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REVIEW ARTICLE Qinqin Shi, Hui Huang *et al.* The design, synthesis and application of rubicene based polycyclic aromatic hydrocarbons (PAHs)



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The design, synthesis and application of rubicene based polycyclic aromatic hydrocarbons (PAHs)

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Rubicene, a key nanofragment of C_{70} , is attracting great attention owing to its unique molecular structure and physicochemical properties. As an indeno-annelated polycyclic aromatic hydrocarbon (indeno-PAH), rubicene itself has a planar p-orbital surface that could provide increased intermolecular electronic coupling, affording interesting optoelectronic properties. Interestingly, most of the substituted and aryl annulated rubicene PAHs possess twisted structures, which may demonstrate different optoelectronic properties. To date, many efforts have been made in the synthesis of rubicene PAHs, which demonstrate potential applications in organic field effect transistors (OFETs), organic solar cells (OSCs), sensors, lithium batteries, *etc.* However, the functionalization of rubicene remains a long-standing challenge from the synthetic perspective. In this mini-review, we summarized the major synthetic routes to construct rubicene PAHs, their physicochemical properties, and various applications. In the end, we propose a future direction on the development of rubicene PAHs.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) including azulene,¹ perylene diimide (PDI),² diketopyrrolopyrrole (DPP),³ and indenofluorenes⁴ have attracted tremendous attention owing

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to their attractive optoelectronic properties and applications in organic field effect transistors, organic synapses, and organic thermoelectric materials.^{5–10} Rubicene ($C_{26}H_{14}$) is a 26- π -electron and planar PAH, which has been known for over 100 years.^{11,12} In recent years, this red compound has received increasing attention due to its unique optoelectronic properties, including high electron affinity, and highly fluorescent and photostable properties.^{13,14} The chemical structure of rubicene contains fully unsaturated five-membered rings that are externally fused to six-membered ring perimeters (Fig. 1a), which constitutes a nano-fragment of C_{70} -fullerene (Fig. 1b).^{15,16} As an interesting aromatic building block, the resolved rubicene



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Fig. 1 (a) The rubicene chemical structure. (b) PC₇₀BM chemical structure containing rubicene nanofragments. (c) AFM image of rubicene. (d) STM image of rubicene. (c) and (d) reproduced with permission from American Chemical Society and The Royal Society of Chemistry.

molecule has been directly witnessed to possess a completely planar structure based on atomic force microscopy (AFM) and scanning tunneling microscopy (STM) images (Fig. 1c and d) by the Gross and Lu groups, respectively.^{17,18} Interestingly, the substituent groups may disrupt the planarity of rubicene. For example, the introduction of Cl, Br, or CN greatly distorts the conformation.^{19,20} Moreover, the fusion of aryl rings causes the structural chirality.^{21,22} Thus, the variance in rubicene PAH derivatives led to the large geometrical differences from rubicene, endowing the rubicene PAH derivatives with various unexpected properties and potential applications in optoelectronic devices, such as sensors, OFETs, OSCs, *etc.*^{15,20,23}

Rubicene was initially synthesized by Schlenk in 1928.¹¹ Although the synthesis of rubicene-based π -functional materials has been a long standing challenge, the rubicene PAHs have become an important and active field in the chemistry and materials community due to their unique physicochemical properties.^{24–28} In this review, we summarized the progress on the design, synthesis, and applications of rubicene-based π -functional materials. First, synthetic routes of rubicene PAHs are briefly introduced. Second, the properties and applications of rubicene derivatives are discussed in detail. Finally, we provide future focus and perspectives for rubicene PAH studies.

2. Synthetic routes for rubicene PAHs

Since the site selectivity of rubicene substitution is challenging, the synthesis of rubicene derivatives mostly relies on the formation of the rubicene core through the key five- and/or six-membered ring closure that is usually the final step of the synthetic route. Herein, we summarized three major routes to construct rubicene PAHs.

