

Polycyclic Aromatic Hydrocarbons as Potential Building Blocks for Organic Solar Cells

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Dedicated with respect and my deepest affection to the memory of Prof. Michèle Auger who served as a model for many scientists.

Abstract: Since the discovery of graphene in the early 2000's, polycyclic aromatic hydrocarbons (PAHs) have been resurrected and new synthetic tools have been developed to prepare unprecedented structures with unique properties. One application that has been overlooked for this class of molecules is organic solar cells (OSCs). In this account, we present the recent development in the preparation of moderate to low band gap PAHs that could potentially be used as semiconducting materials in OSCs. Our focus is directed toward all-carbon PAHs as well as their polymeric analogs.

Keywords: Polycyclic aromatic hydrocarbons, Carbon-rich molecules, Anthanthrene, Solar cells, Organic semiconductors

1. Introduction

The academic and industrial research on organic solar cells (OSCs) has been a tremendous source of innovation for several areas of science and engineering, including organic synthesis, physical chemistry, solid-state physics and electronics.^[1] Arguably, the development of new materials, both small molecules and polymers, has had one of the most decisive roles in the recent improvement of device performance. In a typical bulk-heterojunction (BHJ) OSCs configuration, a n-type material is mixed in a solvent with a p-type material and the resulting solution is deposited and evaporated on a transparent electrode.^[2] Usually, the p-type material act as both the light-harvesting and the hole-transporting material while the n-type component has the primary purpose of transporting electrons after charge separation in the thin film. The great majority of the materials that have been developed for OSCs in the last ten years obey these “simple” requirements, although an increasing number of publications report n-type materials with

an improved capability of absorbing sunlight, leading to better device efficiency.^[3] Still, the design rules for the ideal materials for OSCs have not changed much in that time span,^[4] leaving the researchers with very few innovative approaches to generate the next breakthrough that will make large-scale production of OSCs a reality. In fact, many (most?) of the known heterocycles and other π -conjugated units that possess at least one heteroatom (N, O, S, Se and even Te) have been used as building blocks, and the number of possible combinations of different moieties that have not been tested is becoming scarce. As a consequence, strategies such as side-chain engineering,^[5] atom replacement^[6] and polymer backbone halogenation,^[7,8] which can be seen as rather subtle structural changes, are widely studied to improve already performing materials in the hope to increase efficiency, often by few tenths of percent.

Because low band gap (~1.6 eV) p-type materials are needed to absorb sunlight efficiently, chemists favor the creation of an intramolecular donor-acceptor complex by coupling strong donor and acceptor functional groups and heterocycles.^[9] Although this strategy has been successful and progress is still being recorded in terms of device performance, we believe that other strategies that did not receive as much attention deserve to be explored. One of them is the use of large polycyclic aromatic hydrocarbons (PAHs) as the main component of light-harvesting materials. The advantages of PAHs for OSC applications are

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many and include remarkable thermal and chemical stability due to the high carbon content (no or few heteroatoms), extended conjugation, planar conformation that yields to strong intermolecular interactions in the solid state and the possibility of tuning the band gap through topological organization of the carbon atoms, especially on the edges. In spite of all these benefits, chemists are still recalcitrant to explore the use of PAHs as potential building blocks for OSC materials, mostly due to their poor solubility, the absence of chemical handles for further functionalization and their “neutral” electronic nature (not donor nor acceptor except few cases). Obviously, changing the various π -conjugated units that the researchers in OSCs area have been dealing with for several years by PAHs or other carbon-rich building blocks is unlikely to eliminate all the limitations associate to the use of organic semiconductors. Nonetheless, PAHs can be seen as nanographenes due to their structural similarities to parent graphene, which exhibit outstanding electronic properties with charge mobility values surpassing silicon. Thus, the legitimate question that we ask is: why not trying to exploit the graphene’s wonderful properties by mimicking its structure to prepare the next generation of materials for OSCs? Some researchers spent a big deal of efforts in this direction, but the use of PAHs has never been more than a potentially interesting alternative in the eyes of the OSCs community. Time will tell if this strategy is fruitful or not, but we would be foolish not to at least take a closer look at it.

In this personal account, we summarize the latest work in the area of PAHs for OSC applications and we share to the readers our vision of the directions that could take the quest

for better materials. We present some families of carbon-rich molecules that we think could be the object of particular interest for OSCs due to their unique optoelectronic properties even though they have never been tested as active component in OSCs. Well-known classes of heteroatom-bearing PAHs such as perylendiimide (PDI), indigo and diketopyrrolopyrrole will not be discussed here.

2. Zigzag-Edged PAHs for OSCs

PAHs with strong acene character are particularly interesting as they usually show low band gap values due to the small number of Clar sextets within their structure.^[10] In fact, increasing the size of an acene (ex. from anthracene to tetracene and further to pentacene) through linear annulation does not add any Clar sextet to the structure, making it less and less stable when the size is increased. This instability comes from their mesomeric form in which a second Clar sextet is created at the expense of the formation of a diradical character.^[11] Thus, under ambient conditions long acenes are easily oxidized, making this class of compound rather difficult to explore for applications that require high environmental stability such as OSCs (Figure 1).

One strategy to increase the stability of such compounds is to fuse them together laterally so the ratio of Clar sextet in the molecule remains the same while keeping the zigzag edge topology. For example, going from anthracene to anthanthrene keeps the Clar sextet ratio identical (1/3 vs 2/6), while



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Jean-François Morin obtained a PhD in chemistry from the Université Laval, Quebec City, Canada, in 2004, under the supervision of Professor Mario Leclerc. His work focused on the design, synthesis and characterization of oligo- and poly (2,7-carbazole)s for organic electronic. He joined Professor James M. Tour’s group at Rice University (Houston, USA) as a postdoctoral research associate where he worked on the development of self-propelled nanomachines on surfaces. In 2006, he moved back to the Université Laval, Department of Chemistry, as a faculty member. His current research activities include the synthesis and characterization of carbon nanomaterials, organic semiconductors and diradical molecules. Prof. Morin has authored more than 80 scientific publications, several book chapters and has 4 patents.

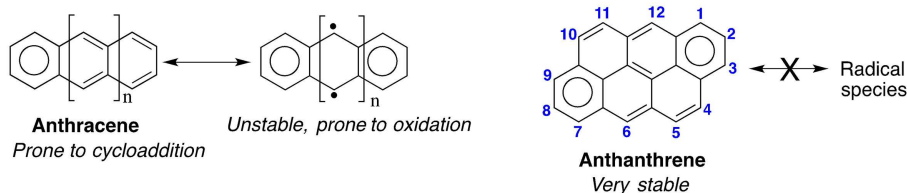


Figure 1. Mesomeric forms of acenes and laterally-fused acenes showing the different stability of both.

