Dedication ((optional))

Functionalization of Pyrene to Prepare Luminescent Materials - Typical Examples of Methodology

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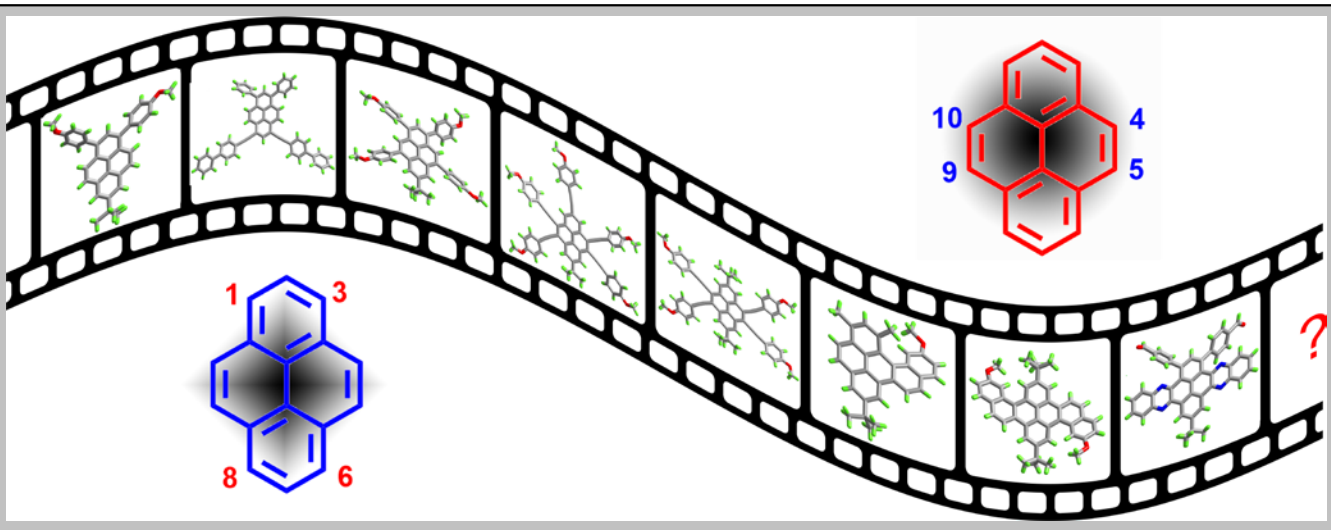

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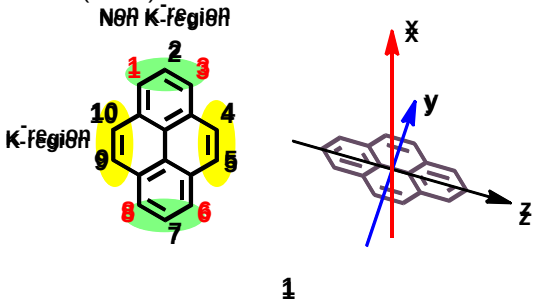
Abstract: Pyrene-based π-conjugated materials are considered to be an ideal organic electro-luminescence material for application in semiconductor devices, such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic photovoltaics (OPVs), etc. However, the great drawback of employing pyrene as an organic luminescence material is the formation of excimer emission which quenches the efficiency at high concentration or in the solid-state. Thus, in order to obtain highly efficient optical devices, scientists have devoted much effort to tuning the structure of pyrene derivatives in order to realize exploitable properties by employing two strategies, 1) introducing a variety of moieties at the pyrene core, and 2) exploring effective and convenient synthetic strategies to functionalize the pyrene-core. Since 20th century, our group mainly focuses on synthetic methodology for functionalization of the pyrene core, we have found that formylation/acetylation bromination of pyrene can selectly functionalization at K-region by lewis acid catalyzed. Herein, this mini-reivew highlights direct synthetic approaches (such as formylation, bromination, oxidation and de-*tert*-butylation reactions, etc) to functionalize the pyrene in order to advance research on luminescent materials for organic electronic applications. Further, this acticle demonstrates the future direction of pyrene chemistry is aysmmetric functionalization of pyrene for organic semiconductor application and highlighting some of the classical asymmetric pyrenes, as well as the latest breakthroughs. In addition, the photophysical properties of pyrene-based molecules are briefly reviewed. To give a current overview of the development of pyrene chemistry, the review selectively covers some of the latest reports and concepts from the period covering late 2011 to the present day.

1. Introduction

The research area of designing and synthesizing molecules as semiconductor materials from PAHs has progressed rapidly,[1] due to their potential application as molecular electronic materials in organic electroluminescent and photoluminescent devices, OFET, as well as in liquid crystal lasers. Even since the first generation of organic electroluminescence (EL) diodes was discovered by Tang and co-workers,[2] more and more highly efficient materials/devices have appeared alongide the rapid developments that have occured in more everyday life technology. For example, organic light-emitting diodes (OLEDs) have found extensive use, particlularly in full-color displays[3] (including full-flat panel and flexible displays) and solid state lighting (SSL).[4,5]

Pyrene[6] is a member of the polycyclic aromatic hydrocarbons (PHAs) family and plays both an electron-donating and an electron-withdrawing role. It exhibits intense blue fluorescence with good quantum yields in solution given its excellent optical properties. The fluorescene properties of pyrene and its derivatives has been employed in detecting guest molecules.[7,8] More importantly, pyrene has exhibited potential for application in organic EL devices due to possessing several advantages: (1) solution processable, (2) good thermal stability, (3) high charge carrier mobility, and (4) intense luminescence efficiency. However, due to pyrene possessing a large planar conjugated aromatic system, it shows a high tendency towards π-stacking and excimer formation and is subject to quenched emission with low photoluminescence quantum yields (PLQYs) in condensed media. Therefore, more recent research has focused on functionalization of the pyrene core with a view to further improving the optical properties. The result has been an extention in their use to fields involving OLEDs,[6,9] organic photovoltaics (OPVs)[10] and solar cells.[11]



Scheme 1. Structure of pyrene (left) and (right) in Cartesian coordinates.

Generally, examples have focused on the construction of highly efficient emitting materials based on the pyrene core by introducing various substitutions at the 1-, 3-, 6- and 8-positions.[6] Given that the 1,3,6,8-positions are significantly more active than the other positions (the 4,5,9,10-positions or the 2-,7-positions), it is not easy to directly substitute at these latter positions over the 1,3,6,8-positions. According to theoretical calculations, the energy of the 1,3,6,8-positions are lower by 8.8 kcal mol^{-1} than the 2,7-positions, and so the substitution order follows the order of positions as follows 1->8->6->3-.[12]

In the development of pyrene chemistry, our laboratory has over the last 30 years made great strides in functionalizing pyrene and employing it as an efficient luminescence material. Our recent work has involved traditional synthetic techniques, (such as formylation, bromination, oxidation and de-*tert*-butylation reactions, etc) in order to offer a facile methodology for functionalization of the pyrene core at both the active sites (the 1,3,6,8-positions) and the K-region (the 4,5,9,10-positions). The synthesized pyrene-based star molecules exhibited air-stability and highly efficient luminescence and are thus considered interesting materials for semiconductor applications.

Recently, a number of review have been published that cover the synthetic and application aspects of pyrene chemistry, including the synthesis of substituted pyrenes by indirect methods.[13] The main distinction here is that we provide a comprehensive overview of direct methodologies, mostly our own work, to modify the pyrene-core to afford intriguing architectures for semiconductor applications. To more fully represent the broad area of pyrene-based luminescent materials, a number of typical, simple and convenience synthetic strategies for modifying the pyrene core both at the active sites (1,3- and 6,8-positions), the non-active sites of the K-region (4-, 5-, 9-, and

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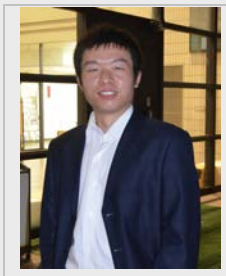

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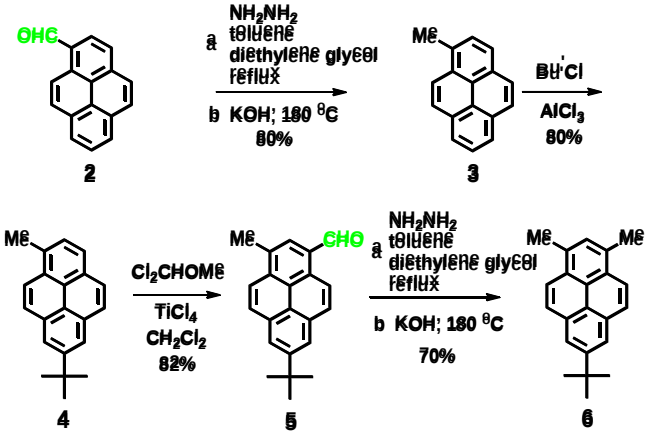
10-positions) and the nodal plane (2,7-positions) have been employed. These include formylation/acetylation, bromination, de-*tert*-butylation,, oxidation and borylation reactions. Furthermore, the preparation of a variety of topologically related molecules allowed us to further investigate the relationship between their optical properties, crystal packing and electrochemistry. Such methodologies in pyrene chemistry are attracting increased interest from both academic and industrial research groups.

2. Formylation/acetylation of pyrene

2.1 Lewis acid catalyzed formylation of pyrene

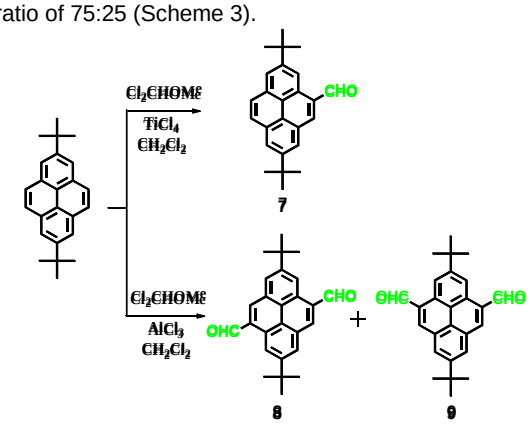
Metal-catalyzed reactions as a mainstream synthetic tool have attracted much attention in organic synthesis in recent years, due to the low cost, high-efficiency and ease of manipulation. Importantly, judicious choice of metal complex allows for regio-selective functionalization to the desired product.[14] Given that the active 1-position site preferentially undergoes electrophilic substitution, the pyrene-1-carbaldehyde **2** is directly obtained from pyrene using either the Vollmann approach[15] or by a Lewis acid-catalyzed method in good yield.[16] To further develope the formylation of pyrene, Yamato explored numerous synthetic routes for formylation of pyrene, not only at the active sites (1-, 3- positions), but also at the K-region (4-, 5-, 9- and 10-positions).



