed electronic absorption spectra similar to those of the corresponding free bases **86** and **87**. In contrast to the reduced biscorrole **87·2Co** with a well-resolved ^{1}H NMR spectrum, the oxidized biscorrole **86·2Zn** had nearly no resonance signals in CD_2Cl_2 and THF-d$_8$, even at −90 °C, suggesting a different ground electronic state for these two biscorroles. Complex **86·2Zn** was confirmed to have a singlet diradical ground state based on the observation of a single ESR peak at room temperature and temperature-dependent magnetic susceptibility in SQUID measurements. The singlet diradical character of **86·2Zn** was estimated to be approximately 87% by theoretical calculations at the BLYP/631TZVP level and the singlet–triplet energy gap was determined to be −0.94 kcal mol^{-1}. Curiously, both compounds exhibited quite planar structures, including the center COT core, based on X-ray crystallographic analysis. Despite the existence of a planar anti-aromatic COT core,[93] **87** and **87·2Co** have a closed-shell ground state and retain the aromaticity of the two corrole units. The oxidized forms **86** and **86·2Zn** however have 4*n* π-electrons and tend to become diradicals.

Very recently, Anand *et al.* reported a stable (4*n* + 1) π pentathiophene macrocyclic radical **88** (Fig. 23), which is regarded as an unusual state between aromatic 4*n* + 2 and anti-aromatic 4*n* π-electronic circuits.[94] The 25 π-electron nature of **88** was responsible for the amphoteric features along with their respective alternative colours in the electrochemical and chemical process, because this neutral macrocycle is ready to

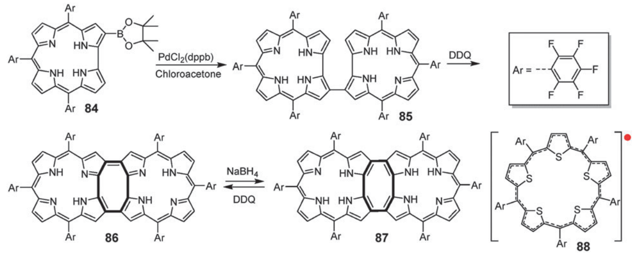

Fig. 23 Synthesis of biscorrole derivatives and chemical structure of the penta-thiophene 25 π-electron radical.

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be a 24-πe anti-aromatic cation or a 26-πe aromatic anion after one-electron oxidation or reduction.

8. Conclusions and perspectives

Although the term aromaticity introduced by Hofmann dates back to the 19th century, it is still an important and powerful concept for organic chemistry in modern time. The development of the aromaticity concept has been growing very fast because it explains well the special stability of the π-conjugated molecules as well as their electronic structures and physical properties. Hückel aromaticity is applied to planar monocyclic systems while Möbius aromaticity is applied to molecules with a Möbius twist. Compared to those aromatic compounds which exhibit a high degree of chemical and thermal stability, anti-aromatic molecules are generally destabilized. Accordingly, an anti-aromatic π system tends to reduce anti-aromaticity by altering its electronic or conformational structure, and becomes aromatic bearing unpaired electrons within the planar framework or non-aromatic within the distorted molecular skeleton. If one non-aromatic π-conjugated molecule tends to become aromatic in a diradical form or zwitterionic form, it can be called pro-aromatic. Many quinoidal systems discussed in this critical review can be classified into this category. In this sense, aromaticity reflects the essential molecular reactivity and π-conjugated molecules tend to be aromatic for stronger stabilization. So, in principle, both anti-aromatic and pro-aromatic π-conjugated molecules have an irresistible wish to be diradicals.

The diradical character and singlet–triplet energy gap are important parameters to describe a singlet diradicaloid. Although they can be theoretically calculated, recent experimental studies indicated that they can be nicely correlated to the factors such as aromaticity and steric hindrance. For benzenoid PAH molecules with the same molecular composition, the stability and physical properties can be simply predicted by Clar's aromatic sextet rule, that is, the molecule with more aromatic sextet rings shows higher stability and larger HOMO–LUMO energy gap. Such a rule can be further extended to the benzenoid PH-based singlet diradicaloids to predict their relative diradical character. Besides the aromaticity, steric hindrance is another important driving force as demonstrated in many quinoidal diradicaloids. By tuning these parameters carefully, it is now possible to do tailored design of the diradical character and singlet–triplet energy gap. More importantly, the diradical character determines the intrinsic electronic, optical and magnetic properties as well as chemical reactivity of a π-conjugated molecule. We would like to say that diradical character is a very important concept to understand most of the organic opto-electronic materials, probably as important as the concept of aromaticity.

