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Conjugated Polymers: Where We Come From, Where We Stand, and Where We Might Go

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Conjugated polymers (CPs) are electronic materials which always attract the joint attention of synthetic chemistry, physics, and engineering. The present article deals with "classical" CPs such as polyacetylenes and polyarylenes, and also with more sophisticated cases such as ladder polymers and graphene nanoribbons. CPs exhibit a wide variety of fascinating electrical and optical properties which qualify them as active components of devices. Their performance, however, is shown to sensitively depend upon structural perfection and purity as well as on the thin-film morphology, which is also influenced by processing procedures. Nowadays, the need for innovative energy technologies and sustainable materials and processes as well as the emerging new opportunities of quantum technologies, are adding further momentum to CP research.

1. Introduction

Most traditional polymers contain saturated chain structures within their backbone and are electrical insulators. That is why their practical applications depend upon their mechanical and thermal properties. Conjugated polymers (CPs), in contrast, possess large domains of mobile π-electrons which qualify them as chromophores and "electrophores." That is, they can transport or even store charges. Not surprisingly, CPs can be constructed from aromatic, olefinic, or acetylenic repeat units. Polyacetylene (PA) and its smaller oligoene model oligomers are textbook cases that can be described with the "electron in a box" model, while a second CP prototype, polyphenylene (PP), is looked upon as a string of benzene rings connected through single bonds (**Figure 1**).

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2. Immense Structural Versatility

The immense structural variations of CPs are fascinating: i) various "hybrids" of PA and PP are possible with poly(phenylene vinylene) (PPV) as the most famous case; ii) benzene can be incorporated in a *para-*, *meta-* or *ortho*-mode which changes not only the steric situation, but also the mode of conjugation; iii) benzene can be replaced by other aromatic units which also offer pathways toward electron-rich and electron-demanding CPs; iv) the connection of aromatic or olefinic moieties can also include exocyclic heteroatoms such as in polyaniline (PANI); v) transition from single-stranded to double- or multi-stranded CPs will not only influence conformation but also create new modes of conjugation such as in graphene nanoribbons (GNRs). This whole scenario will become even more complex in the case of backbone substitution whereby the groups attached exert a profound electronic influence or, as with the case of alkyl chains, modulate solubility- and assembly-related features. Conjugated macrocycles and catenanes are possible as well which raises further electronic and conformational issues because a large "open" ring may also, for example, give rise to the shape of an eight.[1]

From its early times, CP synthesis has come a long way, and structural imagination is tightly connected with the toolbox of synthetic methods. This can best be explained by looking at how the field of CP materials has developed: while there is no doubt that CPs define a strongly interdisciplinary field, "synthesis comes first." Regarding CP synthesis, sound structure–property relationships are only accessible if structural defects can be excluded. Further, polymers come as polydisperse materials so that molecular weight and molecular weight distribution are essential parts of structure proof because they can well–influence the performance of electronic devices.