Scheme 2. Synthetic route to 1,3-dimethylpyrene **6**.

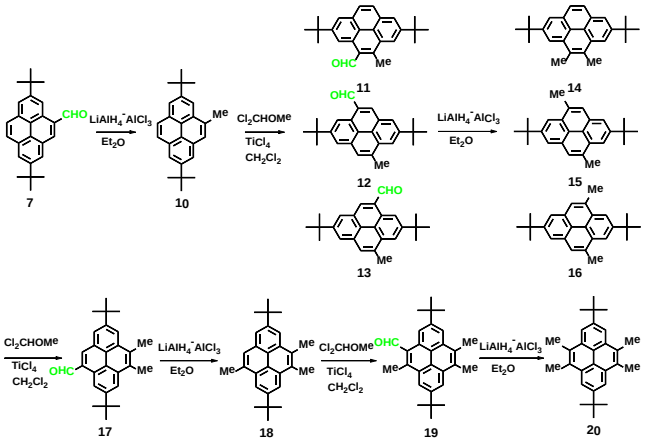
As shown in Scheme 2, the reaction of pyrene with dichloromethyl methyl ether in CH_2Cl_2 solution using $TiCl_4$ as a catalyst,afforded **2** in 90% yield, and a subsequent Wolff-Kishner reduction led to 1-methylpyrene **3** in 80% yield. Subsequently, 7-*tert*-butyl-1-methylpyrene **4** was prepared from **3** by introducing a bulky blocking *tert*-butyl group at the 7-position as a protecting group to avoid reaction at the 6,8-positions. Further formylation of **4** proved possible, such that the -CHO group can be selectively located at the 3-position to afford the corresponding 7-*tert*-butyl-3-methylpyrene-1-carbaldehyde **5** in 82% yield. Wolff-Kishner reduction then afforded 7-*tert*-butyl-1,3-dimethylpyrene **6** in 70% yield.[17]

Yamato et al.[18] have noted that a –CHO group can selectively be attached at the 4- or 4,9-positions of pyrene under different Lewis acid catalyzed conditions. For instance, using the *tert*-butyl group as a positional protective group, the $TiCl_4$-catalyzed formylation of 2,7-di-*tert*-butylpyrene with dichloromethyl methyl ether to afford 2,7-di-*tert*-butylpyrene 4-carbaldehyde **7** was achieved in 84% yield. However, in the presence of $AlCl_3$, a mixture of isomers, namely 2,7-di-*tert*-butylpyrene-4,9-biscarbaldehyde **8** and 2,7-di-*tert*-butylpyrene-4,10-biscarbaldehyde **9** were isolated under the same conditions in the ratio of 75:25 (Scheme 3).



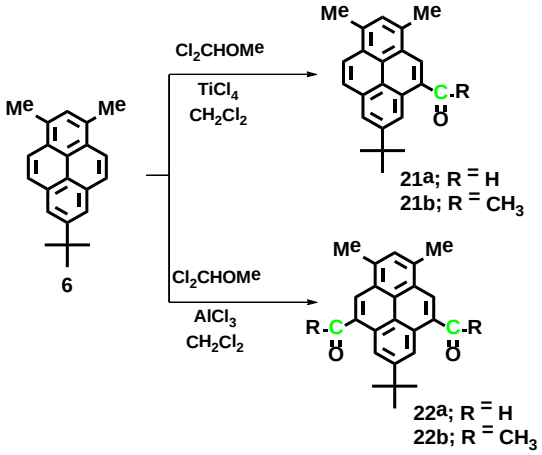
Scheme 3. Synthesis of mono- and diformylpyrenes **7** and **8/9.**

As shown in Scheme 4, Miyazawa[19] developed a stepwise synthetic route to 4,5,9,l0-tetramethylpyrene **20** from 2,7-di-*tert*-butylpyrene-4-carbaldehyde **7** as start material. Reduction of **7** with $LiAlH_4$ in ether afforded 2,7-di-*tert*-butyl-4-methylpyrene **10** in 87% yield. Subsequently, treatment of **10** with Cl_2CHOCH_3 in the presence of $TiCl_4$ as a catalyst, afforded a mixture of the formylated pyrenes **11**–**13**. By repeating the two steps of reduction and formylation, a single 2,7-di-*tert*-butyl-4,5,9-trimethylpyrene **18** was obtained, which can be further involved in formylation and reduction to afford 2,7-di-*tert*-butyl-4,5,9,10-tetramethylpyrene **20**. This methodology offers a clear strategy to methylated pyrene building blocks via a Lewis acid catalyzed process at the K-region, *ie* the 4-, 5-, 9- and 10-positions.



Scheme 4. Synthetic route to afford 4,5,9,10-tetramethylpyrene **20.**

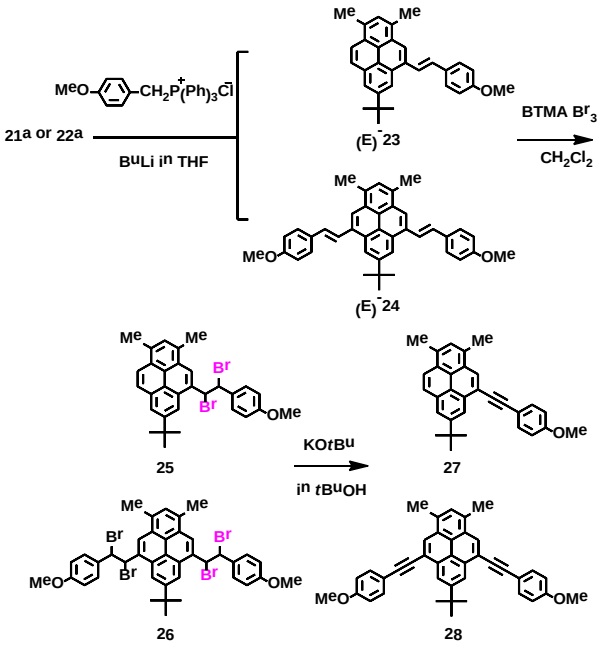
Similarly, we have observed that the regio-selectivity of formylations/acetylations can be controlled by the Lewis acid employed. For example, combining **6** with dichloromethyl methyl ether in the presence of $TiCl_4$ afforded only 7-*tert*-butyl-5-formyl-1,3-dimethylpyrene **21a** in 93% yield, however, in the presence of $AlCl_3$, compound **6** can be converted to 7-*tert*-butyl-5,9-diformyl-1,3-dimethylpyrene **22a** in 80% yield arising from a two-fold formylation at the 5,9-positions. Similar results were observed for aceylation, for example. mixing **6** with acetyl chloride in the presence of $TiCl_4$ afforded 5-acetyl-7-*tert*-butyl-1,3-dimethylpyrene **21b** in 85% yield. By contrast, use of $AlCl_3$ as catalyst resulted in 5,9-diacetyl-7-*tert*-butyl-1,3-dimethyl pyrene **22b** in 95% yield (Scheme 5).[20] It is possible here that the activity of the entire framework has been reduced when the 4-position is occupied by an electron-withdrawing group. In order to furnish further regio-selectivity and electrophilic substitution at the 9-position, a stronger Lewis-acid catalyst should be used. This methodology offered a direct approach for modifying the K-region of pyrene and allowed access to more sophisticated molecules.



Scheme 5. Synthesis of mono- and di-formylpyrene **21** and **22.**

3.2 Witting reaction for substituted pyrene derivatives

The aldehyde-containing compounds can undergo a Wittig reaction, followed by bromination and dehydrobromination to afford arylethynylpyrenes. For example, the pyrene-5-carbaldehyde **21a** and pyrene-5,9-dicarbaldehyde **22a** were converted to the corresponding mixture of the desired (*E*)-/(*Z*)-**23** and **24** by a Wittig reaction with 4-methoxyphenylmethyl phosphoniumylide. Subsequent bromination and dehydrobromination afforded the target compounds 7-*tert*-butyl-1,3-dimethyl-5-(4-methoxyphenylethynyl) pyrene **27** and 7-*tert*-butyl-1,3-dimethyl-5,9-bis(4-methoxyphenylethynyl)-pyrene **28**. Both **27** and **28** displayed high stability, good solubility, and deep-blue fluorescence as well as reversible electrochemical characteristics in solution (Scheme 6).[21] Similarly, following this synthetic strategy, we can introduce the 4-methoxyphenylethynyl group at the 4,9- or 4,10-positions to afford the 4,9- and 4,10-bis(4-methoxyphenylethynyl)pyrenes.[18] The compounds **27** and **28** exhibit bright, deep blue fluorescene in solution(Φ_f = 0.62 for **27** and 0.80 for **28**), and have good solubility and high stability.

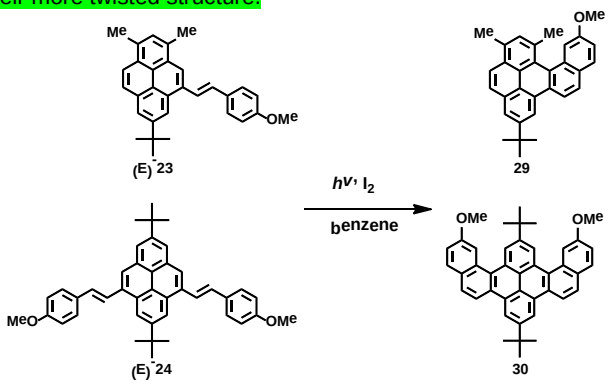


Scheme 6. Synthetic route to 5-mono /5,9-di-substituted pyrenes **27** and **28.**

3.3 Cyclization reaction for substituted pyrene derivatives

PAHs play an important role in synthetic organic chemistry, organic electronic devices,[22] supramolecular chemistry[23] and are also theoretically interesting molecules.[24] Recent efforts have been devoted to the development of new large π-conjugated PAH compounds based on benzene,[25] thiophene,[26] and benzothiophene.[27] Their involvement in Friedel–Crafts-type cyclizations,[28] Zr-mediated and Stille-type biphenylation reactions,[29] and photochemically mediated cyclizations, as well as Scholl reactions has been studied.[30] Recently, various examples focus on the synthesis of extended pyrene skeletons for PAH construction that contained heteroatoms (such as N, O and S). In particular, *pyrene-based heteropolycyclic aromatic hydrocarbons* have been widely reported,[31] but their use to construct large π-conjugated PAH cores is rare.