Different from the typical closed-shell π-conjugated molecules with negligible diradical character, singlet diradicaloids with small and moderate diradical character exhibited very different physical properties and have many useful applications in electronics, non-linear optics, spintronics and energy storage devices: (1) they have a small energy gap and show amphoteric redox behaviour; therefore, they can be used as active materials in ambipolar OFETs with a small hole/electron injection barrier and balanced hole/electron transport; (2) they show enhanced third order NLO response and large TPA cross sections in the NIR region, which opens the opportunities for photonic applications (*e.g.* optical limiting) and optical modulation in the telecommunication region; (3) they show unique magnetic activity and thermo-/photo-magnetic behaviour, and thus can be used as a new type of responsive magnetic materials; (4) they can be used as both charge and spin transporting materials, which are desirable for organic spintronics; (5) they show unique singlet fission phenomenon,[95] which opens opportunities to push the theoretical power conversion efficiency of organic solar cells from 32% to 44%; and (6) they can store lithium ions and charges, and thus can be used for energy storage devices. To achieve these applications, it is of importance to obtain stable materials with controlled molecular order in thin films. Recent studies have developed different synthetic methods and stabilizing strategies (either thermodynamic or kinetic) and now it is not a very big challenge to obtain diradicaloids with similar photo-/thermo-stability to the normal closed-shell π-conjugated materials. For some applications such as organic electronic and spintronic devices, it is important to achieve very ordered intermolecular packing in solid state and for that we still need to do very careful design since in many cases kinetic blocking by bulky groups alleviates the intermolecular interactions.

So far, the diversity of stable diradicaloids is impressive. One challenging task in the near future is to develop stable/persistent π-systems with quarter radical character and even polyradical character. The geometry can vary from the current linear form to macrocyclic structure, which may raise interesting questions on possible global aromaticity (super-aromaticity), ferromagnetism and superconductivity. One of the most interesting applications of these diradicaloids would be organic spintronic devices and it is important to take the first step along this direction. Such spin-dependent electronic devices can go further from thin-film to nanoscale and even to molecular scale and all these need a very good cooperation between chemists, physicists and device engineers and that is the only way we can move the area forward.

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Notes and references

1 (*a*) A. Rajca, *Chem. Rev.*, 1994, **94**, 871; (*b*) A. Rajca, *Adv. Phys. Org. Chem.*, 2005, **40**, 153; (*c*) N. Gallagher, A. Olankitwanit and A. Rajca, *J. Org. Chem.*, 2015, **80**, 1291.

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2 (*a*) W. T. Borden, *Reactive Intermediates*, Wiley-Interscience, New York, 1982; (*b*) L. Salem and C. Rowland, *Angew. Chem., Int. Ed.*, 1972, **11**, 92.

3 (*a*) T. Balley and S. Masamune, *Tetrahedron*, 1980, **36**, 343; (*b*) W. T. Borden, *J. Am. Chem. Soc.*, 1975, **97**, 5968.

4 W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, 1980, **102**, 7958.

5 (*a*) H. S. Kaufman, I. Fankuchen and H. Mark, *Nature*, 1948, **161**, 165; (*b*) M. Kertesz, C. Ho Choi and S. Yang, *Chem. Rev.*, 2005, **105**, 3448.

6 (*a*) D. P. Craig and A. Maccol, *J. Chem. Phys.*, 1949, **11**, 964; (*b*) A. Falchi, C. Gellini, P. R. Salvi and K. Hafner, *J. Phys. Chem.*, 1995, **99**, 14659.

7 A. E. Tschitschibabin, *Chem. Ber.*, 1907, **40**, 1810.

8 J. Thiele and H. Balhorn, *Chem. Ber.*, 1904, **37**, 1463.

9 (*a*) W. T. Borden, H. Iwamura and J. A. Berson, *Acc. Chem. Res.*, 1994, **27**, 109; (*b*) P. Karafiloglou, *J. Chem. Educ.*, 1989, **66**, 816.

10 (*a*) M. Nakano, R. Kishi, T. Nitta, T. Kubo, K. Nakasuji, K. Kamada, K. Ohta, B. Champagne, E. Botek and K. Yamaguchi, *J. Phys. Chem. A*, 2005, **109**, 885; (*b*) M. Nakano, R. Kishi, S. Ohta, H. Takahashi, T. Kubo, K. Kamada, K. Ohta, E. Botek and B. Champagne, *Phys. Rev. Lett.*, 2007, **99**, 033001.

11 K. Kamada, K. Ohta, A. Shimizu, T. Kubo, R. Kishi, H. Takahashi, E. Botek, B. Champagne and M. Nakano, *J. Phys. Chem. Lett.*, 2010, **1**, 937.