3. Early Synthetic Access to Conjugated Polymers

A CP material known since the middle of the 19th century, is polyaniline (PANI), but at this time without any idea on its polymeric nature.[2] More than 100 years later, polymer science was fully established as an independent and interdisciplinary research field especially covering chemistry, physics, and engineering. In the 1970s, Shirakawa and co-workers succeeded in producing compact polyacetylene films through surface-catalyzed polymerization of acetylene gas.[3] MacDiarmid, Heeger, and co-workers later demonstrated that these PA films could be doped, either oxidatively or reductively to achieve metallic electrical
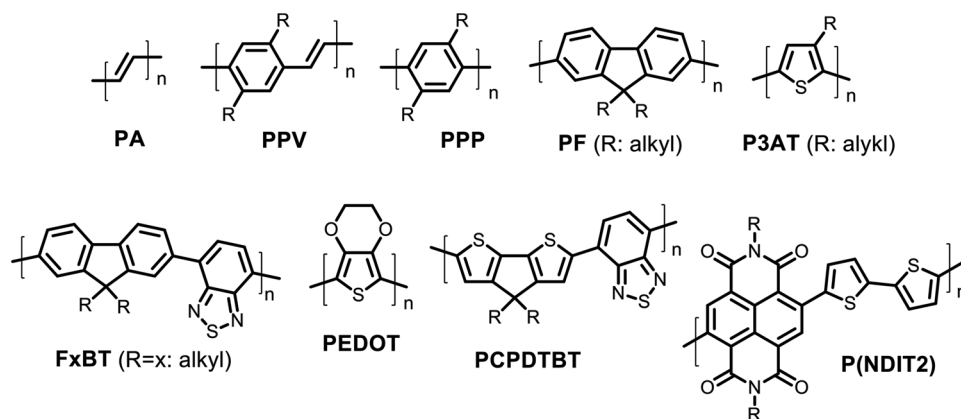
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Figure 1. Chemical structures of CPs discussed in the first paragraphs (R: H, alkyl, or alkoxy of different side chain length).

conductivity.[4] Some years later, Naarmann and co-workers succeeded in increasing the conductivity values of doped PA films up to 20 000 S cm^{-1}, one third of the electrical conductivity of silver or copper.[5] It is, indeed fascinating to blow a stream of acetylene over a catalyst-containing liquid layer, here silicone oil, and to observe how the metallic luster of the solid PA film appears. While this has led to a whole new research field, that of synthetic metals, initial hopes regarding broad technical applications or even replacing copper were not fulfilled due to the low mechanical and chemical stability of the organic conductors. Ways for increasing stability would include encapsulation of the CP chains as "molecular wires" or the design of CPs that are more stable in their doped state rather than in their neutral state (see below). For PA, the main breakthrough was the fabrication of high-quality films of an otherwise insoluble polymer because processability has been and still is the key to device applications. An approach taken toward this end was the development of a so-called precursor route for PA (the Durham route) and this would not have been possible without the input from synthetic organic chemistry: polymerization of a tricyclic monomer through ring-opening metathesis of its strained cyclobutene moiety delivers a soluble but non-conjugated precursor polymer. This film-forming polymer can be thermally converted into the target PA by a polymer-analogous cycloreversion in the solid state, under removal of a volatile benzene species.[6]

Another insoluble lead structure within the class of CPs is the already mentioned poly(*para*-phenylene vinylene)s (PPVs) with alternating phenylene and vinylene moieties. Two main ways for finally processing PPVs into thin films had been developed. First, the polymer films were processed from soluble, ionic PPV precursors, with a thermal post-polymerization step of converting the non-conjugated precursor polyelectrolyte film into the insoluble and non-substituted parent PPV. This approach was developed by Wessling and Zimmermann[7] and later used by Holmes, Friend, and co-workers upon fabrication of the first CP-based organic light-emitting diodes (OLEDs), based on neutral (undoped) PPV films that were stacked between an anode and cathode.[8] Holes and electrons injected from both ends could recombine to form excitons whose energy was released by emission. In simple terms, OLED means "charge in, light out;" which is thus, the reverse of the photovoltaic process. In high efficiency OLEDs, the devices do not only consist of an emitting layer be-

cause charge transport and localization of the charge recombination zone need careful adjustment by additional charge-transport and charge-blocking layers that are assembled into a multilayer stack. In a second synthesis, solubilizing side-groups were directly attached to the PPV backbone which went back to the work of Ballauff and Wegner on polyesters: this has become famous as the "hairy-rod" concept.[9] A somewhat related principle is the attachment of alkyl chains to polycyclic aromatic compounds (PAHs) to be discussed below. There, the substitution does not only promote solubility in organic solvents but also induces the formation of discotic liquid crystals due to the nanophase separation between the hard aromatic cores and soft alkyl shells. The hairy-rod approach was also employed for the synthesis of soluble PPV derivatives by refining an older substituent-free procedure developed by Gilch and co-workers,[10] with poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene] MEH-PPV, first made by Wudl and co-workers in 1993, as prominent example.[11] The polymer-forming step is here, as in the mechanistically related Wessling–Zimmermann approach, a 1.6-polymerization of an in situ-formed, reactive benzoquinone bismethide intermediate. The "improved" Gilch protocol has culminated in the generation of Super Yellow, a copolymeric PPV derivative developed by Covion (now Merck). There, the side-chain pattern of a random PPV copolymer was carefully optimized. Super Yellow was widely used for the fabrication of solution-processed OLEDs.[12]