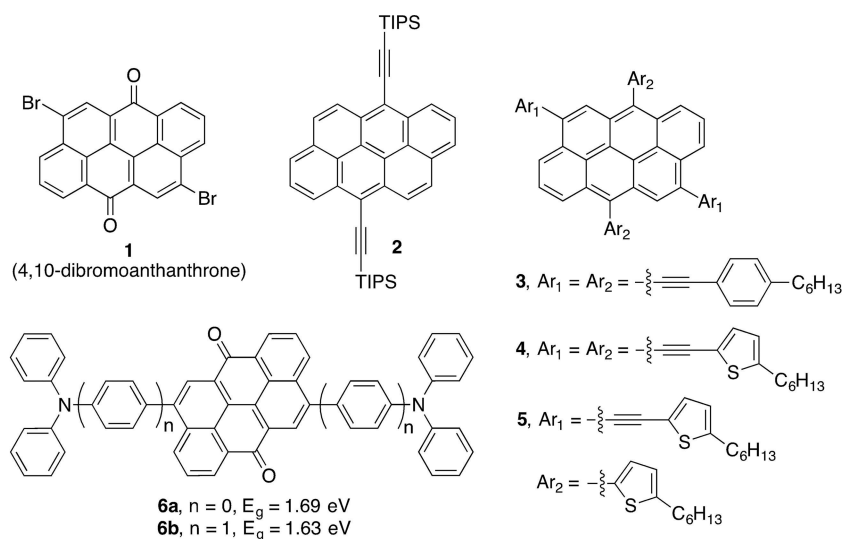


Figure 2. Anthanthrene and anthanthrene-based small molecules for OSCs application.

increasing the overall conjugation significantly. Moreover, unlike linear acenes, mesomeric forms of laterally-fused acenes, called zigzag-edged PAHs (zPAHs) from now on, do not lead to the formation of extra Clar sextets, meaning that they do not exhibit a significant diradical character (Figure 1). Although their band gap values might not be as low as the one of linear acenes with the same number of rings, zPAHs represent a good compromise in terms of stability. Nonetheless, zPAHs have not drawn their fair share of attention for organic electronics, even though they absorb light efficiently in the visible part of the spectrum, organized easily owing to strong intermolecular interactions and exhibit, in several cases, high charge mobility values.^[12,13]

2.1. Anthanthrene-Based PAHs

Anthanthrene and its reduced form, anthanthrene, have been our group's favorite for the past 5 years. Four reasons explain our affection for this molecule: 1) 4,10-dibromoanthanthrone, also named vat orange 3, is a very cheap derivative that is used for multiple applications, mainly textile coloring. In our case, we never had to buy anthanthrene as it has been given

generously by the kilograms by a producer (Heucotech Ltd); 2) with two brominated positions and two ketones, 4,10-dibromoanthanthrone possesses very useful synthetic handles that allowed the functionalization of the aromatic core to modulate the electronic and optical properties, and to perform C–C cross-coupling reactions to make oligomers and polymers; 3) it possesses 6 fused benzene rings, making it a very conjugated molecules with high optical density in the visible region ($\lambda_{\text{max}} \sim 520 \text{ nm}$, $\epsilon \sim 15\,000 \text{ M}^{-1}\text{cm}^{-1}$);^[14] it can be made either electron-accepting or electron-donating by a simple chemical modification at the 6 and 12 positions, making it a highly versatile building blocks for the preparation of donor-acceptor complexes.

Despite all these qualities, relatively few research groups spend efforts to study anthanthrene and its derivatives to prepare organic semiconductors that would be suitable for BHJOSCs applications. To the best of our knowledge, Briseno and coworkers have been the first to demonstrate that anthanthrene could be used as a building block to prepare light-harvesting, p-type materials for BHJOSCs.^[15] In one simple bisalkynylation step, they prepared 6,12-bis(triisopropylsilyl)ethynylanthanthrene (compound **2**, Figure 2) and

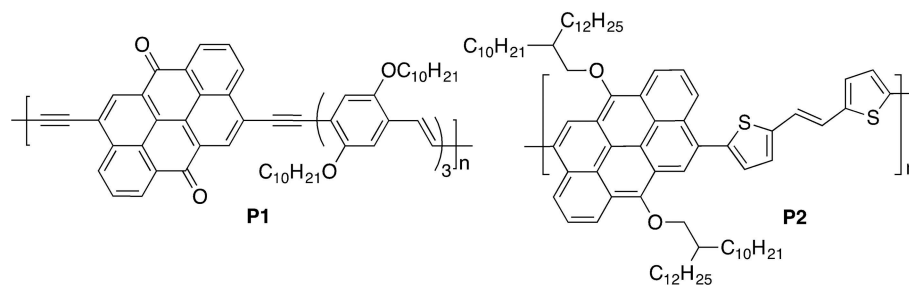


Figure 3. Anthanthrone-based copolymers for OSC applications.

obtained, when mixed with PC_{71}BM in a 1:1 ratio, a PCE value of 1.95 % with a V_{OC} of 0.80 V and a FF value of 0.45 in BHJOSC. Obviously, this value is far from the best reported to date for small molecules due, in part, to poor light absorption beyond 600 nm, but it shows that anthanthrene derivatives can efficiently produce a photocurrent in the thin film. Two years later, our group, in collaboration with Prof. Sariciftci (LIOS, Austria), reported the synthesis and photovoltaic properties of anthanthrene derivatives flanked with either thiophene or phenyl units (compounds **3–5**).^[16] Compounds **3** and **5** gave the best result in BHJOSCs with PCE values slightly over 2%. Again, the low absorption in the low energy region limited the current generation.