12 (*a*) S. Gronowitz and B. Uppström, *Acta Chem. Scand., Ser. B*, 1974, **28**, 981; (*b*) M. L. Kaplan, R. C. Haddon, F. B. Bramwell, F. Wudl, J. H. Marshall, D. O. Cowan and S. S. Gronowitz, *J. Phys. Chem.*, 1980, **84**, 427.

13 (*a*) K. Yui, Y. Aso, T. Otsubo and F. Ogura, *J. Chem. Soc., Chem. Commun.*, 1987, 1816; (*b*) K. Yui, H. Ishida, Y. Aso, T. Otsubo, F. Ogura, A. Kawamoto and J. Tanaka, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 1547; (*c*) A. Galindo, A. Hills, D. L. Hughes and R. L. Richards, *J. Chem. Soc., Chem. Commun.*, 1987, 1816; (*d*) K. Takahashi, T. Suzuki, K. Akiyama, Y. Ikegami and Y. Fukazawa, *J. Am. Chem. Soc.*, 1991, **113**, 4576.

14 T. Kawase, N. Ueno and M. Oda, *Tetrahedron Lett.*, 1992, **33**, 5405.

15 (*a*) H. Higuchi, T. Nakayama, H. Koyama, J. Ojima, T. Wada and H. Sasabe, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2363; (*b*) J. Casado, L. L. Miller, K. R. Mann, T. M. Pappenfus, H. Higuchi, E. Orti, B. Milian, R. Pou-Amerigo, V. Hernandez and J. T. L. Navarrete, *J. Am. Chem. Soc.*, 2002, **124**, 12380.

16 T. Takahashi, K. Matsuoka, K. Takimiya, T. Otsubo and Y. Aso, *J. Am. Chem. Soc.*, 2005, **127**, 8928.

17 R. Ponce Ortiz, J. Casado, V. Hernandez, J. T. Lopez Navarrete, P. M. Viruela, E. Orti, K. Takimiya and T. Otsubo, *Angew. Chem., Int. Ed.*, 2007, **46**, 9057.

18 S. R. González, Y. Ie, Y. Aso, J. T. López Navarrete and J. Casado, *J. Am. Chem. Soc.*, 2011, **133**, 16350.

19 R. P. Ortiz, J. Casado, V. Hernandez, J. T. L. Navarrete, E. Orti, P. M. Viruela, B. Milian, S. Hotta, G. Zotti, S. Zecchin and B. Vercelli, *Adv. Funct. Mater.*, 2006, **16**, 531.

20 Q. Wu, R. Li, W. Hong, H. Li, X. Gao and D. Zhu, *Chem. Mater.*, 2011, **23**, 3138.

21 M. Uno, K. Seto and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, 1984, 932.

22 (*a*) See for example: T. M. Pappenfus, R. J. Chesterfield, C. D. Frisbie, K. R. Mann, J. Casado, J. D. Raff and L. L. Miller, *J. Am. Chem. Soc.*, 2002, **124**, 4184; (*b*) R. J. Chesterfield, C. R. Newman, T. M. Pappenfus, P. C. Ewbank, M. H. Haukaas, K. R. Mann, L. L. Miller and C. D. Frisbie, *Adv. Mater.*, 2003, **15**, 1278; (*c*) S. Handa, E. Miyazaki, K. Takimiya and Y. Kunugi, *J. Am. Chem. Soc.*, 2007, **129**, 11684; (*d*) D. E. Janzen, M. W. Burand, P. C. Ewbank, T. M. Pappenfus, H. Higuchi, D. A. da Silva Filho, V. G. Young, J. L. Brédas and K. R. Mann, *J. Am. Chem. Soc.*, 2004, **126**, 15295; (*e*) J. C. Ribierre, T. Fujihara, S. Watanabe, M. Matsumoto, T. Muto, A. Nakao and T. Aoyama, *Adv. Mater.*, 2010, **22**, 1722.

23 (*a*) Y. Suzuki, E. Miyazaki and K. Takimiya, *J. Am. Chem. Soc.*, 2010, **132**, 10453; (*b*) T. Mori, N. Yanai, I. Osaka and K. Takimiya, *Org. Lett.*, 2014, **16**, 1334.

24 E. V. Canesi, D. Fazzi, L. Colella, C. Bertarelli and C. Castiglioni, *J. Am. Chem. Soc.*, 2012, **134**, 19070.

25 K. Takahashi and T. Suzuki, *J. Am. Chem. Soc.*, 1989, **111**, 5483.

26 (*a*) Z. Sun, Q. Ye, C. Chi and J. Wu, *Chem. Soc. Rev.*, 2012, **41**, 7857; (*b*) Z. Sun, Z. Zeng and J. Wu, *Chem. – Asian J.*, 2013, **8**, 2894; (*c*) M. Abe, *Chem. Rev.*, 2013, **113**, 7011; (*d*) Z. Sun, Z. Zeng and J. Wu, *Acc. Chem. Res.*, 2014, **47**, 2582.