The most common synthesis of rubicene PAHs is through the closure of five-membered ring in the final step.²⁹ Five different synthetic routes towards rubicene PAHs are illustrated in Fig. 2. Starting from 1,5-dichloroanthraquinone 2 and aryllithium reagents, the resulting diol adducts are reduced to afford the diarylanthracenes 4, followed by cyclization to produce the substituted rubicenes 5a-5d in good overall yields by palladium catalyzed Heck intramolecular ring closure reactions (Fig. 2a). However, suffering from polymer formation and decomposition in the Heck reaction step, the synthesis of a heterocyclic analogue of rubicene (named here emeraldicene 5d) is less efficient in DMF solvent.^{30–32} Afterwards, Wudl reported a dramatic yield improvement of 5d by switching the solvent to CH₃CN.³³ The successful synthesis of emeraldicene 5d allowed the various pre-functionalization, which is beneficial for accessing all kinds of rubicene derivatives, including polymers.³⁴ In 2011, Siegel reported a C-F activation method through an intermediate silyl cation, which becomes a useful expansion for the synthesis of rubicene 1 from inert fluoride aryl 6 (Fig. 2b).³⁵ Thus, it could be a complementary method to close the five-membered-ring via inert C-F activation. In 2009, Liu and coworkers reported an efficient synthesis of dibenzo[a,m]rubicenes (**11a**) and tetrabenzo[a, f, r, m]rubicenes (**11b**) involving ICl-mediated benzannulation of 1,4-diphenyl-2,5-dialkynylbenzene 8, Suzuki coupling and Scholl oxidation (Fig. 2c).^{29,36} Later, Müllen developed a similar strategy to obtain rubicene derivatives 14 (Fig. 2d),³⁷ which adopted a unique Scholl reaction of 6,7,13,14-tetraarylbenzo[k]tetraphene, "unexpectedly" forming five-membered rings through highly selective 1,2-shift of aryl groups. It is of note that the Scholl reaction is a substrate dependent reaction, which requires detailed optimization for the ring closure. Therefore, the overall steps for Müllen's synthetic route are simplified in comparison with Liu's routes. Although most methodologies provide access to all-carbon variants, fewer strategies readily furnish their nitrogen-doped analogues. Gorodetsky and coworkers reported a cross coupling reaction of bis(aldimine) with phenylacetylene in the presence of $BF_3 \cdot OEt_2$ as a Lewis acid mediator and chloranil as an oxidant to obtain (1E,1'E)-N,N'-(2,5-dichloro-1,4-phenylene)bis(1-(4-octylphenyl)methanimine) 15. After aza-Diels-Alder reaction, the resulting chloride precursor 16 was used for the Heck coupling reaction to afford a nitrogen-doped rubicene analogue 17 (Fig. 2e).38

The other common strategy to form rubicene PAHs is through a six-membered ring closure in the last step (Fig. 3). Miao reported a novel synthesis of dibromodibenzo[a,m] rubicene (21) *via* Diels–Alder reaction, Corey–Fuchs reaction and intramolecular Heck reaction (Fig. 3a). Thereinto, the starting material terephthalate (18) was prepared from condensation between dimethyl acetonedicarboxylate and benzil and the subsequent Diels–Alder reaction with diphenylacetylene. It is of note that the intramolecular Heck-type reaction should be completed within 15 min. Otherwise, prolonged heating time led to debromination. Thus, various unsubstituted dibenzo[a,m]rubicenes were easily synthesized from 21. Plunkett and coworkers reported a challenging synthesis of much more contorted rubicene PAHs 24a and 24b, which can be prepared *via* a palladiumJournal of Materials Chemistry C



Fig. 2 The synthetic procedures of rubicene PAHs *via* five-membered ring closure. (a) The synthesis of various substituted rubicene PAHs **5** through Friedel–Crafts reaction, followed by reduction reaction and intramolecular Heck reaction. (b) The synthesis of rubicene **1** *via* Suzuki coupling and Friedel–Crafts reaction. (c) The formation of rubicene **11** through ICI mediated cyclization, Suzuki reaction and Scholl reaction. (d) The formation of rubicene **14** through ICI mediated cyclization. (e) The synthesis of a nitrogen-doped rubicene analogues **17** from aza-Diels–Alder reaction and intramolecular Heck reaction.