From a mechanistic point of view, the polymerization of acetylene into PA and the precursor routes to PPV are two eye-catching examples where CP syntheses use typical chain-growth polymerization procedures for polymer generation, based on unsaturated, non-aromatic monomers.

4. Transition Metal-Catalyzed Couplings Come Into Play

Not surprisingly, soluble PPVs can also be synthesized by classical methods of connective C–C-double bond formation through the reactions of electrophilic and nucleophilic carbon species. A breakthrough in the CP field was the development of powerful transition metal-catalyzed C–C-bond formation schemes allowing aryl–aryl, aryl–vinyl, and aryl–ethinyl couplings as novel polycondensation methods. The importance of these synthetic techniques for organic chemistry can hardly be overestimated as

indicated also by the related Nobel prizes. The Suzuki–Miyaura coupling for connecting two arenes combines a boronic acid or ester with a halo or triflate component. Schlüter, Wegner, Feast and co-workers employed this method toward the synthesis of soluble 2,5-dialkyl-substituted poly(1,4-phenylene)s PPPs by an AA+BB polycondensation scheme. These 2,5-dialkylated PPPs represent another prime example of the "hairy-rod" concept in transferring the Suzuki–Miyaura reaction to the world of polymer chemistry.[13] Importantly, this protocol is not restricted to homocoupling but can also connect different arenes in an alternating fashion. Polyarylenes and polyheteroarylenes are of key importance for the whole CP field because they do not contain thermally or photo-reactive double or triple bonds, as present in PA, PPVs, or in the also established CP class of poly(para-phenylene ethynylene)s (PPEs) with their alternating phenylene and ethynylene units.[14] Poly(arylene ethynylene)s with bulky arylene groups are characterized by a high amount of free volume in the solid state and their fluorescence has been used for the design of thin-film sensor devices.[15]

A next pioneering step forward was the synthesis of regioregular 3-alkyl-substituted poly(2,5-thiophene)s (P3ATs), with the best known P3HT having hexyl side chains, by adapting Kumada-type cross-coupling procedures (McCullough and co-workers),[16] or related protocols using zinc-organic compounds (Rieke and co-workers).[17] Interestingly, these polycondensation reactions produced narrowly distributed polymer samples (PDI < 1.3) as result of a unique catalyst-transfer coupling mechanism. This principle could also be applied to Suzuki–Miyaura-type PPP syntheses,[18] as demonstrated by Yokozawa and co-workers. Such catalyst-transfer procedures due to their quasi-living character, allow for a proper molecular weight control, as well as the stepwise generation of conjugated diblock copolymers that contain different polyarylene and polyheteroarylene blocks.[19] Polythiophenes are inherently electron-rich and 3,4-disubstitution of the thiophene repeat units with alkoxy groups further increases the electron-donating character as realized in the PT derivative poly(3,4-ethylenedioxy-2,5-thiophene) (PEDOT). PEDOT exhibits a high stability in its p-doped state (often PEDOT-PSS with polystyrene sulfonate PSS as polymeric counterion) if compared to neutral PEDOT.[20] PEDOT-PSS is commercially distributed as film-forming dispersion for the formation of electrically conductive coatings or electrodes. The percolation mechanism for charge–carrier transport is remarkable because relatively short conjugated chains are embedded in PPS of rather high molecular weights.[21] Very recently, the electrical conductivity of p-doped PEDOT-based materials could be improved to values of >3000 S cm^{-1},[22] which is still ≈one order of magnitude below the record values for doped PA.[5a] PEDOT-related electron-rich poly(3,4-dialkoxythiophene)s have been widely used for the generation of electrochromic films that display distinct color changes when switched between their neutral and oxidatively doped (polaronic and bipolaronic) states.[23]