The results obtained by Brisenio and us revealed that strategies to lower the band gap of anthanthrene derivatives had to be developed in order to make these derivatives suitable for sunlight absorption. However, lowering of the band gap in anthanthrene derivatives is not as trivial as for other π -conjugated moieties since the four positions that can be modified (4, 6, 10 and 12) all suffer from steric hindrance from the protons in *peri* positions. Thus, the extension of conjugation through these positions has only a slight effect on the band gap (high dihedral angle).^[17] We have shown that the dihedral angle between anthanthrene and other π -conjugated units can be reduced by forming intramolecular H-bonding, but this strategy required the presence of a heteroatom directly attached to the anthanthrene, which limits the choice of functional groups that can be used to modulate the electronic properties.^[18]

One way to reduce the band gap of anthanthrene-based materials is to create an intramolecular donor-acceptor complex between the electron-accepting anthanthrene and electron-rich unit. Our collaborator Daniel Ayuk Mbe Egbe and his coworkers prepared various anthanthrene-based polymers for BHJOSCs applications and they showed that the combination of anthanthrene with a tris(ethylhexyl-*p*-phenylenevinylene) unit, linked together by an alkyne spacer to reduce the dihedral angle, yielded to polymers (ex. **P1**, Figure 3) with band gap values as low as 1.6 eV, which is close to the optimal value for sunlight absorption.^[19] Transforma-

tion of the ketones at the 6 and 12 positions of the anthanthrene by ethylhexyloxy groups to provide the electron-rich 6,12-ethylhexyloxyanthanthrene unit increased the band gap value to 2.0 eV, supporting the hypothesis of the presence of a donor-acceptor complex when anthanthrene is used. As a comparison, Kim and coworkers reported that **P2**, which has a significantly higher band gap value at 2.28 eV due to the lack of a donor-acceptor complex, can be used in BHJOSCs with PC_{71}BM as the acceptor, leading to a PCE value of 3.04 %, mainly due to an optimal film morphology.^[20]

The formation of donor-acceptor complexes with anthanthrene has also been exploited in small molecules to obtain low band gap materials. In our first report on anthanthrene-based semiconductors, we showed that 4,10-bis(diphenylamino)-anthanthrene (compound **6a**), obtained in only one step from commercially available products from a Buchwald-Hartwig coupling, possesses a bandgap of 1.69 eV due to the presence of strong electron-donating diphenylamine moieties at the 4 and 10 positions.^[14] However, this compound did not yield to efficient photovoltaic properties in BHJOSCs. Sellinger showed that the addition of a phenyl between the diphenylamine and the anthanthrene unit yield to a molecule (**6b**) with a slightly lower band gap value ($E_g = 1.63$ eV), consequence of an extended conjugated system.^[21]

Recently, alkoxy-substituted 4,10-bis(diphenylamino)-anthanthrene derivatives were prepared and used as hole-transporting material (HTM) in perovskite solar cells. In one simple synthetic step, Sonar and coworkers created a relatively low band gap D-A-D structure to replace the efficient, yet very expensive Spiro-OMeTAD as HTM.^[22] PCE values of up to 11.5 % have been obtained and interestingly, better reproducibility and environmental stability were observed compared to similar devices using Spiro-OMeTAD as the HTM. Upon structure optimization, the same group showed in a follow-up paper that anthanthrene-based HTMs surpassed Spiro-OMeTAD with PCE value of 17.5 %. The increased efficiency may be attributed to a better electronic match between the perovskite's valence band and the HOMO energy level of the anthanthrene-based HTM.^[23]

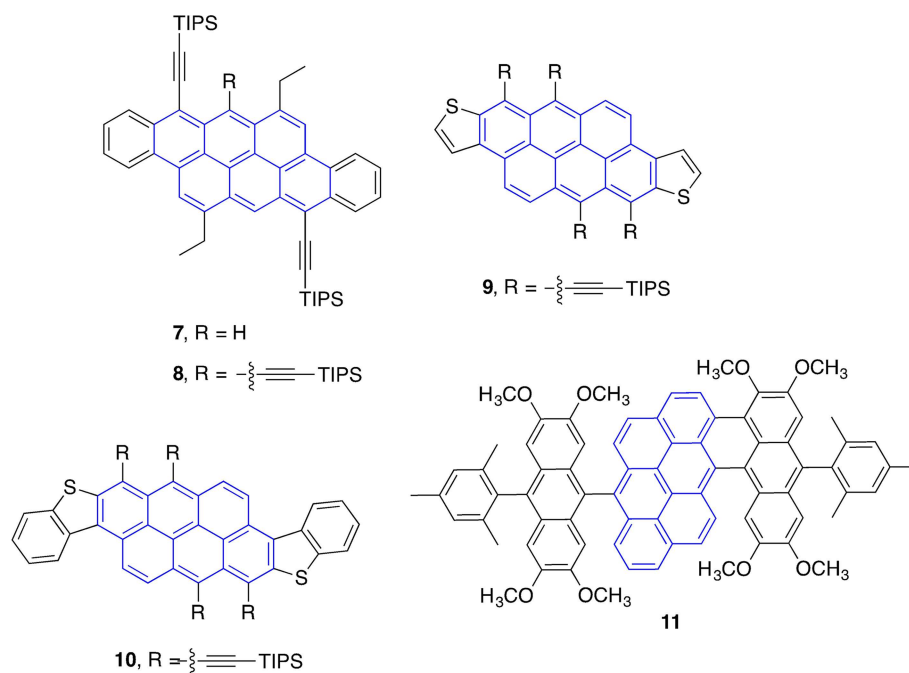


Figure 4. Annulated anthanthrene derivatives. The anthanthrene core is shown in blue.

Another way of decreasing the band gap value of PAH is to extend the conjugation through annulation with other conjugated rings. Tykwinski and coworkers reported in 2016 the synthesis of anthanthrene derivatives annulated with an unsubstituted phenyl at the 2,3 and 8,9 junctions (compounds **7** and **8**, Figure 4).^[24] Through this simple structural modification, PAHs with λ_{max} values as high as 708 nm with a bandgap of 1.65 eV (estimated in solution) have been obtained. However, compound **7** is the result of a side reaction in the synthesis of **8** (11% yield), making difficult its large-scale production for OSC testing.

The anthanthrene core has also been annulated at the 1 and 12 positions using the Scholl reaction of an anthracene-modified anthanthrene derivatives (compound **11**, Figure 4), which absorption band is red-shifted by 181 nm relative to the non-annulated precursor ($E_g = 1.85$ eV from the solution).^[25] All attempts to obtain the all-fused molecule failed due to the high HOMO energy level of the intermediates, leading to oxidation of the aromatic core.

Chen and coworkers exploited the same annulation concept, but used the electron-rich thiophene and benzothiophene moieties instead of phenyl for the annulation (compounds **9** and **10**, Figure 4).^[26] Both compounds absorb light at λ_{max} around 650 nm with band gap values of 1.86 and 1.62 eV (estimated in solution) for **9** and **10**, respectively. Despite their high acene character, both of these compounds exhibit very high photostability, making them promising candidates for OSCs applications. Field-effect transistors

(OFETs) using these molecules as the semiconductor in the thin film state exhibit charge mobility values of $0.019 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $0.012 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **9** and **10**, respectively.