As described aboved, key pyrenecarbaldehyde intermediates play an important role in the construction of intriguing molecules. In particular, we have synthesized novel types of pyrene-cored blue-light emitting [4]helicenes *via* intramolecular photocyclisations in the presence of iodine (as oxidant) in good yields. The methodology for preparing pyrene-based [4]helicenes is displayed in Scheme 7. A solution of (*E*)-**23** and a stoichiometric amount of iodine in benzene was irradiated at λ > 590 nm, and the photocyclized product 7-*tert*-butyl-1,3-dimethyl-13-methoxydibenzo[ij,no]tetraphene **29** was afforded in only 10% yield. However, the product yield can be much improved (to 70%) by prolonging the reaction time and adding large amounts of iodine and propylene oxide.[32] Similarly, (*E*)-**24** can be functionalized to the corresponding [4]helicenes **30** in good yields by intramolecular photocyclization.[33] This approach opened the door to the preparation of more attractive pyrene-based extended π-conjugation polycyclic aromatic hydrocarbons. The compounds **29** and **30** exhibited a maxmuin emission peak at 419 and 408 nm, compared with **(E)-23** and **(E)-24**, the considerable hypsochromic blueshift of **29** and **30** is ascribed to their more twisted structure.

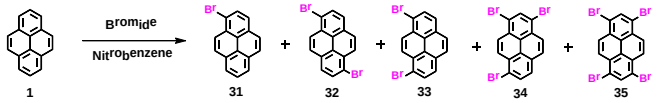


Scheme 7. Intramolecular photocyclisation to afford pyrene-based [4]helicenes **29**–**30.**

4. Bromination of pyrene

4.1 Regio-selective bromination of pyrene

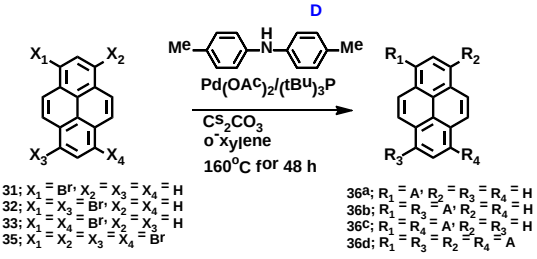
Bromo-containing precursors play a significant role in synthetic chemistry. In particular, the bromine atom of a C-Br bond can easily be converted to a C-C bond, C-N bond or other group by Pd-catalyzed cross-coupling reactions.[34] Given this, it is desirable to explore the effect of this approach on bromopyrene, and to identify key intermediates and thereby open up other avenues for potential future applications.



Scheme 8. Bromination of pyrene to afford **31**–**35**

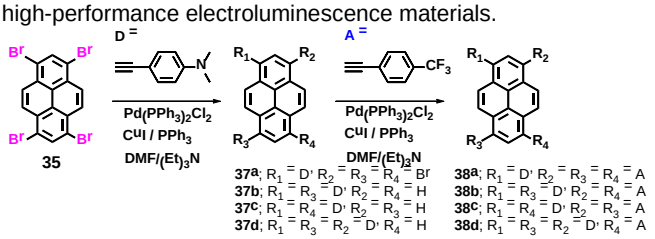
Due to the rather special electronic structure of pyrene, the 1-, 3-, 6- and 8-positions preferentially undergo electrophilic aromatic substitution (S_EAr) reactions, but this does not occur at the other positions (the 2, 7- or 4-, 5-, 9-, 10-positions). Bromination of pyrene **1** with a stoichiometric equivalent of bromide in nitrobenzene afforded 1-bromo- **31**, and the isomers 1,6- and 1,8-dibromo- (**32**) and (**33**) as well as 1,3,6-tribromo- (**34**), and 1,3,6,8-tetrabromopyrene (**35**) (Scheme 8).[15] In this system, on increasing the number of bromine atoms, the solubility of the bromo-substitution pyrenes decreased in the following order **31**>**32**>**33**>**34**>**35**.

Bromopyrenes as key precursors have been thoroughly investigated by our group and others. These bromopyrenes **31–35** as common compounds play a pivatol role in opening up new avenues for constructing highly efficient luminescent materials. The new pyrene-based materials can be obtained by Pd-catalyzed coupling reactions, such as Suzuki,[35] Sonogashira,[36] or Heck,[37] as well as the Buchwald–Hartwig amination reaction[38]. The mono-, di-, tri- and tetra-substituted pyrenes have been thoroughly investigated by chemists.[6a] In particular, 1,3,6,8-tetrasubstituted pyrenes as host materials have been widely applied in OLEDs and OFETs devices as well as in solar cells.[38] For instance, the Buchwald–Hartwig amination reaction of 1,3,6,8-tetrabromopyrenes **31**–**35** with *N,N*-di(4-methylphenyl)amine afforded the 1-, 1,6- and 1,8- and 1,3,6,8-*N,N*-di(4-methylphenyl)amino substituted compounds **36a–e** in good yields (Scheme 9).[39] All compounds of type **36** exhibit bright fluorescent emission from sky-blue to green in solution (λ_{max}=464–500 nm in CH_2Cl_2) and exhibit high emission efficiency (Φ_f= 0.84–0.96 in dichloromethane).



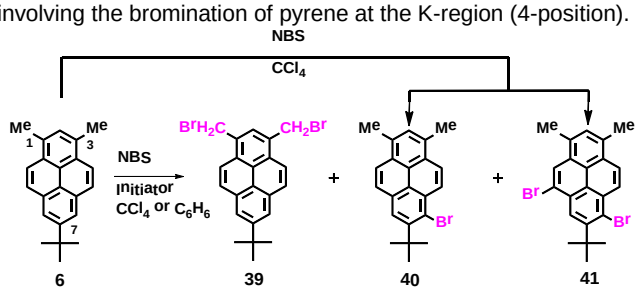
Scheme 9. Buchwald–Hartwig amination reaction to afford *N,N*-di(4-methylphenyl)amino substituted derivatives **36.**

Given that the active positions at the carbons 1-, 3-, 6- and 8- of pyrene have an equal propensity to be attacked, there is a tendency for random substitution to occur, which can result in a multitude of products, the make up of which is determined by the stoichiometric ratio of the starting materials. As shown in scheme 10, Kim et al[40] showed that *N,N*-dimethylaniline and 1-(trifluoromethyl)benzene groups are randomly attached at the 1-, 3-, 6- and 8-positions of pyrene via a stepwise Sonogashira coupling. In this case, although the strategy can offer a set of donor-pyrene-acceptor molecules **38a–d**, the substituent groups and substituted positions are randomly arranged. The above examples inspired us to develop a novel stereocontrolled method for the functionalization of pyrene in order to access high-performance electroluminescence materials.



Scheme 10. Synthetic route to the donor-pyrene-acceptor molecules **38.**

Firstly, on mixing compound **6** with *N*-bromosuccinimide (NBS) in CCl_4 solvent, and using benzoyl peroxide (BPO) as an initiator, we isolated the 1,3-bis(bromomethyl)-7-*tert*-butylpyrene **39** in 10% yield along with products resulting from bromination of the pyrene ring, namely 1-bromo-2-*tert*-butyl-6,8-dimethylpyrene **40** and 1,4-dibromo-2-*tert*-butyl-6,8-dimethyl pyrene **41**. However, in the absence of BPO, we isolated **40** and **41** in 83 and 8% yield, respectively. Meanwhile, the reaction of compound **6** with NBS in the presence of 2,2'-azo(2,4-dimethylvaleronitrile) (V-65) in benzene solution under irradiation by a tungsten lamp afforded the desired bis(bromomethyl) compound **39** in 70% yield. In addition, in the absence of initiator, bromination of compound **6** with *N*-bromosuccinimide (NBS) in carbon tetrachloride resulted in compounds **40** in 83% yield and **41** in only 8% yield. Similarly, in benzene, bromopyrene **41** was obtained in only 7% yield along with recovered starting material (Scheme 11).[41] These results seem to indicate that the solvent and initiator used play a significant role in this bromination process. Based on our knowledge, this is the first example involving the bromination of pyrene at the K-region (4-position).

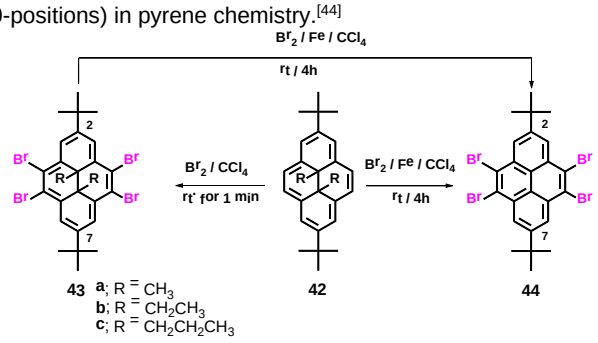


Scheme 11. Bromination of **6** leading to position-substituted bromopyrenes **39**–**41.**