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Fig. 3 The multistep synthesis of rubicene PAHs via six-membered ring closure. (a) The synthesis of substituted rubicene PAH 21 via Diels-Alder reaction, Corey-Fuchs reaction and intramolecular Heck reaction. (b) The synthesis of contorted rubicene PAH 24 through pentannulation reaction and Scholl reaction. (c) The synthesis of rubicene 29 via Negishi coupling, Friedel-Crafts cyclization, Riley oxidation and condensation reactions. (d) The synthesis of B₂N₂-rubicene 33 via condensation, oxidative aromatization and bora-Friedel-Crafts-type reaction.

catalyzed cyclopentannulation followed by Scholl cyclodehydrogenation (Fig. 3b).^{21,39} First, the annulation chemistry can be accomplished between a di-arylethynylene and an appropriate aryl-dibromide **22** to form 1,2,6,7-tetraarylcyclopenta[h,i]aceanthrylenes **23a** and 4,10-dihexyl-1,2,7,8-tetrakis(3methoxyphenyl)cyclopenta-[6,7]aceanthryleno[4,3-*b*:8,9-*b*']dithiophene **23b**. Subsequently, the Scholl cyclodehydrogenation to close the externally fused aryl groups was accomplished only with properly arranged alkoxy substitutions. Unsurprisingly, 3,10-(di-*tert*-butyl)rubicene **29** was difficult to access from the



Fig. 4 The one step synthesis of rubicene PAHs. (a) The synthesis of rubicene **1** *via* electrophilic aromatic substitution. (b) The synthesis of rubicene **1** through Suzuki–Heck cascade coupling. (c) The synthesis of rubicene PAHs **36** through Scholl reaction. (d) The synthesis of rubicene **38** *via* domino thermal radical cycloaromatization.

general deprotonation methods. Thus, Shuler and coworkers developed a ruthenium-catalyzed butadiene-mediated benzannulation to enable the synthesis (Fig. 3c) of substituted rubicene and N-doped derivatives.⁴⁰ Owing to the low lowest unoccupied molecular orbital (LUMO) energy and emission properties for B–N doped PAHs, the B₂N₂-doped dibenzo[*a*,*m*]rubicene (B₂N₂-DBR) and derivatives possessing C_{2h} -symmetrical geometry are synthesized on a multigram scale *via* a two-step synthetic route (Fig. 3d) using commercially available indole, ketone, and dichloroborane, which opens a new direction for the development of rubicene derivatives.⁴¹

To simplify the two different synthetic routes, one-step reactions from the commercial chemicals have been extensively exploited (Fig. 4). In 1990, Langhals and coworkers reported a simple one-step synthesis of highly pure rubicene (1) from fluorenone (34) and magnesium in a 24% yield (Fig. 4a).42 Later, a Suzuki-Heck-type cascade protocol was developed (Fig. 4b),⁴³ which mainly relies on the Suzuki coupling reaction to join two rings simultaneously and a sequential intramolecular Heck-type arylation to close the five-membered ring. In 2021, Huang, Shi and coworkers reported a Scholl oxidation cascade to build rubicene PAHs 36a-36c from trisubstituted aryls alkenes (Fig. 4c).^{24,26} Based on the mechanism studies, it was noticed that this method started from closing the six-membered rings, followed by forming the fivemembered rings. Overall, these chalcogen doped rubicenes were synthesized under slightly different Scholl oxidation conditions in modest to good yields. Interestingly, the non-conjugated aromatic heptaynes may undergo domino thermal radical cycloaromatization at 25 °C to yield indenol ring-fused benzo[a]rubicene skeletons with helicity (Fig. 4d).44 This multicyclization reaction proceeded regio-selectively to yield [6]helicene derivatives 38 via multi-annulation in the final step.

3. The applications of rubicene PAHs

The fused and substituted rubicene π -functional PAHs show photophysical and chemical properties that are different from

rubicene. Thus, constructing a new rubicene PAH molecule is an opportunity to tune the optoelectronic properties. Herein, we summarized the design, properties and applications of all carbon and heteroatom doped rubicenes, which will provide a guideline for developing novel rubicene PAHs.

3.1 All carbon rubicene functional materials

Carbon-based materials, such as acenes, fullerenes, and graphene nanoribbons, are viewed as the potential successors to silicon in the next generation of electronics. Therefore, various substituted rubicenes and aryl fused rubicenes were synthesized, which demonstrated interesting optoelectronic properties.