2.2. Other Zigzag-Edged PAHs

Besides anthanthrene, other zPAHs have been investigated for OSC applications in the past few years. Briseno and Watkins were the first to comprehensively explore the properties of this class of compounds for organic electronics applications.^[27] In 2009, Watkins reported the photovoltaic properties of dibenzo [*b,def*]chrysene derivatives (Figure 5) in a BHJ configuration with PCBM as the acceptor.^[28,29] For the best device, a PCE value of 2.25% was obtained (with compound **13**), which were at that time one of the highest values ever reported for a small molecules-based OSCs. The good results have been attributed to the film morphology that exhibit nanoscale phase separation.

To the best of our knowledge, no zPAH with more than six fused rings have been tested in OSCs, presumably due to a lack of efficient synthetic methods to prepare them and for stability issues. Yet, recent progress in the area of synthesis of PAHs could change the way zPAHs are perceived by the organic electronic community. For instance, Amsharov and coworkers reported a very elegant and efficient synthetic method, called the dehydrative π -extension (DPEX), to prepare zPAHs in grams scale (compounds **14–18**, Fig-

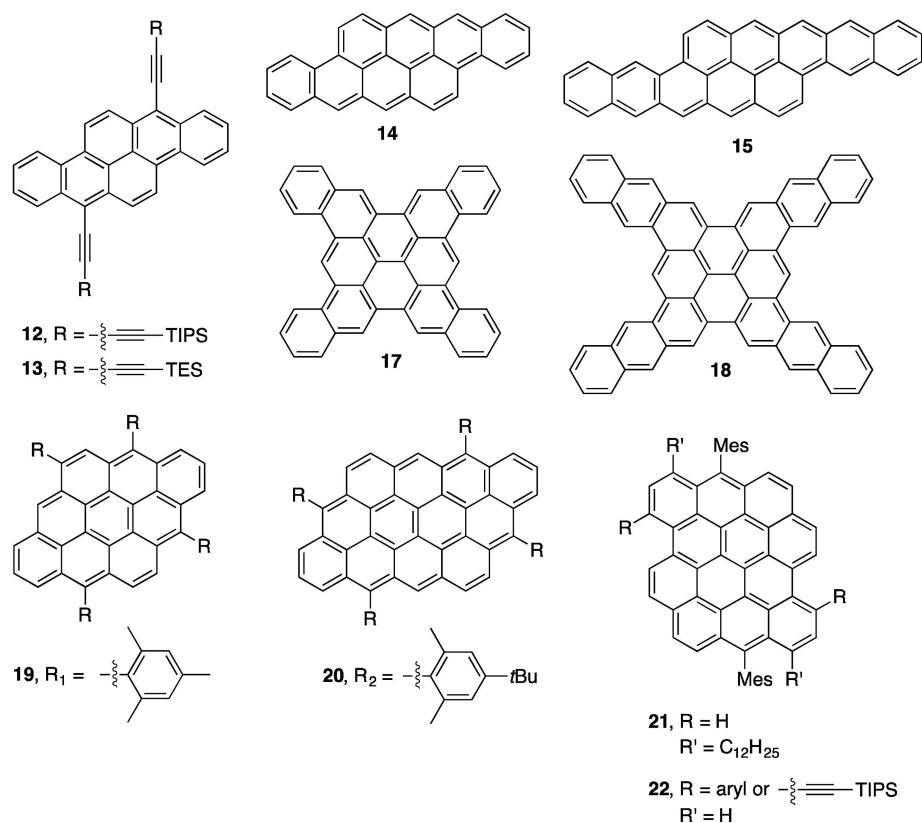


Figure 5. Various zPAHs exhibiting moderate to low band gap values.

ure 5).^[30] Starting from small, properly functionalized naphthalene and pyrene building blocks, they have prepared several stable zPAHs containing up to sixteen fused rings with band gap values as low as 1.62 eV. Because of their acene character, some of these molecules exhibit a moderate diradical character that harm their stability. Addition of bulky substituents such as mesityl or triisopropylsilylacetylene group could be used to further increase the kinetic stability of these compounds.

In this line, Wu and coworkers prepare a series of zPAHs consisting of three rows of fused acenes (compounds **19** and **20**) decorated with bulky substituted aryl groups (Figure 5).^[31] Compound **20**, which possesses twelve rings, is stable despite its bandgap value of 1.40 eV. Interestingly, these compounds can be reversibly oxidized and reduced, making them, along with their strong absorption in the visible region, very promising candidates for OSC applications.

One way to gain extra stability in zPAHs is to disrupt the zigzag pattern at the edge of the molecule. Using this strategy, Narita and coworkers synthesized ovalene derivatives (compounds **21** and **22**, Figure 5) whose upper and lower edges have a zigzag topology while the left and right edges are of armchair type.^[32] Band gap values as low as 1.91 eV have been

obtained with a strong, sharp absorption peaking at *ca.* $\lambda_{\text{max}} = 625$ nm. Most importantly, these derivatives showed excellent stability under ambient conditions.^[33] Again, these derivatives have not been tested in OSCs.

Periacenes is another class of zPAHs that possess low bandgap values.^[34] However, periacene derivatives tend to oxidize rapidly as a consequence of a relatively high diradical character. Even relatively small or annulated periacenes that exhibit good stability under ambient conditions suffer from relatively poor photostability, making them unsuitable for OSC applications.^[35]

In the light of the recent reports discussed above, one can argue that some zPAHs have all the necessary requisites to be efficient semiconducting materials in OSCs: low band gap, good electrochemical properties and high molar absorptivity in the visible region. Nonetheless, the need to attach bulky side groups to stabilize them might prevent good π - π interactions, which is necessary for good charge transport properties. Yet, the presence of bulky side groups is not necessarily detrimental for molecular organization and charge transport as it has been shown several times in John Anthony's seminal work on acenes and their packing properties.^[36] Moreover, little is known about the photostability of zPAHs and more work needs to be

performed before we can count this class of compounds as a member of the OSC materials family.

3. Nanographenes and Graphene Nanoribbons

Since the isolation and characterization of graphene in the early 2000's, there has been a renaissance in the chemistry of large PAHs, commonly known these days as nanographenes. A plethora of new synthetic methods have been developed to prepare novel, unprecedented structures with unique properties, including low band gap and high molar absorptivity. Moreover, efficient strategies have been established to make these molecules soluble, enabling solution processing for fabrication of thin films on large surface. Thus, everything is set for these molecules to be tested in solar cells. Yet, an impressively low number of reports have been published on this topic. Somehow, nanographenes have been overlooked by the organic electronics community who prefer to keep optimizing traditional π -conjugated molecules and polymers. In the following section, we will present some recently reported structures which, to our opinion, could be highly promising for solar cells applications based on their physical properties. Some classes of compounds, which have been reviewed elsewhere such as hexabenzocoronene (HBC) and acenes, will not be discussed here. Also, PAHs and other carbon-rich molecules that possess a low band gap but exhibit a strong diradical (open-shell) character will not be presented as their inherent instability under ambient conditions make them irrelevant for OSC applications.