4.2 Iron(III) bromide catalyzed bromination of pyrene

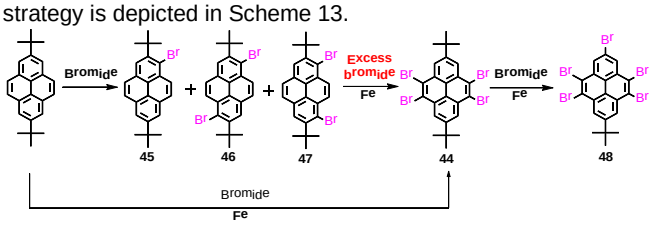
Iron-catalyzed reactions as efficient, clean, environmentally friendly and selective methods have been well-utilized by organic chemists.[42] Iron is an abundant and inexpensive metal, which has been widely used in the field of catalysis[43]. Iron(III)

bromide has been widely used as a Lewis acid for electrophilic aromatic substitutions, and numerous parallel bromination experiments of pyrene were carried out using iron powder / iron(III) bromide / iron(III) chloride catalysts, and the results were fruitful. We observed that iron powder can play a crucial role in the preparation of bromopyrene derivatives. As shown in Scheme 12, in the presence of iron powder, treating **42** with bromine in carbon tetrachloride at room temperature surprisingly afforded the dealkylated compound 2,7-di-*tert*-butyl-4,5,9,10-tetrabromopyrene **44** in good yield. However, in the absence of iron powder, under the same experimental conditions, only **43** was formed within 1 minute and in more than 90% yield. Interestingly, tetrabromopyrene **44** is also obtained by treatment of **43** with bromine in the presence of iron powder, whereas neither $FeBr_3$ nor $FeCl_3$ in CCl_4 reacted with **42**. This is the first example of full halogenation at the K-region (the 4-, 5-, 9- and 10-positions) in pyrene chemistry.[44]



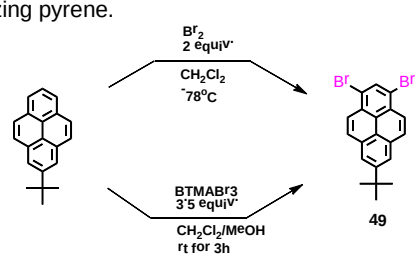
Scheme 12. Bromination of **42** to afford 4,5,9,10-tetrabromopyrenes **43** and **44.**

In our experience, the 4-position undergoes electrophilic substitution via Lewis acid catalysis, to afford 4,9-substituted pyrene products, where the *tert*-butyl group acts as a position protecting group. We carefully examined the experimental conditions for the bromination of 2,7-di-*tert*-butylpyrene and the strategy is depicted in Scheme 13.



Scheme 13. Synthetic route to tetrabromopyrene **44** and pentabromopyrene **48**.

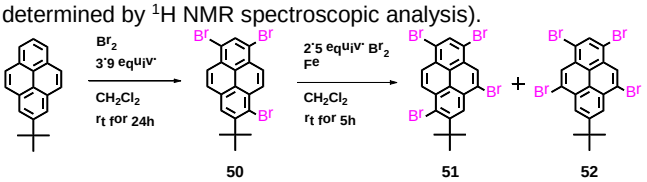
Bromination of 2,7-di-*tert*-butylpyrene with 1.1 moles and 2.2 molar equivalents of bromine in the presence of iron powder afforded 1-bromo-2,7-di-*tert*-butylpyrene **45** and a mixture of 1,6-dibromo-2,7-di-*tert*-butylpyrene **46** and 1,8-dibromo-2,7-di-*tert*-butylpyrene **47** in 85% and 73%, respectively, which can be further brominated with excess bromine under Fe-catalyzed conditions to afford **44**.[45] On the other hand, conducting the same reaction with 6.0 mol equiv. of bromide in the presence of iron powder afforded tetrabromopyrene **44** in 90% yield. Interestingly, on further prolonging the reaction time, a *tert*-butyl group is replaced by a bromide atom and the *ipso*-bromination product 7-*tert*-butyl-4,5,7,9,10-pentabromopyrene **48** is obtained in 85% yield.[46] To the best of our knowledge, this is a first direct bromination approach at the K-region (the 4,5,9,10-positions) of pyrene, which has not only opened up a new pathway to a broad family of C-functionalized pyrenes via Suzuki or Sonogashira coupling reactions, but also offers a new strategy for functionalizing pyrene.



Scheme 14. Synthesis of 1,3-dibromopyrene **49.**

Generally, 1,3-dibromopyrenes cannot be synthesized due to the preference for electrophilic substitution at the 1,6- and 1,8-positions rather than the 1,3-positions. However, by selectively protecting at the 7-position by introducing a *tert*-butyl group as a positional protective group the reactivity behavior can be changed. With this in mind, 7-*tert*-butyl-1,3-dibromopyrene **49** was prepared from 2-*tert*-butylpyrene with bromine (2 equiv.) at -78°C.[47] However, the established experimental conditions are hard to control and tend to afford complex by-products. Fortunately, Yamato et al. established a route which employs milder conditions for the preparation of **49** with an equal yield to the previous route. Compound 2-*tert*-butylpyrene was then treated with $BTMABr_3$ (3.5 equiv.) in dry CH_2Cl_2 at room temperature to give the desired compound **43** in 76% yield (Scheme 14). [48]

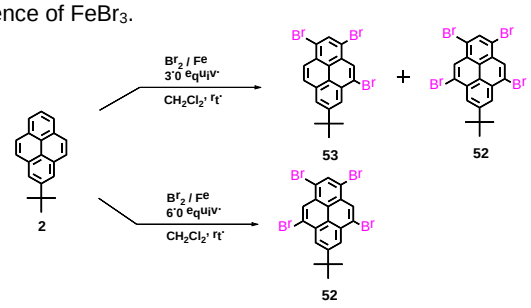
Interestingly, Nakasuji[49] reported a new tri-substituted bromopyrene **50** by direct bromination. Treatment of 2-*tert*-butylpyrene with a large excess of Br_2 (>3.9 equiv.) in CH_2Cl_2 afforded the 1,3,6-tribromopyrene **50** in 67% yield (Scheme 15). We further treated this product with bromine in the presence of iron powder, and observed a number of novel bromopyrene precursors. For instance, reaction of **50** with Br_2 (1:2.5) was carried out in the presence of iron powder, and the isomers 1,3,5,8-tetrabromo-7-*tert*-butylpyrene **51** and 1,3,5,9-tetrabromo-7-*tert*-butylpyrene **52** were obtained in the ratio of 7:3 (as determined by ^1H NMR spectroscopic analysis).



Scheme 15. Synthesis of 1,3,6,-tri-substituted pyrene **50** and tetrabromopyrenes **51** and **52**.

More detailed investigations into the conditions required for the bromination of pyrene using iron powder were conducted. As shown in scheme 16, under iron powder catalysis conditions, a mixture of 2-*tert*-butylpyrene with a stoichiometric amount of Br_2 (1:3~5) in CH_2Cl_2 gave the 1,3,5-tribromo-7-*tert*-butylpyrene products **62** and **63**. When the same reaction was carried out with 6.0 equiv. of bromine in the presence of iron powder, the isolation of 1,3,5,9-tetrabromo-7-*tert*-butylpyrene **62** was achieved in 84% yield.[50] Furthermore, we observed that **62** can be obtained by bromination of **61** in the presence of iron powder in CH_2Cl_2. According to the experimental observations, we speculated that the bromide atom was introduced at the 1-, 3- and 6-positions by a step-by-step procedure to afford the corresponding bromopyrenes.[51] It is also thought that the bromide atom at the 6-position can transfer to the 5-position via a rearrangment process under Fe-catalyzed conditions. To the best of our knowledge, this is the first example of a method to halogenate the pyrene ring both at the active sites (the 1- and 3-positions) and at the K-region (the 5- and 9-positions).

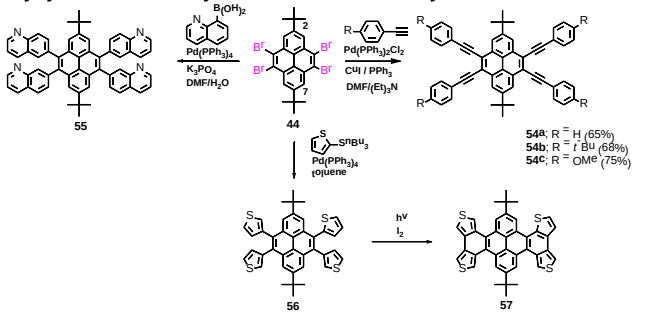
Generally, Iron complexes can be used for ring rearrangements and double bond isomerizations.[19] Here, we present an example of iron complexes employed for intramolecular bromine rearrangement. For this process, when conducting the bromination of 2-*tert*-butylpyrene without iron powder present, only the active sites of pyrene (the 1-, 3- and 6-positions) are substituted by bromide atoms, whereas, with iron powder, compounds **53, 51** and **52** are formed, where the bromine is directed to the K-region (positions 5- and 9-) instead of the more active 6- and 8-positions. There are two reasons that can explain this phenomenon of $FeBr_3$-induced intramolecular bromine rearrangement: one possible reason is a release of the steric hindrance at the *peri*-positions, which could be the driving force for this rearrangement, which is also possible in the absence of $FeBr_3$ where no rearrangement is observed. Another possible reason is that the activation energy of the rearrangement induced would be decreased in the presence of $FeBr_3$.



Scheme 16. Synthetic route of tri-bromopyrene **53** and tetrabromopyrenes **52**

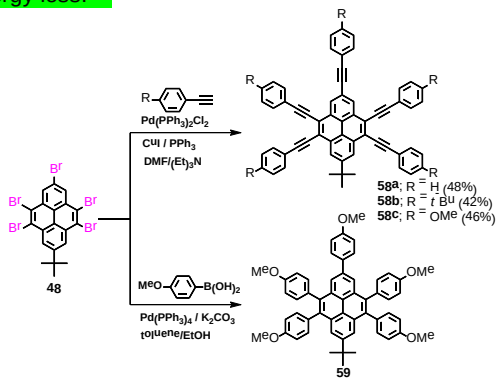
4.3 Coupling reaction for substituted pyrene derivatives

The 4,5,9,10-tetrabromopyrene **44** has undergone Suzuki, Sonogarashi and Migita-Kosugi-Stille coupling reactions, and resulting cruciform-shaped pyrene derivatives have been reported. Sonogashira reaction of 2,7-di-*tert*-butyl-4,5,9,10-tetrabromopyrene **44** with various phenylacetylenes afforded 2,7-di-*tert*-butyl-4,5,9,10-tetrakis(p-R-phenylethynyl) pyrenes **54** in 65–75% yield, which have been used as blue-emitters in light-emitting diodes (Scheme 17).[52] A Suzuki coupling reaction of **44** with quinolinylboronic acid yielded 2,7-di-*tert*-butyl-4,5,9,10-tetraquinolinylpyrene **55** as binucleating ligands,[53] whilst Müllen reported a four-fold stille coupling of **44** with tri-*n*-butyl(thiophen-2-yl)stannane to afford 2,7-di-*tert*-butyl-4,5,9,10-tetra(thien-2-yl)pyrenes **56** in 48% yield. The subsequent irradiation of the cruciform-shaped **56** in the presence of iodine as an oxidant instead of iron(III) chloride afforded, via a photoinduced cyclization reaction, a large non-planar π-system, namely the polycyclic aromatic hydrocarbon **57** in 60% yield.[54]