5. The Problem of Backbone Conformation

In polyarylenes, the steric hindrance of the three ortho-substituents (H, alkyl, and alkoxy) causes torsion about the inter-ring bonds; and thus, hampers an extended conjugation. In the initial poly(2,5-dialkyl-1,4-phenylene)s of Schlüter and co-workers, the 2,5-dialkylated phenylene subunits are almost orthogonally arranged; thus, leading to a negligible amount of intrachain conjugative interaction. Further, this interaction is always reduced in single-stranded CPs due to the existing conformational freedom. Exclusively hydrogens in the ortho-positions of the phenylene-phenylene linkages in polyphenylenes and related polyarylenes or one ortho-alkyl substituent in CPs from 5-ring heteroaromatic units (e.g., polythiophenes as P3HT) ensure an effective conjugative interaction along the backbone.

A partial solution of this problem for PPPs is to avoid solubilizing alkyls in the ortho-positions. This can be realized in polyfluorenes as prototypical "hairy-rod" CPs without ortho-alkyls at the aryl–aryl connections. High molecular weight and structurally defined polyfluorenes (PF) could be made in Suzuki–Miyaura-type polycondensations by using AA + BB-type monomer couples, as first demonstrated for 9,9-di-n-octyl-substituted PF (PFO or PF8, "O" or "8" for octyl) by Inbasekaran and Woo (Dow Chemicals) in 1997.[24] In addition, a reductive, transition-metal-mediated homocoupling of 2,7-dibromofluorene monomers has been developed, first in 1996 with Ni(II)/Zn as transition metal/reducing agent couple,[25] and 3 years later in an elegant approach with Ni(COD)$_2$ in stoichiometric amounts as single coupling agent (Yamamoto-reaction).[26]

Polyfluorenes PFs and copolymers derived thereof have played an important role for polymer OLEDs due to their emission in the blue; although, at a slightly too low wavelength for human vision. Using larger planarized oligophenylens such as indenofluorenes en route to so-called step-ladder polymers caused the desired bathochromic shift.[27] Interestingly enough, fully ladderized polyphenylenes, which marked our own access to the field, came before the step-ladder polymers.

Polyfluorenes PFs have also served as suitable model systems for the study of supramolecular chirality. Many works toward circularly polarized photo- or electroluminescence (CPL, CPEL) emitters were focused on CPs that carry alkyl side chains with stereogenic carbon centers.[28] Here, the side chains induce a chiral, supramolecular packing of helically arranged main chains which is achieved in the condensed state.[29] In solution, the high conformational freedom of the PF main chains prevents the occurrence of chiroptical effects on the level of isolated polymer chains. During the last years, this supramolecular chirality of bulk polyfluorenes and related fluorene-based copolymers (especially alternating fluorene-benzothiadiazole copolymers FxBT, see Figure 1) came into focus, mainly because of the observed very large chiroptical anisotropy values of circularly polarized photoluminescence. Recently, the formation of so-called blue liquid crystalline (LC) phases ("blue phases") was postulated for corresponding polyfluorenes and copolyfluorenes with chiral alkyl chains as well as for their achiral counterparts where the (co)polymers were doped with suitable chiral additives/helical twisting agents.[30] However, a final and conclusive interpretation of the experimental findings is still missing and the nature of the LC phases formed is still a matter of debate. In constructing chiral polymers with "intrinsic" chirality, giving rise to chiroptical effects already in the non-aggregated state, chirality of CPs can be achieved by incorporating suitable, mostly axial or planar, chirality elements into their main chain. However, the observed chiroptical effects at the single-chain level are only moderate.[31]