Simple PAHs such as naphthalene, pyrene and chrysene possess band gap values that are way too high to be used as building blocks for light-harvesting materials. In fact, very few small molecules and conjugated polymers based on these units show high efficiency in OSCs. In addition to their intrinsically high band gap values, these units are generally "electronically neutral", meaning that they cannot be part of a donor-acceptor complex, which is the predominant strategy used to prepare low band gap organic materials. One of the best ways to decrease the band gap value of a given PAH is to perform annulation reactions that will extend its effective conjugation length.^[37] Depending on the nature of the annulated unit and the direction of the π extension, significant change can be induced on the electronic properties.

Chalifoux and coworkers recently used a bay-region-selective alkyne benzannulation reaction on different small PAHs to prepare nanographenes whose absorption spectra extend to the red region.^[38,39] Starting from properly functionalized pyrenes, they prepared pero- and teropyrene derivatives through a four-fold benzannulation reaction using either InCl_3 or a Brønsted acid as the catalyst (Figure 6).^[40,41] Teropyrene derivatives (ex. **24**) are the ones showing the lowest band gap

values at ca. 2.1 eV with strong absorption ($2.8 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) peaking at $\lambda_{\text{max}} = 572 \text{ nm}$. Interestingly, pero- and teropyrene possess an oligorylene core (shown in red in Figure 6), which are known to have low band gap value.^[42] The same group extended the scope of this reaction by showing that domino benzannulation reactions can be used to prepare a series of larger PAHs with different optical properties.^[43,44] Owing to the efficiency and high yield of the alkyne benzannulation reaction, the polymeric analog of these pyrene has been prepared from a poly(*p*-phenylene) derivative (**25**), resulting in a graphene nanoribbon (GNR, **26**) (Figure 6).^[45] This GNR, which is the first example of a polyrylene made from solution-phase synthesis, exhibit a low band gap value of 1.03 eV with an absorption edge of 1200 nm. Information such as the value of the HOMO and LUMO energy level and the thin-film morphology need to be gathered to assess the potential of this material for OSC applications, but based solely on the band gap value, the GNR could be a promising candidate.

Alkyne benzannulation has also been used in combination with cyclodehydrogenation (Scholl) reaction by Dichtel and coworkers to prepare large PAHs that exhibit rather strong absorption in the visible range (compounds **27–29**, Figure 6).^[46] This method was also employed to prepare a wide variety of small, highly functionalized PAHs that could be used as building blocks for larger PAHs.^[47] A GNR using this method has been reported by the same group and tested in OFET, but its limited solubility makes its use in BHJOSC rather difficult to implement.^[48]

Photocyclization is also a very useful tool to form intramolecular C–C bonds, allowing the preparation on large PAHs in few synthetic steps. Nuckolls and coworkers published several reports in this regard in which they used the Katz-modified Mallory reaction to prepare contorted PAHs for various applications, including OFETs and OSCs.^[49] Among others, PAH **30** (Figure 7) has been tested in BHJOSC in combination with PC_{70}BM and a PCE value of 2.9% was obtained.^[50] In another report, the same authors have exploited the high affinity between the contorted hexabenzocoronene **31** and PC_{70}BM to create a self-assembled molecular-scale p-n junction that yield, in optimized conditions, to OSCs with PCE values up to 2.4%.^[51] This result is particularly surprising considering that compound **31** possesses quite a high band gap whose absorption bands are confined in the UV and blue regions.

As illustrated with many examples above, the most intuitive strategy to decrease the band gap value of PAHs is to extend the effective conjugation length through annulation reaction. However, there are cases where reducing the number of conjugated double bonds for a given series of PAHs can also lead to a decrease in the band gap value. This has been exploited very recently by Müllen and coworkers who