27 (*a*) C. A. Coulson, D. P. Craig, A. Maccoll and A. Pullman, *Discuss. Faraday Soc.*, 1947, **2**, 36; (*b*) M. Szwarc, *Discuss. Faraday Soc.*, 1947, **2**, 46; (*c*) N. S. Hush, *J. Polym. Sci.*, 1952, **11**, 289.

28 D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, 1962, **84**, 3370.

29 (*a*) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, 1974, **7**, 232; (*b*) J. G. Laquindanum, H. E. Katz, A. Dodabalapur and A. J. Lovinger, *J. Am. Chem. Soc.*, 1996, **118**, 11331.

30 T. Yanagimoto, K. Takimiya, T. Otsubo and F. Ogura, *J. Chem. Soc., Chem. Commun.*, 1993, 519.

31 (*a*) H. D. Hartzler, *J. Am. Chem. Soc.*, 1964, **86**, 2174; (*b*) A. W. Addison, N. S. Dalal, Y. Hoyano, S. Huizinga and L. Weiler, *Can. J. Chem.*, 1977, **55**, 4191.

32 M. Maxfield, A. N. Bloch and D. O. Cowan, *J. Org. Chem.*, 1985, **50**, 1789.

33 X. Zhu, H. Tsuji, K. Nakabayashi, S.-I. Ohkoshi and E. Nakamura, *J. Am. Chem. Soc.*, 2011, **133**, 16342.

34 (*a*) G. J. Sloan and W. R. Vaughan, *J. Org. Chem.*, 1957, **22**, 750; (*b*) L. K. Montgomery, J. C. Huffman, E. A. Jurczak and M. P. Grendze, *J. Am. Chem. Soc.*, 1986, **108**, 6004.

35 Z. Zeng, Y. M. Sung, N. Bao, D. Tan, R. Lee, J. L. Zafra, B. S. Lee, M. Ishida, J. Ding, J. T. López Navarrete, Y. Li, W. Zeng, D. Kim, K.-W. Huang, R. D. Webster, J. Casado and J. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 14513.

36 K. Zhang, K. Huang, J. Li, C. Chi and J. Wu, *Org. Lett.*, 2009, **11**, 4854.

37 (*a*) M. E. Itkis, X. Chi, A. W. Cordes and R. C. Haddon, *Science*, 2002, **296**, 1443; (*b*) D. Small, V. Zaitsev, Y. Jung, S. V. Rosokha, M. Head-Gordon and J. K. Kochi, *J. Am. Chem. Soc.*, 2004, **126**, 13850; (*c*) S. K. Mandal, S. Samanta,

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Published on 21 mayo 2015. Downloaded by Fail Open on 23/07/2025 8:09:51.

M. E. Itkis, D. W. Jensen, R. W. Reed, R. T. Oakley, F. S. Tham, B. Donnadieu and R. C. Haddon, *Science*, 2005, **309**, 281; (*d*) Y. Morita, S. Suzuki, K. Sato and T. Takui, *Nat. Chem.*, 2011, **3**, 197.

38 T. Kubo, A. Shimizu, M. Sakamoto, M. Uruichi, K. Yakushi, M. Nakano, D. Shiomi, K. Sato, T. Takui, Y. Morita and K. Nakasuji, *Angew. Chem., Int. Ed.*, 2005, **44**, 6564.

39 A. Shimizu, T. Kubo, M. Uruchi, K. Yakushi, M. Nakano, D. Shiomi, K. Sato, T. Takui, Y. Hirao, K. Matsumoto, H. Kurata, Y. Morita and K. Nakatsuji, *J. Am. Chem. Soc.*, 2010, **132**, 14421.

40 A. Shimizu, Y. Hirao, K. Matsumoto, H. Kurata, T. Kubo, M. Uruichi and K. Yakushi, *Chem. Commun.*, 2012, **48**, 5629.