Rubicene itself was well-known for exhibiting intense electrochemiluminescence (ECL) with a maximum emission wavelength of 560 nm.45 In 2015, the electronic emission characteristic of rubicene was investigated to diagnose laserinduced fluorescence (LIF) spectra of PAHs. It was found that the fluorescence signals with the wavelength longer than 500 nm are likely emitted by the PAHs with five-membered rings.46 This study demonstrated the selectivity of PAHs in LIF technology, especially in the visible region. Additionally, rubicene has been used as a sensitizer to estimate the quantum yield of singlet oxygen (¹O₂) owing to its strong intersystem crossing (ISC) properties.⁴⁷ Not surprisingly, the planar geometry of rubicene allows strong π - π stacking, suggesting its good charge transport characteristics. Thus, a bottom-gate/bottomcontact polycrystalline thin-film OFET based on rubicene exhibits a saturation hole mobility of 0.20 cm² V⁻¹ s⁻¹ and a current on/off ratio $(I_{\rm on}/I_{\rm off})$ of 1.0 \times 10⁴.⁴⁸ These results indicate that rubicene can serve as a benchmark organic semiconductor for various organic electronic devices.15

Next, the representative substituted rubicenes are summarized in Fig. 5. The 5-monosubstituted and 5,12-disubstituted derivatives were normally prepared by electrophilic substitution on the rubicene nucleus. For example, introducing two amino-groups into the apolar core structure of a rubicene molecule produced an original conjugated primary diamine

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molecule **38**, exhibiting low affinity for polar solvents. PAH **38** can be used as a common carbonate-based battery electrode, which showed reversible electroactivity and promising performances when using LiPF_6 (1.0 M) in EC (ethylene carbonate): DMC (dimethyl carbonate) (1:1 vol%) as the electrolyte.¹³

Additionally, the dendrimer **39** with a rubicene fluorescent core was synthesized by Schryver and Dehaen, which was used for the determination of the hydrodynamical volume in solvents, since the dendrimers can be used as selective cation sensitive fluorescence indicators.^{32,49} Later, several anomalous non-hexagon arrays of graphitic carbon material **40** with cylindrical shapes were synthesized using 2,5-substituted rubicene.⁵⁰ The single-crystal X-ray diffraction exhibited its curved structure with good conjugation across the pentagons. In 2014, the symmetrical polysubstituted PAH rubicene **41** proved to be an interesting new cytotoxic agent with potential application in drugs.⁵¹

Owing to the large geometrical differences between rubicene and its substituted derivatives, the systematic incorporation of fused-aryl rings at selected positions can also significantly tune the electronic properties (Fig. 5). In 1958, Clar and Willicks reported the first aryl fused rubicene 42, which demonstrated obvious redshift absorption (80 nm) in comparison with that of rubicene 1.52 Later, Miao and coworkers reported an efficient synthesis of a symmetrical dibenzo [a,m] rubicene 21 (Fig. 3a), a new member of nonplanar cyclopenta-fused PAHs (Fig. 6).¹⁹ It is found that the conformation and molecular packing of dibenzo[a,m]rubicenes in the solid state can be tuned by the substituting groups, and the silylethynylated derivatives of dibenzo[*a*,*m*]rubicene **43b** function as p-type organic semiconductors in solution-processed thin film transistors with field effect mobility up to 1.0 cm² V⁻¹ s⁻¹ (Fig. 6). Song revisited the same dibenzo [a,m] rubicene,⁵³ of which charge transport properties were effectively modulated by introducing different substituents into molecules. Specifically, molecules 43d and 43e possess balanced electron and hole mobilities, which can be used as bipolar semiconductors for optoelectronic devices. Another interesting application of p-type rubicene derivatives is as additives in organic photovoltaics (OPVs). The efficiencies of OPVs based on a fullerene acceptor are improved by over 20%



Fig. 6 (a) Side view and (b) top view of the π - π stacking of **43b** in the crystal. (c) Reflection polarized light micrograph for a dip-coated film of **43b**. (d) Drain current (IDS) *versus* gate voltage (VGS) with drain voltage (VDS) at -3 V for the best-performing OTFT of **43b** with an active channel of W = 1 mm and $L = 150 \mu$ m measured in air. Reprinted from ref. 19. All figures reproduced with permission from 2015 American Chemical Society.

upon introducing a high mobility p-type rubicene semiconductor **43b** into the active layers as an additive in only a few weight percent.²³ This observation was attributed to the increased hole mobilities in the devices. Note that the conformation of **43b** is curved. However, the significant efficiency enhancement was not observed when high-mobility planar molecules were introduced into the active layers. In view of the curved p-type semiconductors being more compatible with a fullerene acceptor in their molecular shape than a planar one, the authors