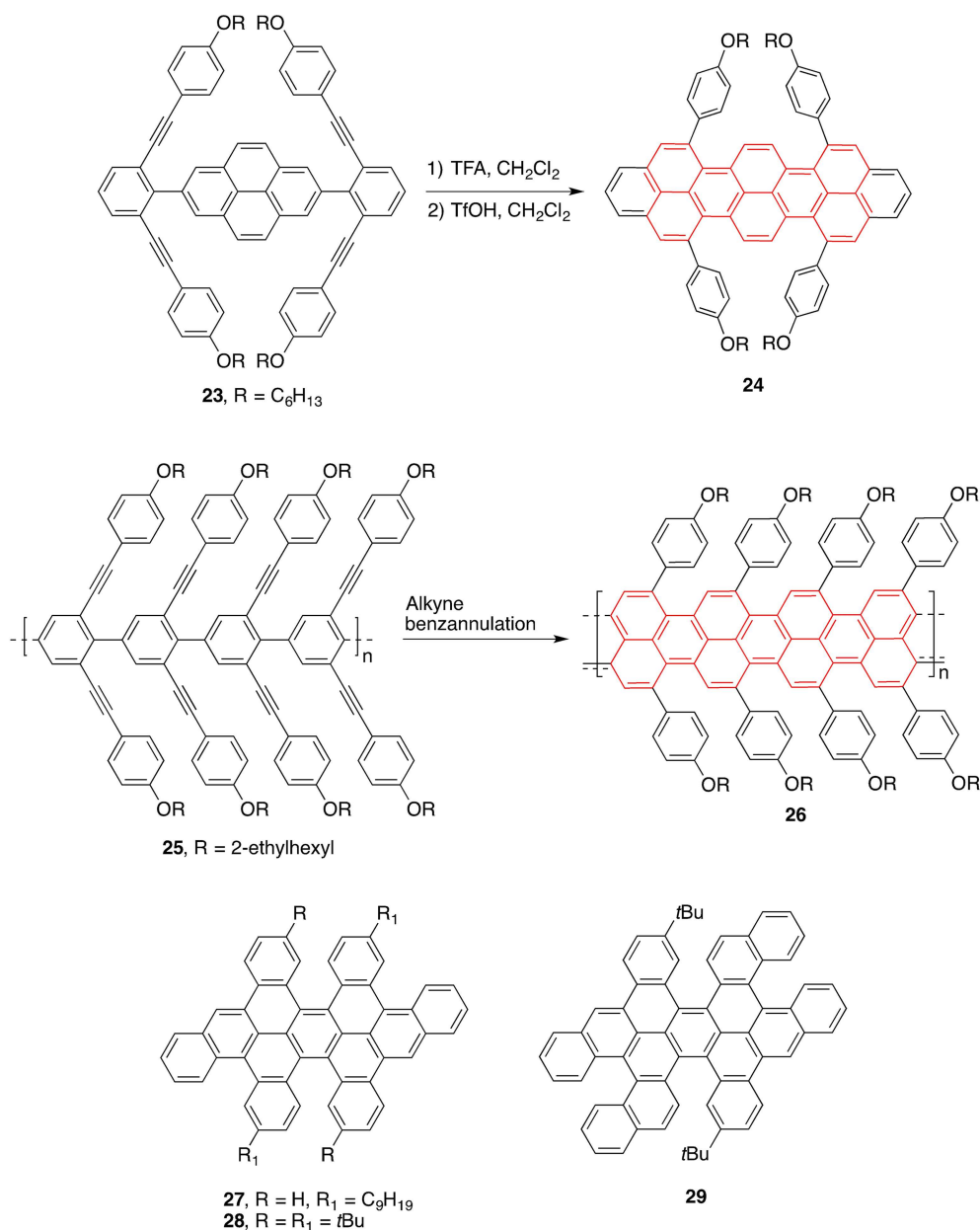


Figure 6. Various PAHs and GNR obtained through alkyne benzannulation.

proceeded to a regioselective edge hydrogenation of the very stable nanographene **32** to give PAH **33** with a circum-biphenyl core whose absorption spectrum in solution is red-shifted compared to the starting nanographene (Figure 7).^[52]

The decrease of the band gap upon edge hydrogenation, called by the authors “ π -truncation”, can partially be explained by the decrease in the number of Clar sextet, from ten in **32** to only two in **33**. Although PAH **33** has not been tested in OSC, this example illustrates that the reduction of the band

gap in PAHs through the reduction of the number of Clar sextets can be an efficient strategy to reduce the band gap.

4. PAHs with Odd-Membered Rings

PAHs with odd-membered rings, especially those possessing 5- or 7-membered rings, are getting more and more popular due to the properties that arise from this structural change.^[53] For example, the introduction of odd-membered rings in a six-

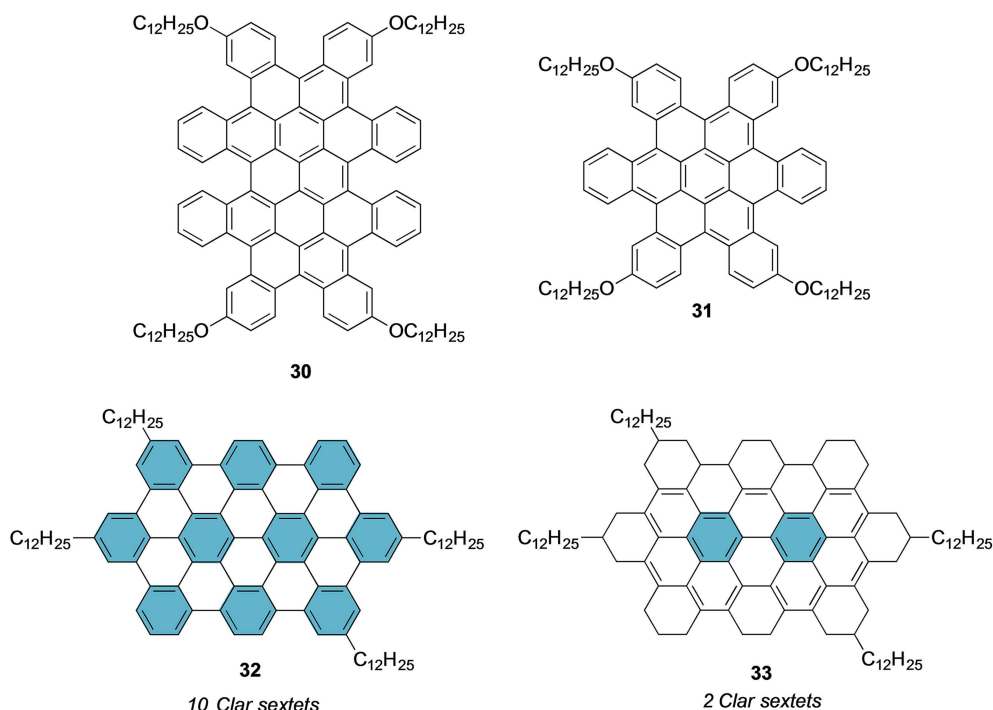


Figure 7. Various all-phenyl PAHs.

membered rings scaffold can induce a significant curvature to the PAH, allowing the synthesis of elegant yet useful molecules.^[54] Corannulene, which consists of a five-membered ring surrounded by five six-membered rings, is probably the most popular structure of all as it is the building block of fullerene C_{60} . In the context of organic electronics, however, the presence of a curvature is not necessarily a desirable feature since the charge transport ability of a given molecule in the thin film state strongly depends on the intermolecular interactions and the π contact. For this reason, chemists usually target flat, symmetrical molecules that self-organized into large array of molecules such as discotic arrangements. To keep the molecule flat with the presence of odd-membered rings, these have to be located at the edge of the PAHs (ex. dicyclopentapyrene) or to be at the core of a linear PAH (ex. indenofluorene). In the following lines, we will focus our attention on recently reported flat PAHs that contain odd-membered rings and possess a relatively low band gap. In some cases, the low band gap values measured can be attributed to formal or partial anti-aromaticity of the PAHs, which can be seen as a drawback for their use in OSCs. Nonetheless, several means of stabilization have been developed and there are good reasons to believe that this class of PAHs could one day become a highly used one in organic electronics.