Another issue is the occurrence of defects in polymer synthesis, whether in a direct process or in a precursor route. Thus, failure to form a double bond in PPV synthesis via the Wessling–Zimmermann- or Gilch-process can not only interrupt the conjugation[32] but also furnish defects acting as traps of excitation energy. A related problem has been seen for poly(9,9-dialkylfluorene)s where oxidatively generated fluorenone defects can severely obstruct the optical and OLED device properties of polyfluorenes, especially in the solid state.[33]

6. From Homopolymers to Alternating Donor–Acceptor Copolymers

Leaving the world of homopolymers, donor–acceptor (DA) copolymers that are composed of alternating electron-rich and electron-poor subunits have defined another milestone in the CP field. They are often characterized by shifting electronic transitions toward lower excitation energy due to the occurrence of intrachain charge–transfer interactions. For their synthesis, Stille-type (hetero)aryl-(hetero)aryl couplings are often adapted. The DA approach has significantly contributed to the performance progress of potential device applications for CPs: For organic field-effect transistor devices (OFETs), for example, an alternating naphthalene diimide–bithiophene copolymer P(NDIT2) has defined a breakthrough for n-type-conducting, polymer-based OFETs.[34] Already before that, alternating cyclopentadithiophene-benzothiadiazole copolymers PCPDTBT with different lengths of their solubilizing alkyls had been used as active layer in very high mobility p-type polymer OFETs[35] as well as allowing for the generation of improved organic photovoltaic (OPV) devices. OPV devices built from PCPDTBT/PCBM have been the first with power conversion efficiencies (PCEs) exceeding 5%; thus, outperforming P3HT/PCBM-based OPV cells as the record holder at that time.[36] After the introduction of non-fullerene acceptors as replacement of PCBM as fullerene-derived acceptor components, the power-conversion efficiencies (PCEs) of OPV cells have been continuously increased during the last 15 years, up to values of >19% for single and tandem cells today; for some examples, see ref. [37]. Despite the continuous and impressive progress in device performance, other questions arise, for example, with regard to the reproducibility of materials syntheses and manufacturing processes, an upscaling of both procedures, the price of materials, devices and modules, the operational and shelf lifetime of the OPV solar cells/modules, as well as the overall ecological footprint of such an OPV technology. Without any doubt, these issues will become increasingly important when trying to put CPs to work.

During the last decade, several research groups developed a modified polycondensation procedure aiming to replace the toxic, environmentally questionable tin-organic monomers of Stille-type cross-coupling polycondensations. The approach is called direct arylation polycondensation (DAP) and uses non-activated monomers instead of substituted ones.[38] Until now, several of these approaches are hampered by the formation of defects such as misconnections, branches or crosslinks[39] and more work is needed to demonstrate the real potential of direct arylation protocols for producing CPs acceptable for sophisticated device applications.
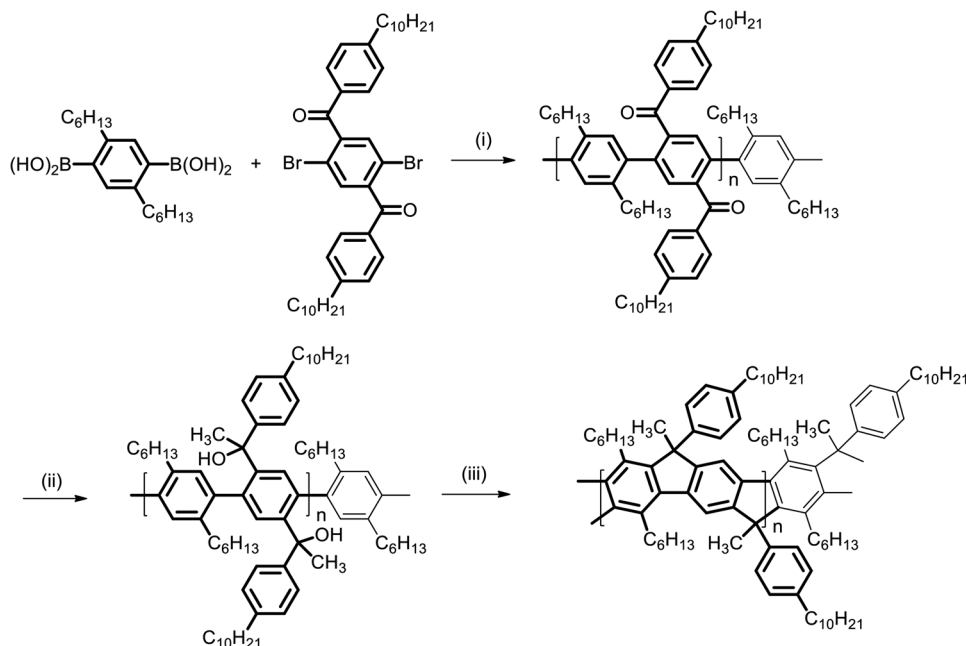
7. The Ladder Polymer Approach