The compound diindeno[1,2-g:1',2'-s]rubicene (44) has been prepared in three steps from 1,5-dichloroanthraquinone (Fig. 5).⁵⁴ Single crystallographic analysis indicated that 44 molecules pack in a manner hindering π - π stacking in the crystalline state, thus preventing strong electronic coupling between molecules. Thus, those derivatives have bulk mobilities of 10⁻⁷ cm² V⁻¹ s⁻¹. In 2015, Chen and coworkers processed bulk-heterojunction organic solar cells with a mixture of molecule 44 and P3HT as electron acceptor and donor materials, which afforded a PCE of 3.05% with a relatively high $V_{\rm OC}$ of 1.22 V.⁵⁵ Recently, an azulene fused rubicene material 45 was synthesized via a Scholl reaction and dehydrogenation.⁵⁶ The incorporation of two formal azulene moieties has an effect on the physiochemical properties. First, the π -electrons of benzenoid and pentagon rings are more delocalized. Second, molecule 45 exhibits unusual S₀ to S₂ absorption and abnormal anti-Kasha S₂ to S₀ emission. Finally, crystal 45 exhibits semiconducting behavior with a hole mobility of up to 0.082 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

3.2 Heteroatom doped rubicene functional materials

The cooperation of heteroatom into the rubecene derivative may obviously change the physicochemical properties. However, the rational positional heteroatom doping remains a huge challenge from the synthetic perspective.

The sulfur doped rubicene analogue emeraldicene was first reported in 1999 by Smet et al. (Fig. 2a).³¹ In 2011, Wudl and coworkers reported a soluble substituted emeraldicene (5d),³³ which demonstrated a maximum absorption of over 600 nm, redshifted 100 nm in comparison with rubicene 1. The long wavelength band shows no solvent polarity response, indicating that is unlikely a result of intramolecular charge-transfer. Additionally, the cyclic voltammetry (CV) was performed and demonstrated deep LUMO and high highest occupied molecular orbital (HOMO) energy levels. Therefore, a copolymer 46 based on emeraldicene and diketopyrrolopyrrole (DPP) was explored, exhibiting balanced field effect hole and electron mobilities as high as 0.29 cm^{2} V^{$^{-1}$} s^{$^{-1}$} and 0.25 cm^{2} V^{$^{-1}$} s^{$^{-1}$},³⁴ respectively. Such balanced and high mobility values encouraged chemists to develop new emeraldicene molecules to achieve excellent optoelectronic performances. In 2012, Wudl and coworkers developed a unique emeraldicene compound 47. Upon simply decreasing the concentration of 47 in tetrahydrofuran (THF), the selfassembly of the molecules evolved from well-defined ribbons to vesicles to baskets.⁵⁷ Moreover, the elongated supramolecular organization of 47 and the oriented π - π stacking in the ribbons play a crucial role in determining the charge transport properties in thin films. Therefore, the self-assembly of this molecule enables a bottom-up strategy to construct complex nano/microstructures with excellent optoelectronic properties. Additionally, these emeraldicene derivatives with multiply cyano-substituted ethenyl groups at the molecular termini (bisDCNE 48a and bisTCNE 48b) and with a dicyanomethylene-substituted

quinoidal structure (TCNQE **49**) were synthesized for application in n-type organic semiconductors.²⁰ Thanks to the existence of strong electron-withdrawing groups, **48b** and **49** exhibited lowlying LUMO energy levels at around -4.2 eV that allowed easy electron injection and stable electron transfer under ambient conditions. It is of note that bisTCNE-based bottom-gate bottomcontact OFET devices exhibited the highest electron mobility of up to 5.5×10^{-2} cm² V⁻¹ s⁻¹ with I_{on}/I_{off} more than 10^5 under vacuum, and comparable electron mobility ($\mu_e = 3.3 \times 10^{-2}$ cm² V⁻¹ s⁻¹) under ambient conditions.