41 (*a*) K. Nakasuji and T. Kubo, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 1791; (*b*) C. Lambert, *Angew. Chem., Int. Ed.*, 2011, **50**, 1756; (*c*) A. Shimizu, M. Nakano, Y. Hirao and T. Kubo, *J. Phys. Org. Chem.*, 2011, **24**, 876; (*d*) I. Murata, S. Sasaki, K.-U. Klabunde, J. Toyoda and K. Nakasuji, *Angew. Chem., Int. Ed.*, 1991, **30**, 172; (*e*) K. Ohashi, T. Kubo, T. Masui, K. Yamamoto, K. Nakasuji, T. Takui, Y. Kai and I. Murata, *J. Am. Chem. Soc.*, 1998, **120**, 2018; (*f*) A. Shimizu, M. Uruichi, K. Yakushi, H. Matsuzaki, H. Okamoto, M. Nakano, Y. Hirao, K. Matsumoto, H. Kurata and T. Kubo, *Angew. Chem., Int. Ed.*, 2009, **48**, 5482; (*g*) T. Kubo, A. Shimizu, M. Uruichi, K. Yakushi, M. Nakano, D. Shiomi, K. Sato, T. Takui, Y. Morita and K. Nakasuji, *Org. Lett.*, 2007, **9**, 81; (*h*) A. Konishi, Y. Hirao, M. Nakano, A. Shimizu, E. Botek, B. Champagne, D. Shiomi, K. Sato, T. Takui, K. Matsumoto, H. Kurata and T. Kubo, *J. Am. Chem. Soc.*, 2010, **132**, 11021.

42 T. Kubo, M. Sakamoto, M. Akabane, Y. Fujiwara, K. Yamamoto, M. Akita, K. Inoue, T. Takui and K. Nakasuji, *Angew. Chem., Int. Ed.*, 2004, **43**, 6474.

43 M. Nakano, R. Kishi, A. Takebe, M. Nate, H. Takahashi, T. Kubo, K. Kamada, K. Ohta, B. Champagne and E. Botek, *Comput. Lett.*, 2007, **3**, 333.

44 E. Clar, K. F. Lang and H. Schulz-Kiesow, *Chem. Ber.*, 1955, **88**, 1520.

45 (*a*) H. A. Staab, A. Nissen and J. Ipaktschi, *Angew. Chem., Int. Ed.*, 1968, **7**, 226; (*b*) R. H. Mitchell and F. Sondheimer, *Tetrahedron*, 1970, **26**, 2141; (*c*) H. A. Staab, J. Ipaktschi and A. Nissen, *Chem. Ber.*, 1971, **104**, 1182; (*d*) R. Umeda, D. Hibi, K. Miki and Y. Tobe, *Org. Lett.*, 2009, **11**, 4104; (*e*) T. C. Wu, C. H. Chen, D. Hibi, A. Shimizu, Y. Tobe and Y. T. Wu, *Angew. Chem., Int. Ed.*, 2010, **49**, 7059; (*f*) L. Shan, Z. Liang, X. Xu, Q. Tang and Q. Miao, *Chem. Sci.*, 2013, **4**, 3294.

46 (*a*) E. Clar and I. A. Macpherson, *Tetrahedron*, 1962, **18**, 1411; (*b*) R. K. Erünliü, *Liebigs Ann. Chem.*, 1969, **721**, 43.

47 Z. Sun, K.-W. Huang and J. Wu, *Org. Lett.*, 2010, **12**, 4690.

48 Z. Sun, K.-W. Huang and J. Wu, *J. Am. Chem. Soc.*, 2011, **133**, 11896.

49 Y. Li, W.-K. Heng, B. S. Lee, N. Aratani, J. L. Zafra, N. Bao, R. Lee, Y. M. Sung, Z. Sun, K.-W. Huang, R. D. Webster, J. T. Löpez Navarrete, D.-H. Kim, A. Osuka, J. Casado, J. Ding and J. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 14913.

50 S. Das, S. Lee, M. Son, X. Zhu, W. Zhang, B. Zheng, P. Hu, Z. Zeng, Z. Sun, W. Zeng, R. W. Li, K. W. Huang, J. Ding, D. Kim and J. Wu, *Chem. – Eur. J.*, 2014, **20**, 11410.

51 W. Zeng, M. Ishida, S. Lee, Y. Sung, Z. Zeng, Y. Ni, C. Chi, D.-H. Kim and J. Wu, *Chem. – Eur. J.*, 2013, **19**, 16814.

52 Z. Sun, S. Lee, K. H. Park, X. Zhu, W. Zhang, B. Zheng, P. Hu, Z. Zeng, S. Das, Y. Li, C. Chi, R. W. Li, K. W. Huang, J. Ding, D. Kim and J. Wu, *J. Am. Chem. Soc.*, 2013, **135**, 18229.

53 (*a*) B. J. Jung, N. J. Tremblay, M. L. Yeh and H. E. Katz, *Chem. Mater.*, 2011, **23**, 568; (*b*) C. Wang, H. Dong, W. Hu, Y. Liu and D. Zhu, *Chem. Rev.*, 2012, **112**, 2208.