Attempts at optimizing the conjugative interaction, with important consequences for optical properties, have prompted our idea of embedding the conjugated PPP backbone into a double-stranded, geometrically fixed ladder polymer. This polymer deserves some more attention because it has been characterized by defect spectroscopy to possess an essentially defect-free structure.[40] The stepwise synthesis of a planar PPP ladder polymer (LPPP) by bridging neighboring phenylenes of the conjugated skeleton with substituted methylenes, as presented by us in 1991,[41] combined a Suzuki-type polycondensation toward single-stranded polyketone precursors with two consecutive post-polymerization steps (depicted for MeLPPP as most prominent example in **Scheme 1**), the reduction of the carbonyl groups, and last of all, the intramolecular Friedel–Crafts-type cyclization of the polyalcohol toward the ladderized backbone. An optimized substitution pattern at the bridging carbon appeared as crucial for obtaining ladder polymers of the highest possible structural perfection. The challenges were a (nearly) quantitative reduction and the exclusion of interchain side reactions by steric shielding. NMR analysis pointed toward a very high structural regularity of these polymers. The needed solubility and processability were secured by the attachment of four alkyls (hexyls, decyls) per repeat unit by following the "hairy-rod" concept. The length of the chain segment in "effective" electronic conjugation, the "effective conjugation length" of MeLPPP, was extrapolated in a series of corresponding model oligomers to involve ≈20 aromatic rings.[42] The optical spectra of MeLPPP reflect a minimum geometrical disorder (**Figure 2**, left).

Absorption and photoluminescence (PL) spectra are mirror-symmetrically arranged, with a well-resolved vibronic structure and a very small Stokes loss (<150 cm^{-1}). As there are no major polarity changes in the transition from ground to excited state, the optical spectra exhibit only minor solvent-dependence. MeLPPP with its unique electronic and optical properties has been used in several interdisciplinary applications, for example, by pioneering the fields of blue OLED emitters and optically pumped polymer lasers.[43] Later, room-temperature exciton-polariton Bose–Einstein condensates were realized in the strong coupling regime for use in all-optical transistors and switches.[44] The latter scenario has profited from the amorphous morphology and high optical quality of MeLPPP films and paves a possible way toward future organic quantum optical technologies. Other entries to quantum technologies will be presented later.

Recently, also a donor–acceptor-type version of LPPP-type ladder polymers is made available.[45] In the ladder polymer MeLBT-DTPP, a significant contribution of polar resonance structures is expected, especially in the excited state. This is documented in an increased Stokes loss (if compared to MeLPPP) and a positive solvatochromism of the PL (Figure 2, right).