One of the most promising all-carbon building blocks for organic electronics applications has been developed by

Plunkett and coworkers who synthesized cyclopenta[*hi*]aceanthrylene derivatives (Figure 8).^[55] This unit, consisting of an anthracene core annulated with two cyclopentadiene rings at the edge, is a subunit of C_{70} and is highly electro-deficient due to the partial anti-aromaticity of one of its cyclopentadiene ring as shown in Figure 8. In fact, a two-electron reduction leads to a stable, fully aromatic unit. Interestingly, the dibrominated cyclopenta[*hi*]aceanthrylene derivative, which could be used as a comonomer for the synthesis of a large variety of π -conjugated polymers, is obtained from 9,10-dibromoanthracene in two straightforward synthetic steps. When coupled to rather weak electron donors such as a 4-decyloxy-phenylacetylene, the resulting molecule (**35**) exhibits a large absorption band with an onset at 815 nm in solution, corresponding to a low band gap value of 1.52 eV. Surprisingly, extending the conjugation by using a tetracene core (**37**) does not lead to a significant change in the band gap value while the use of pentacene considerably red-shifted the absorption spectrum.^[56,57] When cyclopenta[*hi*]aceanthrylene is polymerized with 2,5-bis(2-octyldodecyloxy)-1,4-diethynylbenzene or 9,9-didodecyl-2,7-diethynylfluorene, polymers with band gap values of 1.27 eV and 1.42 eV, respectively, were obtained.^[58] Such low band gap values are usually obtained for π -conjugated polymers with several heteroatoms and exhibiting a strong intramolecular donor-acceptor complex. It is noteworthy that cyclopenta[*hi*]aceanthrylene-based

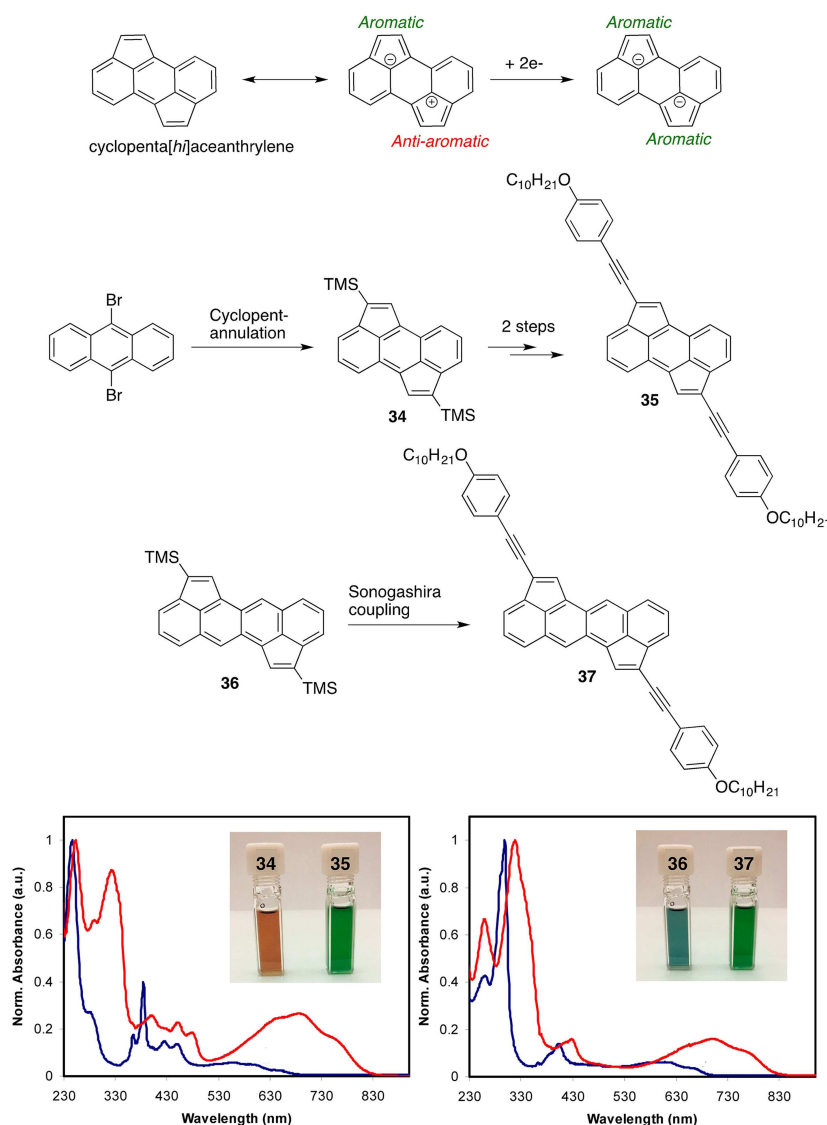


Figure 8. Various cyclopenta[hi]aceanthrylene-based PAHs and their UV-visible spectrum through alkyne benzannulation. Modified from ref. 55 with permission from the American Chemical Society.

polymers possess a LUMO energy level similar to that of PCBM, making them promising candidates as n-type polymers for OSC applications.

Other π -conjugated polymers have been prepared by Plunkett's group by performing with success the cyclopentannulation reaction directly on poly(aryleneethynylene)s (Figure 9).^[59] Conjugated ladder cyclopenta[hi]aceanthrylene-based polymers (ex. 42, Figure 9) have also been obtained by cyclopentannulation between 9,10-dibromoanthracene and 1,4-bis((3-((2-decyltetradecyl)-oxy)phenyl)ethynyl)benzene, followed by a dehydrogenation (Scholl) reaction.^[60] The planarization of the conjugated backbone yielded to the lowest

band gap value ($E_g = 1.17$ eV) ever reported for a cyclopenta[hi]aceanthrylene-based polymer.

In 2013, the same group extended the scope of cyclopenta[hi]aceanthrylene as a building block by preparing orthogonally functionalized derivatives.^[61] When decorated with four thiophene units, absorption bands with onset beyond 1000 nm and band gap values down to 1.22 eV in the solid-state have been obtained. The cyclopentannulation reaction has also been used to extend the conjugation of PAHs such as pyrene in order to prepare new building blocks for π -conjugated polymers^[62] and to prepare contorted PAHs.^[63]

Another way of introducing five-membered rings into PAH is to synthesize pentalene derivatives. Pentalene has been