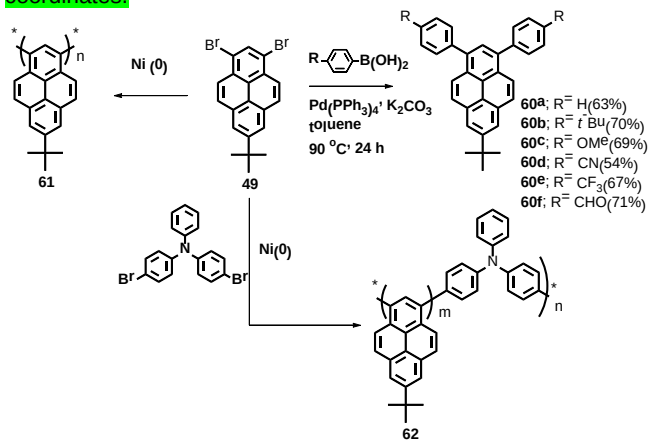
Scheme 17. Synthesis of the pyrene-based derivatives **54–57.**

The 4,5,7,9,10-pentabromopyrene **48** was directly used in Sonogashira/Suzuki couplings as depicted in Scheme 18. We reported the Sonogashira coupling reaction of 7-*tert*-butyl-4,5,7,9,10-pentabromopyrene **48** with various phenylacetylenes to afford the 2-di-*tert*-butyl-4,5,7,9,10-pentakis(p-R-phenylethynyl) pyrenes **58** in moderate yield.[46] The hand-shaped π-conjugated alkynylpyrenes **58** exhibited good stability and blue emission (λ_{em} = 454–463 nm) with high fluorescence quantum yields (Φ_f = 0.46-0.86 in solution, and 0.12-0.32 in thin film), making them potential candidates for optoelectronic applications. However, the Suzuki reaction of **48** with 4-methoxyphenylboronic acid gave 7-*tert*-butyl-4,5,7,9,10-pentakis(4-methoxyphenyl)pyrene **59**, which possessed low solubility and blue-shifted emission (λ_{em} = 414 nm) with low fluorescence quantum yields (Φ_f = 0.24 in solution and 0.17 in thin film); rotation of a single carbon-carbon bond would cause the energy loss.[55]



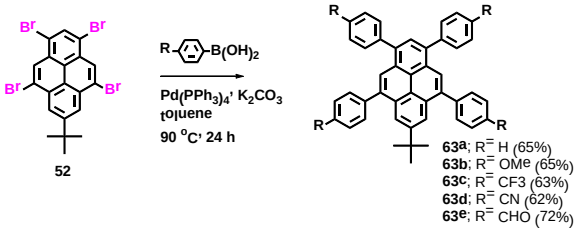
Scheme 18. Synthesis of the hand-shaped pyrenes **58** and **59.**

1,3-Dibrompyrene **49** can be directly used in Suzuki cross-couping or in Yamamoto coupling reactions. As scheme 19 shown, treated bromopyrene **49** with different arylboronic acid in the presence of $Pd(PPh_3)_4$ and potassium carbonate in toluene to provided 1,3-bisaryl substituted pyrenes **60** in good yield.[48] Müllen reported a polypyrene **61**[47a] which was formed by the self-polymerization of monomer **49** via a Yamamoto coupling with a Ni(0) catalyst in 60 yield. The PLED device with the configuration of ITO/PEDOT:PSS30/polypyrene/CsF/Al, exhibited a bright blue-turquoise electroluminescence with a λ_{em} = max = 465 nm and with high efficiencies (0.3 cd/A), luminance values of 300 cd m^{-2} at a bias voltage of 8 V, and the favorable blue color coordinates (CIE coordinates x = 0.15, y = 0.12). Furthermore, the copolymer **62**[56] was synthesized by a Yamamoto coupling with Ni (0) from 1,3-dibromo-7-*tert*-butylpyrene **49** and bis(4-bromophenyl)aniline in 45% yield with weight average molecular weight of M_w = 27400 个 /mol. compared to PLEDs containing pure polypyrene **61**, the PLEDs with copolymer **62** as deep blue emitting layer displayed an enhanced device efficiencies with a high photoluminescence quantum yields of 88%, a maximum luminescence of 0.19 cd/A at 6,4 V, a current density of 1.11 kA/m^2 and (0.13, 0.21) CIE coordinates.



Scheme 19. Coupling reaction to afford the Y-shaped pyrenes **60–62.**

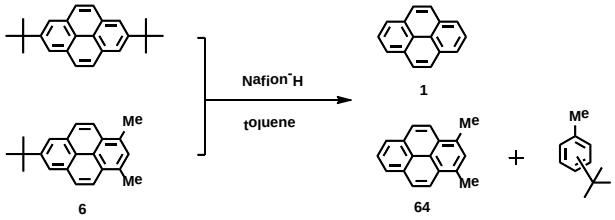
The bromide precursor of 1,3,5,9-tetrabromopyrene **52** can also be employed in Suzuki coupling reactions. Recently, we reported the Suzuki reaction of 1,3,5,9-tetrabromo-7-*tert*-butylpyrene **62** with arylboronic acid to afford aryl-functionalized, butterfly-shaped, highly fluorescent and stable blue-emitting monomers, namely 7-*tert*-butyl-1,3,5,9-tetrakis(*p*-R-phenyl)pyrenes **63** in high yields (Scheme 20).[50,57] These butterfly-shaped pyrene-based compounds possessed high solubility, high stability and blue emission with quantum efficiency (Φ_f) in the range of 0.89–0.92 in solution and 0.72–0.78 in the solid-state, and fluorescence lifetimes (τ = 4.04–12.2 ns) in solution.



Scheme 20. Synthesis of the butterfly-shaped pyrene **63.**

4.4 De-*tert*-butylation of *tert*-butylpyrenes

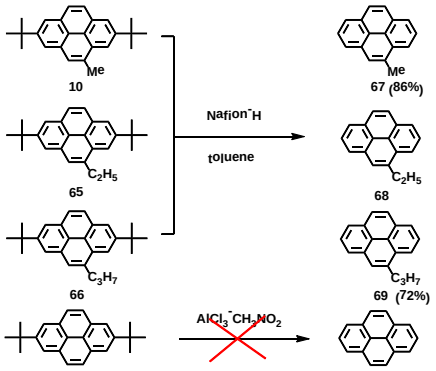
Generally, the bulky *tert*-butyl group in this system could play a significant role, not only in suppressing π-π stacking interactions and preventing excimer formations but also in substantially improving the solubility. Especially, for the pyrene core, a *tert*-butyl group tends to be introduced at the 2,7-positions of pyrene in order to protect the ring against electrophilic attack at the 1-, 3-, 6- and 8-positions. However, the sterically *tert*-butyl group is unfavorable for organic semiconductors, which would influence the packing arrangement and lower the hole mobility in OFET devices. Based on our experience, *tert*-butyl-substituted pyrenes are easily de-*tert*-butylated to the corresponding pyrene derivatives under Nafion-H catalysis.[58-60] For instance, reaction of **6** (or 2,7-di-*tert*-butylpyrene) with Nafion-H in boiling toluene afforded the desired products (**64** or **1**) in 90% and 95% isolated yield, respectively (Scheme 21).[17]



Scheme 21. De-*tert*-butylation of *tert*-butyl-substituted pyrenes to afford **1** and **64.**

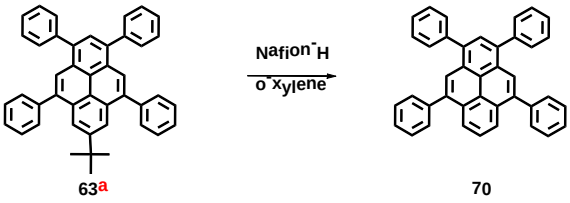
To further investigate the effect of the substituent group at the 4-position for transalkylation, we examined the reaction of 2,7-di-*tert*-butyl-4-methyl-pyrene **10** under Nafion-H catalyzed in boiling toluene, which afforded the 4-methylpyrene **67** in 86% yield (Scheme 22).

In addition, under the same conditions, for 2,7-di-*tert*-butyl-4-ethylpyrene **65** or 2,7-di-*tert*-butyl-4-*n*-propylpyrene **66** in the presence of Nafion-H, the *tert*-butyl group can still be removed in high yield. However, in the presence of $AlCl_3$-CH_3NO_2 as a catalyst, *trans*-*tert*-butylation of 2,7-di-*tert*-butylpyrene does not afford the desired compound **1.**[61] This methodology presents an important strategy for the synthesis of more sophisticated pyrene building blocks.



Scheme 22. De-*tert*-butylation of *tert*-butyl-substituted pyrenes to afford **67**–**69.**

More recently, the bulky *tert*-butyl group has also been removed from 7-*tert*-butyl-1,3,5,9-tetrakisphenyl pyrene **63a** by Nafion-H catalysis to afford 1,3,5,9-tetraphenylpyrene **70** in 51% yield (Scheme 23).[57] However, an attempted de-*tert*-butylation of 7-*tert*-butyl-1,3,5,9-tetrakis(4-methoxylphenyl)pyrene **63b** with Nafion-H under *o*-xylene reflux failed and only a dark viscous residue was obtained. This experience gave us further inspiration to investigate the regio-selective substitution of pyrene along the Z-axis.