Recently, Huang and coworkers developed a simple synthetic route (Fig. 4c) for O, S and Se doped aryl annulated rubicene (36a-36c).²⁴ All chalcogen doped rubicenes possess slightly twisted structures with a torsion angle of less than 10.4 $^{\circ}$ and are relatively more planar than that of all carbon rubicenes. It is noted that the chalcogen-atom doping greatly affected the physical properties such as energy levels, the charge transport mobilities, and intersystem crossing efficiencies (Fig. 7). Meanwhile, these rubicenes presented diradical character and excellent air stabilities,^{18,26} which were manifested by single-crystal X-ray studies, variable-temperature nuclear magnetic resonance (VT-NMR), and electron spin resonance (Fig. 7c). Furthermore, the nucleus independent chemical shifts (NICS) and the anisotropy of the induced current density calculations (ACID) revealed that the formation of a diradical was caused by a pro-aromaticity driving force. Similarly, a tetraindeno-fused bis(anthraoxa)quinodimethane 50 with nine consecutively fused six-membered rings in a row was designed and synthesized,⁵⁸ the structure of which was confirmed by single crystal X-ray diffraction and NMR measurements. Compared with an unfused analogue, the indeno fusion onto the zigzag edges not only enhanced the photostability but also dramatically tuned the electronic properties. Due to the existence of two rubicene units, the compound 50 can also be readily reduced to form a radical anion and dianion.

Although a number of methodologies provide access to allcarbon variants, fewer strategies readily furnish their nitrogendoped analogues. Herein, we summarized the nitrogen containing rubicenes in Fig. 8. Gorodetsky reported a N-doped rubicene 51 featuring a low lying LUMO of -3.25 V, suggesting potential application as an electron transport material.³⁸ Subsequently, a challenging B_2N_2 -doped dibenzo[*a*,*m*]rubicene (52) and derivatives were reported, which possess two B-N units C_{2h} -symmetrically on two edges.⁴¹ The compound 52 possesses a large optical bandgap, and hence blue-shifted absorption and emission with a larger fluorescence quantum yield ($\Phi = 0.88$) and a much smaller Stokes shift than its all-carbon analogue ($\phi = 0.25$). The blue emissive B₂N₂-doped rubicene derivatives are stable under ambient conditions but sensitive to nucleophiles such as fluoride and pyridine. Additionally, 52 reversibly interacts with a fluoride ion to bathochromically shift its emission with a high fluorescence quantum yield, while coordination with pyridine quenches its photoluminescence. The marked changes in luminescence properties and optical bandgap on interaction with a Lewis base along with good chemical stability suggested the application of B2N2-doped rubicene derivatives in colorimetric chemo- and

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Fig. 7 (a), (d) and (g) Chemical structure of **36a–36c**. (b), (e) and (h) Crystal structures of **36a–36c** and the torsion angles. (c) The variable temperatureelectron spin resonance (VT-EPR) spectra of **36b** in solids. (f) Transfer curves of the OFET device based on single crystals of **36b**. (i) The speciesassociated difference spectra (SADS) and concentrations of transient species as a function of time obtained from global target analysis for **36c**. Reprinted from ref. 18 and 20. All figures reproduced with permission from 2018 Wiley-VCH and 2022 Chinese Chemical Society.



biosensors. Meanwhile, a bottom-up synthesis of graphene nanoribbons (GNRs) 53 with embedded fused BN-doped rubicene components on an Au(111) surface using on-surface chemistry was explored.⁵⁹ The structures and electronic properties of the BN-GNRs were characterized by STM and AFM with CO-terminated tips supported by numerical calculations. The periodic incorporation of BN heteroatoms in the GNR leads to an increase of the bandgap compared to its undoped counterpart, which opens avenues for the rational design of semiconducting GNRs.

4. Conclusions and perspectives

Rubicene PAHs are receiving increasing attention due to their unique molecular structures, versatile functional sites, and

unusual photophysical properties. In this minireview, several major synthetic routes are introduced, which demonstrate upto-date progress for the construction of rubicene derivatives. Next, we summarized the design, structures and properties of rubicene functional materials. Moreover, we discussed the difference between all carbon and heteroatom doped rubicene PAHs, highlighting the efficient construction of rubicene is of vital importance. Therefore, the challenges and opportunities of rubicene PAH are proposed. (1) Powerful and universal synthetic methods are required to construct and modify rubicene PAHs. Thus, many advanced synthetic methods, such as electrochemical or photochemical catalysis may provide new solutions to develop rubicene PAHs; (2) rubicene based building blocks are barely applied to construct functional polymers, mainly due to the challenging pre-functionalization of rubicene PAHs. Thus, improving the site selectivity for functionalization of rubicene PAHs is critical; (3) the variety of rubicene PAHs is still limited, restraining their potential applications. More attention should be paid to create various rubicene functional materials, which are beneficial for understanding the structure-property relationship. Overall, this minireview should encourage more chemists to develop the library of rubicene based functional materials and potential applications.

Conflicts of interest

There are no conflicts to declare.

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