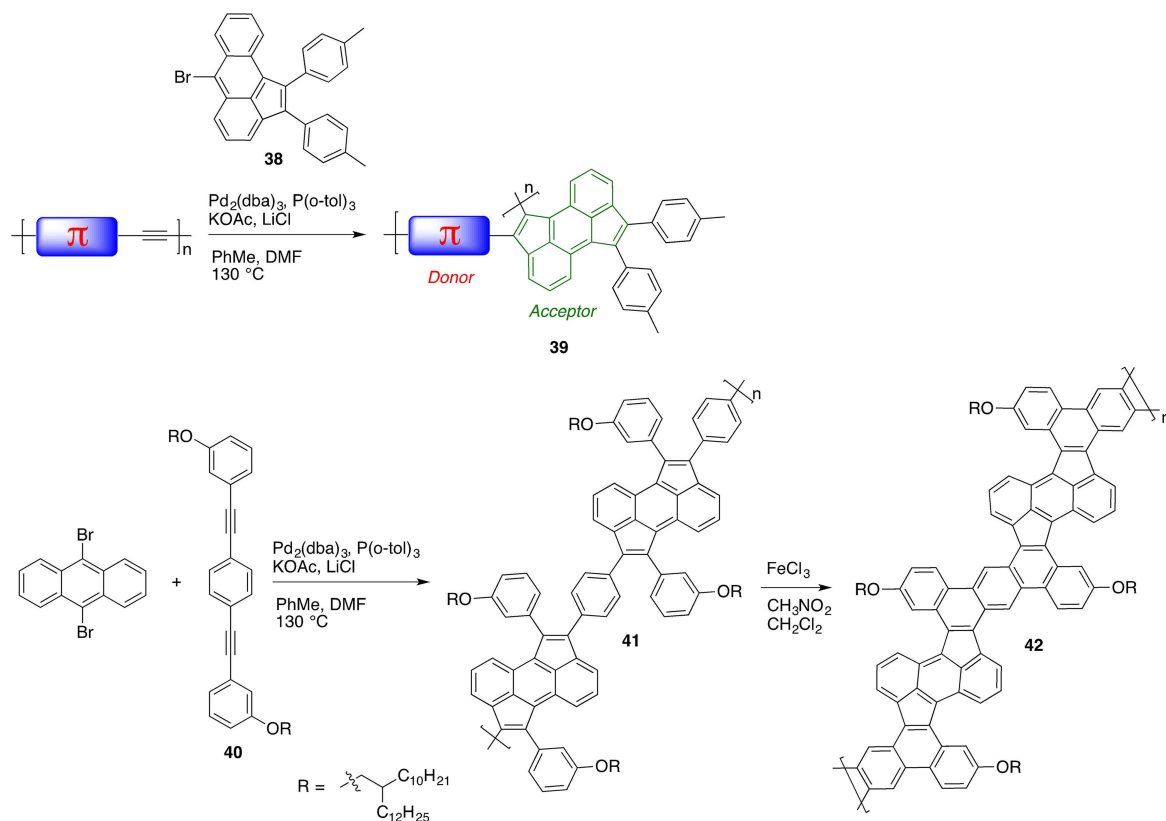


Figure 9. Synthesis of π -conjugated polymers based on cyclopenta[hi]aceanthrylene.

gaining in popularity for the synthesis of low band gap PAHs due to its anti-aromatic (8 π electrons) character. Pentalene itself is not stable enough to be used as a semiconductor, but its annulation with aryl rings increased its stability enough to allow its use as an active component in electronic devices.^[64] Some pentalene derivatives that exhibit a strong diradical character will not be discussed here as they are not likely to be suitable for OSC applications.

The Z-shaped pentaleno-acene dimers reported by Chi and coworkers is a beautiful example of the use of pentalene to obtain low band gap small molecules.^[65] In only four synthetic steps, they have prepared compounds **43** and **44** (Figure 10) which band gap values are 1.41 and 1.17 eV, respectively. Despite their low band gap values, these compounds exhibit surprisingly good photostability with half-life time of up to 54 days (for **44**) upon irradiation under ambient conditions. Both compounds exhibit high optical density in the visible range, and reversible oxidation and reduction electrochemical process.

Dibenzo[*a,e*]pentalenes have been used by Esser and coworkers as a core unit in small conjugated oligomers (**45**, Figure 10).^[66] By changing the nature of the end groups, the electronic properties can be easily modulated, especially the

HOMO energy level. In a separate study, Takamiya and coworkers showed that when dibenzo[*a,e*]pentalenes is copolymerized in either the 6 and 13 or 2 and 7 positions (**46** and **47**), optical band gap values of ca. 1.7 eV are obtained.^[67] Interestingly, the high order of these polymers in the thin film state leads to charge transport mobility values as high as $0.19\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. However, no OSC performance has been reported for these materials.

5. Conclusion and Outlook

The chemistry of PAHs has been resurrecting since the discovery of graphene as an unmatched material for electronic applications. New synthetic tools to prepare unprecedented carbon-rich structures are constantly being reported and chemists' imagination is nowadays the main limitation for the development of new PAHs with unique properties. Nonetheless, the use of all-carbon PAHs in organic electronics, especially solar cells, is still scarce as they suffer from a bad reputation regarding their processability and electronic properties modulation. Yet, we show in this account that many PAHs check all the boxes in regard to the requirements of a

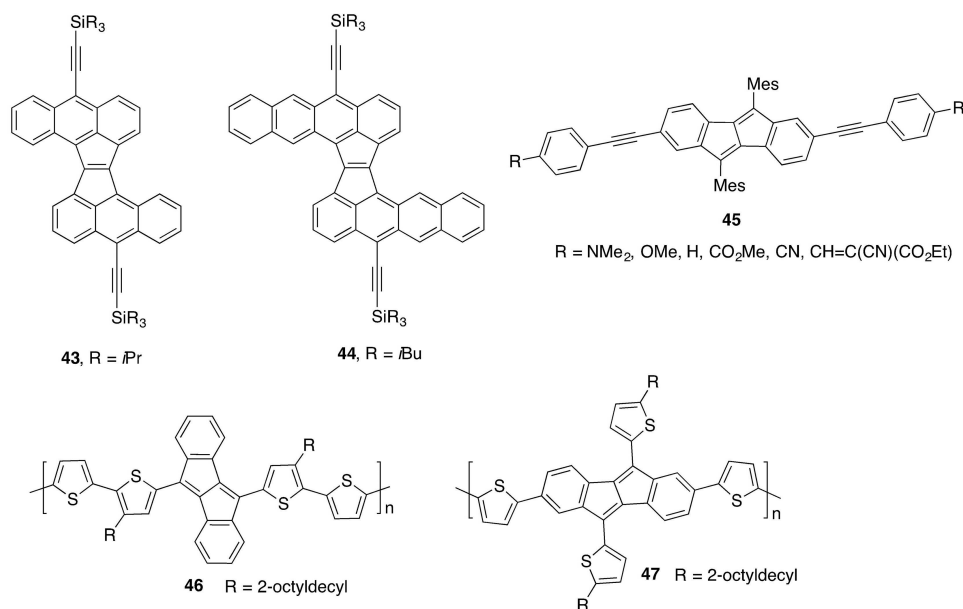


Figure 10. PAHs and π -conjugated polymers based on the pentalene unit.

good organic semiconductor: excellent optical density in the visible range, reversible redox processes, good solubility, tunable band gap and, in some cases, excellent charge transport properties. Obviously, we are not expecting all-carbon PAHs to be the “miracle” materials that will make the traditional π -conjugated polymers irrelevant in solar cells application. However, the researchers involved in semiconducting materials optimization would benefit to include PAHs in their studies and who knows, the next “rare pearl” that could provoke a paradigm shift might be already available.

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