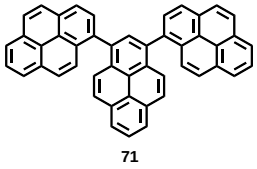


Scheme 23. Synthesis of 1,3,5,9-tetrakisphenylpyrene **79.**

4. 5 Regio-selective substitution of pyrene

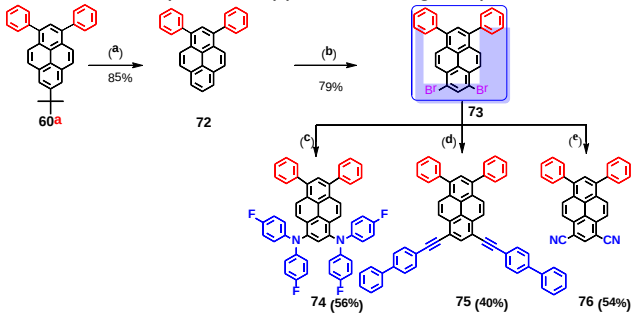
To use pyrene as an effective deep blue-emitter for OLED applications, the most important thing to consider is how to inhibit the formation of the molecular dimer that is responsible for quenching the emission and low quantum yields. The use of a bulky substituent, such as a *tert*-butyl group, is usually adopted, which is introduced at the pyrene skeleton to suppress π–π stacking, thereby preventing excimer formation and improving solubility. However, the *tert*-butyl groups are unfavorable for the desired materials given they may destroy the close packing.[62] On the other hand, although the *tert*-butyl group when located at the 2,7-positions of pyrene can protect the active 1,3,6,8-positions thereby avoiding electrophilic substitution, it has only limited impact on the overall electron distribution of the entire molecule.[63] Therefore, exploring an effective approach for the regio-selective substitution of pyrene at the 1-,3- and 6-,8-positions is an interesting topic in synthetic chemistry.

Although in the absence of a *tert*-butyl group located at the 7-position, 1,3-dibromopyrene cannot be synthesized under experimental conditions, such 1,3-substituted pyrenes have been thoroughly studied by theoretical methods. Zwijnenburg investigated the absorption and fluorescence spectra of 1,3-polypyrene **80** (Scheme 24) by time-dependent density functional theory (TD-DFT) and approximate coupled cluster theory (CC2).[64] The calculations revealed that the lowest singlet excitation is excitonic in nature and that this exciton becomes strongly localized upon excited state relaxation.



Scheme 24. The 1,3-dipyreneyl pyrene **80.**

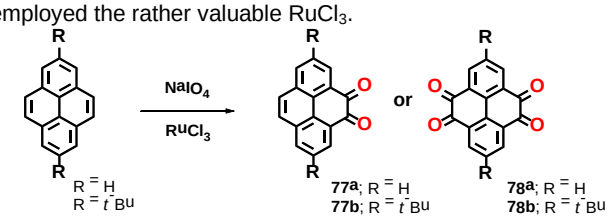
Inspired by this report and our previous work, we explored a new route for the asymmetric selective substitution at the active sites of pyrene. As shown in Scheme 25,[65] three new asymmetric dyes, 1,3-diphenyl-6,8-disubstituted pyrenes were synthesized via efficient regio-selective functionalization at both the 1,3- and 6,8-positions of pyrene. 1,3-Diphenylpyrene **72** was successfully synthesized in 85% yield from 7-*tert*-butyl-1,3-diphenylpyrene **60a** under Nafion-H catalyzed conditions in boiling *o*-xylene. Further, a mixture of **72** with $BTMABr_3$ (1:3.5 equiv.) in CH_2Cl_2 afforded 1,3-dibromo-6,8-diphenylpyrene **73** in 79% yield, which could further be employed in Buchwald–Hartwig amination/Sonogashira/cyanation reactions to afford the 1,3-diphenyl-6,8-disubsituted pyrenes **74**–**76** in 56%, 40%, 54% yields, respectively. The compounds **74**–**76** display blue to sky blue colors with the emission maxima at 488nm, 462nm and 456 nm with high quantum yield (Φ_f = 0.90-0.96) in solution, respectively. Especially, the types pyrenes exhibited obviously an intramolecular charge-transfer (ICT) state. This example presents a revolutionary methodology for the functionalization of the pyrene core along the Z-axis and the resultant dipolar molecules have potential application in organic photonics.



Scheme 25. Regioselective functionalization to dipolar molecules **74**–**76**. (a) Nafion-H, *o*-xylene, 160 °C, 24 h, (b) $BTMABr_3$ (benzyltrimethylammonium tribromide), CH_2Cl_2/MeOH, room temp., 12 h, (c) $NHPh_2F$, $Pd(OAc)_2/(tBu)_3P/K_2CO_3$, toluene, 100 °C, 24 h, (d) 4-Ethynyl-1,1'-biphenyl, $[PdCl_2(PPh_3)_2]$, CuI, PPh_3, Et_3N/DMF (1:1), 48 h, 100 °C, (e) CuCN, NMP, 48 h, 180 °C.

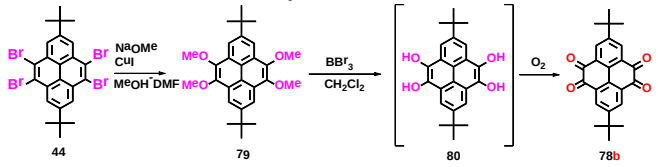
5. Oxidation of pyrenes

No straightforward methodologies had been reported for the oxidation of pyrene at the K-region [17,66] until Harris developed a novel oxidation procedure for the preparation of diteketon and tetraketon in 2005.[67] As Scheme 26 describes, oxidation of pyrene (R = H and *t*-Bu) with $NaIO_4$ catalyzed by $RuCl_3$ in CH_2Cl_2 afforded pyrene diketones **77** and tetraketones **78** on varying the stoichiometry of the bromide reagent. This route employed the rather valuable $RuCl_3$.



Scheme 26. Oxidation of pyrene to afford the ketones **77** and **78.**

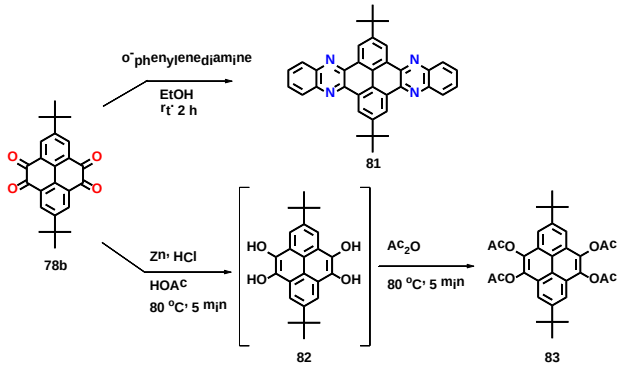
In fact, Yamato reported an indirect approach to oxidation of pyrene at the K-region (the 4,5,9,10-positions) in 1997 (Scheme 27). As an example, the Von Braun reaction of tetrabromopyrene with NaOMe in the presence of CuI afforded the 4,5,9,10-tetrakismethoxy-2,7-di-*tert*-butylpyrene **79** in 78% yield. Following this, demethylation of **79** with BBr_3 in methylene dichloride, followed by air oxidation afforded 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone **78b**.[45] Although the ketones were prepared in two steps, this synthetic route offered a strategy to avoid excessive use of heavy and noble metals.



Scheme 27. Synthetic route for pyrene-4,5,9,10-tetraone **78b**.

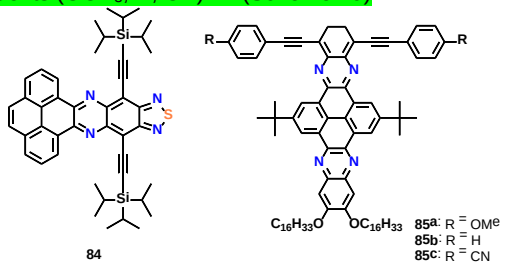
The key intermediate pyrene diketones and tetraketones play a crucial role in the construction of larger π-conjugated pyrene-fused pyrazaacenes, which not only enriches the pool of pyrene-based materials available with unprecedented optoelectronic properties, but also improves the synthetic techniques available for accessing highly efficiency liquid crystalline materials for OLED and OPV applications.[31]

In 1997, we first reported the condensation reaction of 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone **78b** with 1,2-diaminobenzene to afford tetracenes **81** in 90% yield. At the same time, the hydrogenation of **78b** with zinc powder in acetic acid gave quinhydrone **82,** which was not stable and was subjected to a further reduction reaction in acetic anhydride to afford 4,5,9,10-tetraacetoxy-2,7-*tert*-butylpyrene **83** (Scheme 28).[45]



Scheme 28. Synthetic routes for 4,5,9,10-tetra-substituted pyrene derivatives **90** and **91.**

Recently, a popular method involves the design of large π-conjugated pyrene-based luminiscence materials, namely, *pyrene-fused pyrazaacenes* , which were synthesized from pyrene diketones and tetraketones **77** or **78** by condensation.[31a] These intriguing molecules were air-stability, exhibited good solubility and were electron-conducting, attributes that made them potentially good candidates for organic electronics applications.[68] A recent review by Mateo-Alonso has covered the development of *pyrene-fused pyrazaacene*.[31a] For example, the pyrene-fused phenazinothiadiazole **84** exhibits a low LUMO level (-3.83 eV) with higher electron mobilities (μ_e = 0.016 $cm^2 V^{-1} S^{-1}$) in thin films.[69] The T-shaped n-type semiconductor **85** was obtained by a stepwise cyclization and subsequent Sonogashira reaction. The morphologies of the self-assembled structures **85** were profoundly influenced by varying the peripheral substituents (OCH_3, H, CN).[70] (Scheme 29)

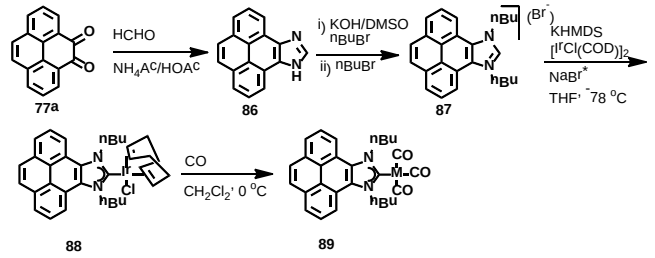


Scheme 29. Pyrene-fused pyrazaacenes **84** and **85.**

On the other hand, pyrene diketones and tetraketones **77** and **78** were involved in a condensation to afford pyrene-imidazole compounds. A set of well defined, pyrene-N-heterocyclic carbene ligands were coordinated with noble metals, such as platinum, rhodium, ruthenium as well as iridium, in order to study the influence of the substitution pattern and stereoscopic effect on the stereoelectronic, photo/electroluminescence properties of the pyrene chemistry.[71]