54 Z. Zeng, M. Ishida, J. L. Zafra, X. Zhu, Y. M. Sung, N. Bao, R. D. Webster, B. S. Lee, R.-W. Li, W. Zeng, Y. Li, C. Chi, J. T. López Navarrete, J. Ding, J. Casado, D. Kim and J. Wu, *J. Am. Chem. Soc.*, 2013, **135**, 6363.

55 Z. Zeng, S. Lee, J. L. Zafra, M. Ishida, X. Zhu, Z. Sun, Y. Ni, R. D. Webster, R.-W. Li, J. T. López Navarrete, C. Chi, J. Ding, J. Casado, D. Kim and J. Wu, *Angew. Chem., Int. Ed.*, 2013, **52**, 8561.

56 Z. Zeng, S. Lee, J. L. Zafra, M. Ishida, N. Bao, R. D. Webster, J. T. López Navarrete, J. Ding, J. Casado, D. Kim and J. Wu, *Chem. Sci.*, 2014, **5**, 3072.

57 M. Nakano, T. Minami, K. Yoneda, S. Muhammad, R. Kishi, Y. Shigeta, T. Kubo, L. Rougier, B. Champagne, K. Kamada and K. Ohta, *J. Phys. Chem. Lett.*, 2011, **2**, 1094.

58 T. Nozawa, M. Nagata, M. Ichinohe and A. Sekiguchi, *J. Am. Chem. Soc.*, 2011, **133**, 5773.

59 H. Braunschweig, V. Dyakonov, B. Engels, Z. Falk, C. Hçrl, J. H. Klein, T. Kramer, H. Kraus, I. Krummenacher, C. Lambert and C. Walter, *Angew. Chem., Int. Ed.*, 2013, **52**, 12852.

60 X. Zheng, X. Wang, Y. Qiu, Y. Li, C. Zhou, Y. Sui, Y. Li, J. Ma and X. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 14912.

61 Y. Su, X. Wang, X. Zheng, Z. Zhang, Y. Song, Y. Sui, Y. Li and X. Wang, *Angew. Chem., Int. Ed.*, 2014, **53**, 2857.

62 K. Kamada, S. Fuku-en, S. Minamide, K. Ohta, R. Kishi, M. Nakano, H. Matsuzaki, H. Okamoto, H. Higashikawa, K. Inoue, S. Kojima and Y. Yamamoto, *J. Am. Chem. Soc.*, 2013, **135**, 232.

63 U. Mayer, H. Baumgärtel and H. Zimmermann, *Angew. Chem., Int. Ed.*, 1966, **5**, 311.

64 Y. Sakaino, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1063.

65 Y. Sakaino, H. Kakisawa, T. Kusumi and K. Maeda, *J. Org. Chem.*, 1979, **44**, 1241.

66 A. Kikuchi, F. Iwahori and J. Abe, *J. Am. Chem. Soc.*, 2004, **126**, 6526.

67 W. W. Porter III, T. P. Vaid and A. L. Rheingold, *J. Am. Chem. Soc.*, 2005, **127**, 16559.

68 J. Casado, S. Patchkovskii, M. Z. Zgierski, L. Hermosilla, C. Sieiro, M. Moreno Oliva and J. T. López Navarrete, *Angew. Chem., Int. Ed.*, 2008, **47**, 1443.

69 U. Scherf and K. Müllen, *Polymer*, 1992, **33**, 2443.

70 Q. Zhou, P. J. Carroll and T. M. Swager, *J. Org. Chem.*, 1994, **59**, 1294.

71 D. T. Chase, B. D. Rose, S. P. McClintock, L. N. Zakharov and M. M. Haley, *Angew. Chem., Int. Ed.*, 2011, **123**, 1159.

72 (*a*) D. T. Chase, B. D. Rose, S. P. McClintock, L. N. Zakharov and M. M. Haley, *Angew. Chem., Int. Ed.*, 2011, **50**, 1127; (*b*) D. T. Chase, A. G. Fix, B. D. Rose, C. D. Weber,

Published on 21 mayo 2015. Downloaded by Fail Open on 23/07/2025 8:09:51.

S. Nobusue, C. E. Stockwell, L. N. Zakharov, M. C. Lonergan and M. M. Haley, *Angew. Chem., Int. Ed.*, 2011, **50**, 11103; (*c*) D. T. Chase, A. G. Fix, S. J. Kang, B. D. Rose, C. D. Weber, Y. Zhong, L. N. Zakharov, M. C. Lonergan, C. Nuckolls and M. M. Haley, *J. Am. Chem. Soc.*, 2012, **134**, 10349; (*d*) B. D. Rose, C. L. Vonnegut, L. N. Zakharov and M. M. Haley, *Org. Lett.*, 2012, **14**, 2426; (*e*) J. Nishida, S. Tsukaguchi and Y. Yamashita, *Chem. – Eur. J.*, 2012, **18**, 8964.

73 A. Shimizu and Y. Tobe, *Angew. Chem., Int. Ed.*, 2011, **50**, 6906.

74 A. G. Fix, P. E. Deal, C. L. Vonnegut, B. D. Rose, L. N. Zakharov and M. M. Haley, *Org. Lett.*, 2013, **15**, 1362.

75 A. Shimizu, R. Kishi, M. Nakano, D. Shiomi, K. Sato, T. Takui, I. Hisaki, M. Miyata and Y. Tobe, *Angew. Chem., Int. Ed.*, 2013, **52**, 6076.

76 G. E. Rudebusch, A. G. Fix, H. A. Henthorn, C. L. Vonnegut, L. N. Zakharov and M. M. Haley, *Chem. Sci.*, 2014, **5**, 3627.

77 X. Shi, P. M. Burrezo, S. Lee, W. Zhang, B. Zheng, G. Dai, J. Chang, J. T. López Navarrete, K.-W. Huang, D. Kim, J. Casado and C. Chi, *Chem. Sci.*, 2014, **5**, 4490.

78 (*a*) P. L. T. Boudreault, S. Wakim, M. L. Tang, Y. Tao, Z. A. Bao and M. Leclerc, *J. Mater. Chem.*, 2009, **19**, 2921; (*b*) Y. L. Guo, H. P. Zhao, G. Yu, C. A. Di, W. Liu, S. D. Jiang, S. K. Yan, C. R. Wang, H. L. Zhang, X. N. Sun, X. Tao and Y. Q. Liu, *Adv. Mater.*, 2008, **20**, 4835; (*c*) P. L. T. Boudreault, S. Wakim, N. Blouin, M. Simard, C. Tessier, Y. Tao and M. Leclerc, *J. Am. Chem. Soc.*, 2007, **129**, 9125; (*d*) K. S. Park, S. M. Salunkhe, I. Lim, C. G. Cho, S. H. Han and M. M. Sung, *Adv. Mater.*, 2013, **25**, 3351.

79 (*a*) S. Hünig and H. C. Steinmetzer, *Liebigs Ann. Chem.*, 1976, 1090; (*b*) L. N. Yudina, M. N. Preobrazhenskaya and A. M. Korolev, *Chem. Heterocycl. Compd.*, 2000, **36**, 1112; (*c*) R. Gu, K. Robeyns, L. van Meervelt, S. Toppet and W. Dehaen, *Org. Biomol. Chem.*, 2008, **6**, 2484.

80 D. Luo, S. Lee, B. Zheng, Z. Sun, W. Zeng, K.-W. Huang, K. Furukawa, D. Kim, R. D. Webster and J. Wu, *Chem. Sci.*, 2014, **5**, 4944.

81 (*a*) J. L. Brédas, D. Beljonne, J. Cornil, J. P. Calbert, Z. Shuai and R. Silbey, *Synth. Met.*, 2002, **125**, 107; (*b*) E. J. Meijer, D. M. De Leeuw, S. Setayesh, E. van Veenendaal, B.-H. Huisman, P. W. M. Blom, J. C. Hummelen, U. Scherf and T. M. Klapwijk, *Nat. Mater.*, 2003, **2**, 678; (*c*) R. Ruiz, D. Choudhary, B. Nickel, T. Toccoli, K. C. Chang, A. C. Mayer, J. M. Blakely, R. L. Headrick, S. Iannotta and G. G. Malliaras, *Chem. Mater.*, 2004, **16**, 4497; (*d*) T. Okamoto, M. L. Senatore, M. M. Ling, A. B. Mallik, M. L. Tang and Z. Bao, *Adv. Mater.*, 2007, **19**, 3381.

82 (*a*) M. Bendikov, F. Wudl and D. F. Perepichka, *Chem. Rev.*, 2004, **104**, 4891; (*b*) J. E. Anthony, *Chem. Rev.*, 2006, **106**, 5028; (*c*) J. E. Anthony, *Angew. Chem., Int. Ed.*, 2008, **47**, 452; (*d*) Q. Ye and C. Chi, *Chem. Mater.*, 2014, **26**, 4046.