As scheme 30 shows, condensation of pyrene 4,5-diketone **77** with formaldehyde, and ammonium acetate in acetic acid, afforded 1H-pyrene[4,5]imidazole **86**. The intermediate **86** was

subsequently bisalkylated to the dibutylated pyrene-imidazole **87** that was then deprotonated prior to the addition of [IrCl(COD)] to afford complex **88**. Furthermore, the COD ligands in complex **88** can be replaced by carbon monoxide in CH_2Cl_2, affording the iridium−carbonyl complex **89**.[72]

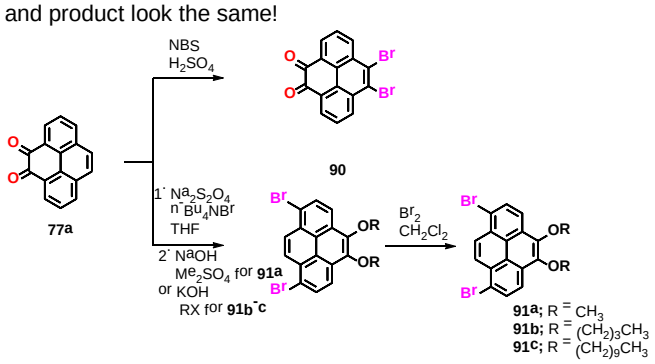


Scheme 30. pyrene-imidazole compounds **89.**

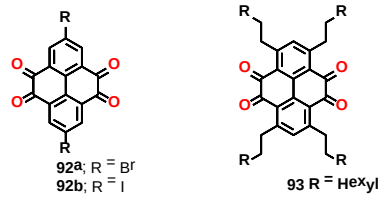
For the pyrene-imidazole complex, the substitution patterns have a negligible effect on the luminescence emission, but the solubility, melting point, and viscosity can be fine-tuned..In particular,, the pyrene-based bisazolium complexes exhibited deep blue fluorescence properties, with emissions in the range of 370–450 nm, and quantum yields ranging from 0.29 to 0.41.[73]

5.1 Asymmetric functionlization of pyrene

As mentioned-above, due to the special electronic structure of pyrene, asymmetric functionlization of the pyrene core remained a challenge in synthetic chemistry. Only a handful of examples have been reported which discuss a synthetic strategy to realize aysmmetric pyrene derivatives for semiconductor material applications. Müllen et al. reported the first example of the direct oxidation and bromination at the K-region of pyrene, producing 9,10-bromopyrene-4,5-dione **90**, which can be utilized as a hole mobility material in OFET devices with high hole mobility.[62,74] For example, bromination of pyrene-4,5-dione **77a** afforded 4,5-dibromo-9,10-diketopyrene **90** in quantitative yield via the use of N-bromosuccinimide (NBS) in concentrated sulfuric acid. Alternatively, alkylation of pyrene-4,5-dione **77a** afforded 4,5-dialkoxy-9,10-dione, which was successively brominated to furnish 4,5-dialkoxy-1,8-dibromopyrenes **91** in liquid bromine.[75] (scheme 31) – check the scheme intermediate and product look the same!



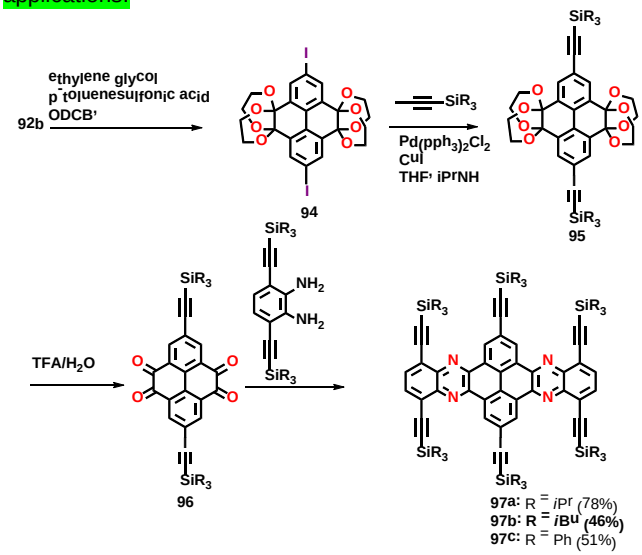
Scheme 31. Synthetic route to asymmetric pyrenes **90**-**91.**



Scheme 32. The reported asymmetric pyrenes **90**-**93**.

Furthermore, new intermediates, namely 2,7-dibromo- and 2,7-diiodopyrene-4,5,9,10-tetraones **92** were synthesized by the halogenation of tetraketones **78a**.[76] Interestingly, oxidation of 1,3,6,8-tetraoctylpyrene followed by Harris's method, afforded a new intermediate tetraketone **93** (Scheme 32) .[77] As mentioned above, the order of the oxidation and halogenation reaction, as well as the bromide reagent are critical for the preparation of pyrene-based precursors.

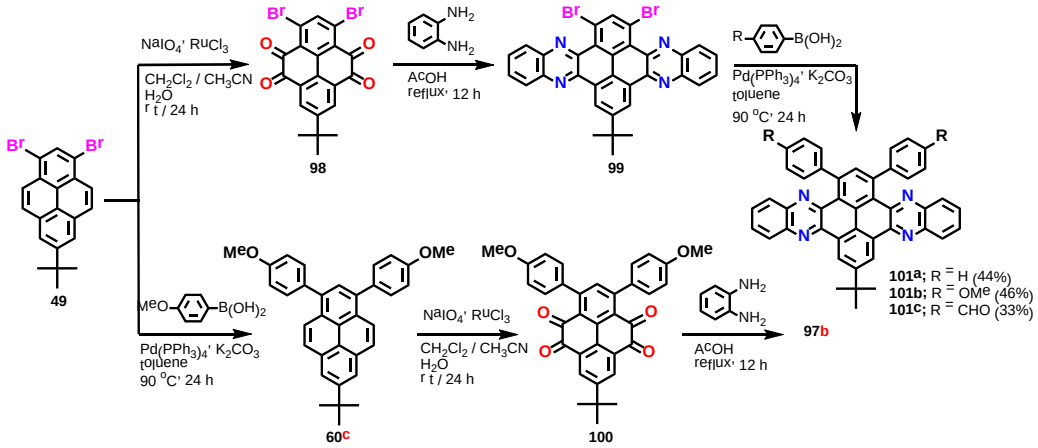
Mateo-Alonso reported twisted pyrene-fused azaacenes.[78] As shown in scheme 33, the ketones were protected by diketals,[79] then, Sonogashira reaction of **94** with acetylenes afforded **95** in good yield (up to 78%), Subsequent deprotection with TFA afforded **96** in >88% yield. Finally, a consdensation reaction of **96** with the requisite diamine afforded **97** in good yield. This type of pyrene-fused azaacene, as electron-deficient organic materials, can be ulitized in electronic and plasmonic applications.



Scheme 33. Synthetic route to twisted pyrene-fused azaacenes **97**.

We explored an innovative methodology to functionalize both the active sites (1,3-) and the K-region (4,5,9,10-) of pyrene by bromination and successive oxidation which proved to be achieveable in considerable yield.[80] As shown in Scheme 34, the key intermediate 1,3-dibromo-7-*tert*-butylpyrene-4,5,9,10-tetraone **98** can be prepared by oxidation of the precursor 2-*tert*-butylbromopyrene **49** using ruthenium(III) chloride ($RuCl_3 \cdot H_2O$) in 35% yield, by a modified Harris method,[70] There are two

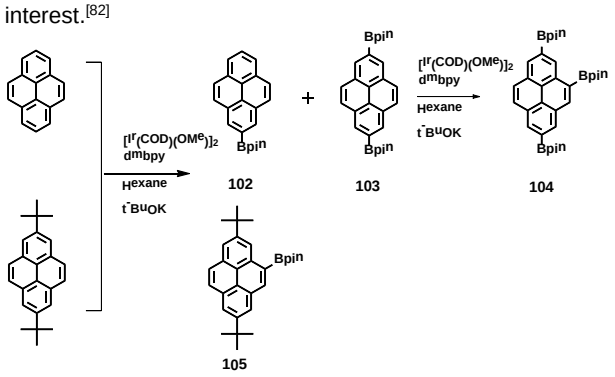
synthetic strategies to access the pyrene-fused azaacenes **101**. Firstly, a condensation reaction of **98** with 1,2-diamine affords **99** in 35% yield, and a subsequent Suzuki cross-coupling reaction of **99** with *p*-substituted phenylboronic acids gave **101** in good yield. The other route is via oxidation of 7-*tert*-butyl-1,3-di-(4-methoxyphenyl)pyrene **60c**, which affords the tetraketone **100** (28%), and then reaction with the 1,2-diamine in acetic acid solution yielding **97b** (80%). This is the first example of both bromination at the active sites (1,3-positions) and oxidation at the K-region (4,5,9,10-positions) of pyrene.



Scheme 34. Synthetic route to the pyrene-fused azaacenes **101.**

6. Borylation of Pyrene

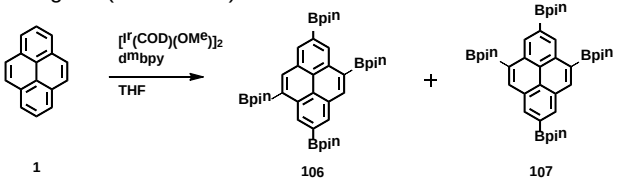
Aryl boronate (boronic acids, boronate esters, and trifluoroborate salts) derivatives are very important synthetic intermediates for the formation of carbon-carbon bonds by transition-metal catalyzed cross-coupling reaction.[81] The development and application of efficient, convenient, selective, and environmentally synthetic routes for the direct borylation of C−H bonds is attracting increasing industrial and academic interest.[82]



Scheme 35. Synthesis of mono-, di- and tri-Bpin-pyrenes **102**-**105**.

Since Marder and co-workers first reported a novel borylation strategy for preparing pyrene-2-boronate esters **102**, and pyrene-2,7-bis(boronate) esters **103** by one-step Ir-catalysis in 68% and 97% yield,[83] many new 2,7-disubstituted pyrene compounds have been reported.[84] Liu reported the regio-selective borylation of pyrene at the 4-position, for example, borylation of pyrene-2,7-bis(boronate) ester **103** with B_2pin_2 in hexane gave 2,4,7-tri-Bpin-pyrene **104** in 62% yield. Similarly, borylation of 2,7-*tert*-butylpyrene under the same conditions, led to 4-Bpin-2,7-di-*tert*-butylpyrene **105** in 45% yield (Scheme 35).[85]

After, Scott et al reported a pure 2,4,7,9-tetrakis(Bpin)pyrene **96** by polyborylation of pyrene using Marders' method in THF solvent, [86] Marder[87] repeated their reaction three times and detected two isomers **106** and **107** in a 2:1 ratio in the absence of t-BuOK. The detailed structures of **106** and **107** have been further confirmed by single-crystal X-ray diffraction. It was claimed that the Ir-catalyzed borylation of pyrene at the 4, 9/10-positions is determined by kinetic selectivity, and that the ligand dmbpy plays a significant role in affecting the Ir-catalyzed C−H borylation by the donor strength of the ligand (Scheme 36).

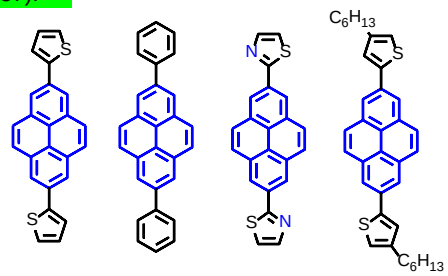


Scheme 36. Synthesis of isomer tetrakis-Bpinpyrenes **106** and **107**.

Boronates not only have open a new possibility in terms of producing new conjugated systems and optical materials by Pd-catalyzed cross-coupling reactions, but also offer an approach for the construction of large π-conjugation system.

For example, a series of 2,7-functionalized pyrene derivatives **108**–**111** have been syntheized by Pd-catalyzed Suzuki coupling reaction of the precursor pyrene-2,7-bis(boronate) esters **103** with the corresponding bromo-substituted (hetero)aryl rings,

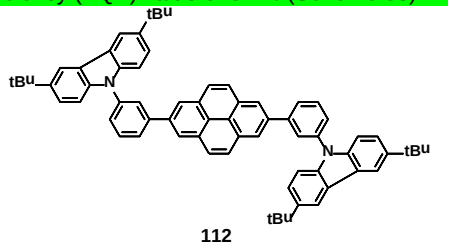
which can be utilize as active layer materials in organic TFTs. The compounds **108**–**111** performed as *p*-type organic semiconductors with a field-effect mobility as high as 0.018 $cm^2 V^{-1} s^{-1}$;, a current on/off ratio of 10^6 for **110** was achieved (Scheme 37).[84b]



108 **109** **110** **111**

Scheme 37. The reported 2,7-substituted pyrenes **108-111**.

On the other hand, 2,7-disubstituted pyrenes show potential for application in OLED devices. Thus, a blue light emitting 2,7-disubstituted pyrene with N-phenyl carbazole moieties was prepared *via* a Suzuki coupling reaction and used as an emitter in OLED devices. The OLED device exhibited deep blue photo-luminescence (CIE: x = 0.16, y = 0.024) and good external quantum efficiency (EQE) value of 3.1% (Scheme 38).[88]



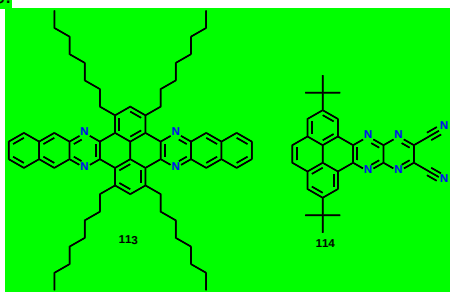
112

Scheme 38. The reported 2,7-substituted pyrene **112**.

4.6 Pyrene-based materials with luminiscence properties

Pyrene-based materials as essential semiconductor materials, have attracted extensive interest in industrial and academic arenas. Due to the planar structure, there is a tendency for pyrene and its derivatives to form excimers in condensed media, and therefore it is necessary to suppress passive π–π stacking interactions by introducing appropriate substituents into the pyrene core. The sterically inhibited, π-stacked 1,3,6,8-tetrakis(2,6-dimethyl-4-methoxyphenyl)pyrenes were explored as blue-emitting materials in OLEDs, with a maximum external quantum efficiency of ca. 3.3%, a maximum luminance efficiency of 2.7 cd/A and with a maximum luminance of 4730cd/m^2.[89] With the increased π-conjugated 1,3,6,8-tetraarylfunctionalized pyrenes, the emission color was shifted from blue to yellow, and the 1,3,6,8-tetrakis(4-butoxyphenyl)pyrene derivative as an active emitter showed high efficiencies (2.56cd/A) with deep blue emission (CIE = 0.15, 0.18), low turn-on voltages (3.0 V) and a maximum brightness of 5015 cd m^{-2}.[90] On the other hand, 1,3,6,8-tetrakis(3,5-dimethylphenyl)pyrene behaved as a host emitter for non-doped OLED devices, and emits excimers of green light with a high maximum luminance of 26670 cd m^{-2} and displays a high maximum current efficiency of 10.8 cd A^{-1}.[91] In addition, on increasing the substituents present, both mono- and tetra-substituted alkynylpyrenes were tested as emitting dopants with the host material 4,4'-bis(9H-carbazol-9-yl)biphenyl (CBP) in a multilayered OLED and exhibited bright blue to yellow electroluminescence.[92]

On the other hand, substituents at the K-region of pyrene can exert interesting optical properties, due to their involvement in $S_1 \leftarrow S_0$ and $S_3 \leftarrow S_0$ transitions, which can cause a hypochromic shift in the emission spectra.[63] For example, 4,5,9,10-tetrakis[(4-methoxyphenyl)ethynyl]pyrene **58c** exhibited pure blue emission with a maximum band at 453 nm, whereas the emisson of 1,3,6,8-tetrakis[(4-methoxyphenyl)ethynyl]pyrene shows a large red-shift with a maximun peak at 477 nm.[52] Similarly, compared with 1,3,6,8-tetrakis(4-methoxyphenyl) pyrene (λem max = 434 nm in solution and (λem max = 488 nm in thin film), the emission of 1,3,5,9- tetrakis(4-methoxyphenyl) pyrene **63b** shows an obvious hypsochromic shift both in solution (λem max = 421 nm) and the solid-state (λem max = 443 nm). [50,57] In addition, in this system, due to the presence of the *t*-Bu group located at the 2- or 2,7-positions, this conformation effectively suppresses any π-π stacking in the solid state.



113 **114**

Scheme 38. The reported pyrene-fused azaacenes **113** and **114**.

According to the literature, most pyrene-fused azaacenes show intensity emission from sky blue to a red color depending on the size of the π-conjugation in the molecule and appended substituents.[31,77-79,93] For instance, the emission spectra of compound **113** showed a peak centered at 478 nm with a shoulder at 454 nm, and the emission bands of **114** display a featureless emission band to the NIR region of 860 nm.[94] However, compound **101** did not emit any fluorescence spectra; this issue will need to be further explore.

7. Conclusions

This mini-review mainly highlights the methodologies employed to functionalize the pyrene core both at the active sites (the 1,3,6,8-positions, the K-region (the 4,5,9,10-positions) and the nodal plane (the 2,7-position) with the aim of constructing fluorescent probes and organic semiconductor materials by

employing formylation/acetylation, bromination, de-*tert*-butylation, oxidation and borylation reactions. This work opens up a promising and active field not only for academic research, but for techological advances in chemsensors, solid-state lighting, and full-color-displays, as well as OPVs and OFETs. Due to the deficiencies in the nature of pyrene, work in our laboratory has mainly concerned optimization of the synthetic methods required for the modification of pyrene. According to our experiments, 1) *tert*-butylation of pyrene at the 2,7-positions can improve the solubility and inhibit π-π stacking - use of Nafion-H as a catalyst can efficiently remove the *tert*-butyl group in this system 2) electrophilic substitution can directly occur at the K-region (the positions 5- and 9-) instead of the more reactive 6- and 8-positions when using iron powder catalysis via a rearrangement process that uses a *tert*-butyl group for protection 3) in the formylation reaction, use of the strong Lewis acid catalyst $AlCl_3$ is more benefical to introduce the aldehyde/acetyl group at the 5,9-positions than use of $TiCl_4$ 4) halogenation and oxidation can be employed to realize asymmetric substitution at the pyrene core, however, the reaction order should be rigorously regulated to afford the desired products. For instance, the 1,3-positions and the 4,5,9,10-positions can undergo regio-selective bromination followed by oxidation, respectively, using a *tert*-butyl as protecting position group, however, if the first step is oxidation at the K-region (partial substitution at the 4,5-positions or full substitution at the 4,5,9,10-positions) of pyrene, then the halogen atom would be attached at the 1,8-positions, 4,5-positions or the 2,7-positions, affording 9,10-dibromopyrene-4,5-dione **90**, 1,8-bromo-4,5-dialkoxypyrenes **91**, 2,7-dibromo- or diiodo-pyrene-4,5,9,10-tetraone **92** depending on the experiment conditions. 5) borylation of pyrene not only occurred at the 2,7-positions, but also can take place at the K-region (4- and 9- or 10-position). The key methodologies mentioned above are central to the synthesis of a variety of pyrene derivatives for application as organic electronics. Examples discussed include *Y*-shaped, butterfly-shaped, hand-shaped and linear molecules all of which have potential application in OLEDs, OFETs and as chemsensors.

Until now, investigations by materials chemists had focussed on the 1,3,6,8-tetrabromopyrenes, however the development of 1,3,5,9-substituted pyrenes has led to a renewed drive to develop new materials based on pyrene chemistry. On the other hand, as syntheses improve, more and more chemists are starting to exploring new synthetic strategies for the asymmetric functionalization of pyrenes, a trend which is likely to prevail in future pyrene chemistry development. Indeed, the design and synthesis of asymmetric pyrene-based luminescence material is becoming a hot research topic and a number of novel D-pyrene-A molecules have appeared over the past five years.[75,95] Herein, this review presents typical methodologies for the functionalization of pyrene to prepare asymmetric luminescent materials. As progress continues, we believe that the mentioned methodologies will become a power synthetic tool, and will have wide impact in supramolecular and materials chemistry.

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Keywords: Pyrene and pyrene derivatives • regio-selective substitution • methodology • organic electronics

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