83 (*a*) A. Maliakal, K. Raghavachari, H. Katz, E. Chandross and T. Siegrist, *Chem. Mater.*, 2004, **16**, 4980; (*b*) S. H. Chan, H. K. Lee, Y. M. Wang, N. Y. Fu, X. M. Chen, Z. W. Cai and H. N. C. Wong, *Chem. Commun.*, 2005, 66; (*c*) Y. Wang, N. Fu, S. Chan, H. Lee and H. N. C. Wong, *Tetrahedron*, 2007, **63**, 8586; (*d*) C. P. Bénard, Z. Geng, M. A. Heuft, K. VanCreg and A. G. Fallis, *J. Org. Chem.*, 2007, **72**, 7229.

84 (*a*) G. M. Badger and R. Pettit, *J. Chem. Soc.*, 1951, 3211; (*b*) H. Beecken and A. Musso, *Chem. Ber.*, 1961, **94**, 601; (*c*) J. Manassen and S. Khalif, *J. Am. Chem. Soc.*, 1966, **88**, 1943; (*d*) J. K. Stille and E. L. Mainen, *Macromolecules*, 1968, **1**, 36; (*e*) S. A. Jenekhe, *Macromolecules*, 1991, **24**, 1; (*f*) M. A. Goyette and M. Leclerc, *J. Electroanal. Chem.*, 1995, **382**, 17; (*g*) Y. Ma, Y. Sun, Y. Liu, J. Gao, S. Chen, X. Sun, W. Qiu, G. Yu, G. Cui, W. Hu and D. Zhu, *J. Mater. Chem.*, 2005, **15**, 4894.

85 Q. Tang, J. Liu, H. S. Chan and Q. Miao, *Chem. – Eur. J.*, 2009, **15**, 3965.

86 Q. Ye, J. Chang, X. Shi, G. Dai, W. Zhang, K. W. Huang and C. Chi, *Org. Lett.*, 2014, **16**, 3966.

87 B. S. Young, D. T. Chase, J. L. Marshall, C. L. Vonnegut, L. N. Zakharov and M. M. Haley, *Chem. Sci.*, 2014, **5**, 1008.

88 A. Osuka and S. Saito, *Chem. Commun.*, 2011, **47**, 4330.

89 (*a*) F. Sondheimer, R. Wolovsky and Y. Amiel, *J. Am. Chem. Soc.*, 1962, **84**, 274; (*b*) M. K. Cyranski, T. M. Krygiwski, M. Wisioroski, N. J. R. van E. Hommes and P. von R. Scheyler, *Angew. Chem., Int. Ed.*, 1998, **37**, 177; (*c*) M. G. P. M. S. Neves, R. M. Martins, A. C. Tomé, A. J. D. Silvestre, A. M. S. Silva, V. Félix, M. G. B. Drew and J. A. S. Cavaleiro, *Chem. Commun.*, 1999, 385; (*d*) S. Mori and A. Osuka, *J. Am. Chem. Soc.*, 2005, **127**, 8030.

90 T. Koide, G. Kashiwazaki, M. Suzuki, K. Furukawa, M. C. Yoon, S. Cho, D. Kim and A. Osuka, *Angew. Chem., Int. Ed.*, 2008, **47**, 9661.

91 T. Koide, K. Furukawa, H. Shinokubo, J.-Y. Shin, K. S. Kim, D. Kim and A. Osuka, *J. Am. Chem. Soc.*, 2010, **132**, 7246.

92 S. Hiroto, K. Furukawa, H. Shinokubo and A. Osuka, *J. Am. Chem. Soc.*, 2006, **128**, 12380.

93 (*a*) Y. Nakamura, N. Aratani, H. Shinokubo, A. Takagi, T. Kawai, T. Matsumoto, Z. S. Yoon, D. Y. Kim, T. K. Ahn, D. Kim, A. Muranaka, N. Kobayashi and A. Osuka, *J. Am. Chem. Soc.*, 2006, **128**, 4119; (*b*) S. Hiroto, N. Aratani, N. Shibata, Y. Higuchi, T. Sasamori, N. Tokitoh, H. Shinokubo and A. Osuka, *Angew. Chem., Int. Ed.*, 2009, **48**, 2388.

94 T. Y. Gopalakrishna, J. S. Reddy and V. G. Anand, *Angew. Chem., Int. Ed.*, 2014, **53**, 10984.

95 (*a*) M. B. Smith and J. Michl, *Chem. Rev.*, 2010, **110**, 6891; (*b*) T. Minami and M. Nakano, *J. Phys. Chem. Lett.*, 2012, **3**, 145; (*c*) J. C. Johnson, A. J. Nozik and J. Michl, *Acc. Chem. Res.*, 2013, **46**, 1290; (*d*) J. Lee, P. Jadhav, P. D. Reusswig, S. R. Yost, N. J. Thompson, D. N. Congreve, E. Hontz, T. van Voorhis and M. A. Baldo, *Acc. Chem. Res.*, 2013, **46**, 1300.