Moreover, the generation of diarylvinylene-bridged phenylene ladder polymers in 1992 (**Scheme 2**, left) with a fully unsaturated backbone of sp^2-hybridized carbons can be seen as an early example of a graphene nanoribbon (GNR) synthesis.[46] These ladder polymers were initially made in a two-step sequence of reductive Yamamoto-type polycondensation of 2,5-dibromo-1,4-dibenzoylbenzenes with Ni(COD)$_2$ and a post-polymerization

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Scheme 1. MeLPPP synthesis: i) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, toluene/H$_2$O; ii) CH$_3$Li, and iii) BF$_3$·Et$_2$O.[41]
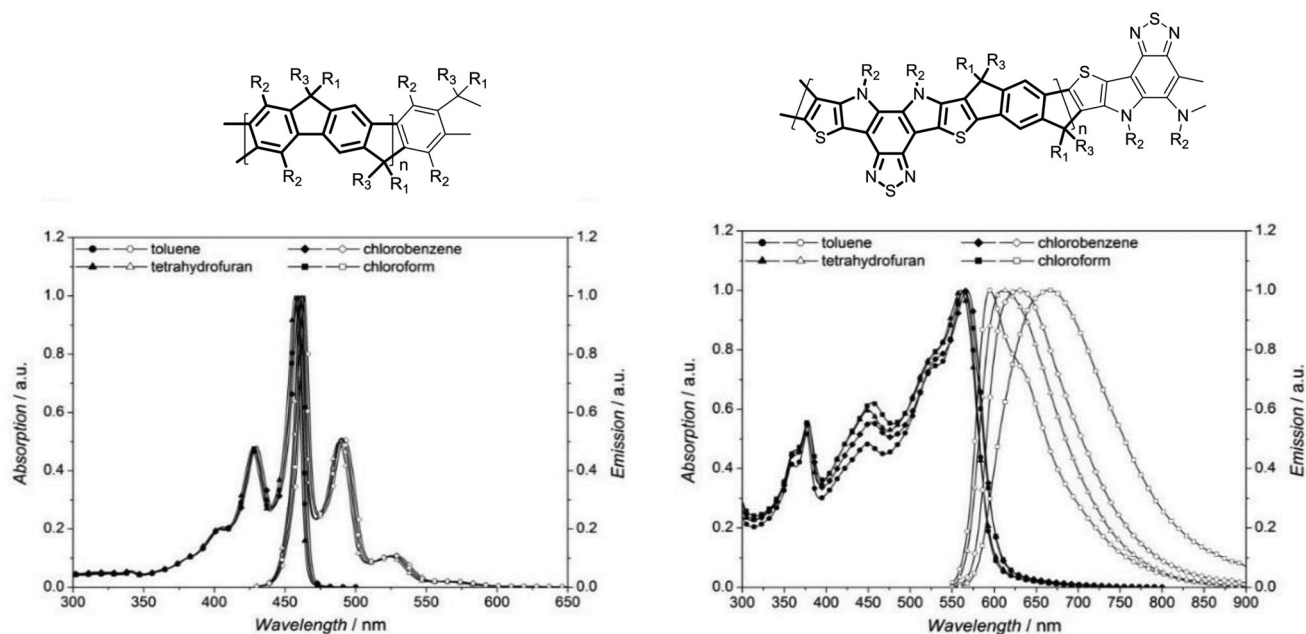

Figure 2. (Left) UV–vis and photoluminescence (PL) spectra of MeLPPP in different solvents; (right) UV–vis and PL spectra of MeLBTDTPP in different solvents (for the chemical structures, see the depicted structures on top. Adapted with permission.[45] Copyright 2016, Wiley-VCH GmbH); R$_1$: 4-alkylaryl; R$_2$: alkyl; and R$_3$: methyl.

ring closure of neighboring carbonyl functions with in situ-generated boron sulfide B$_2$S$_3$. As an alternate procedure, we recently developed a post-polymerization condensation of single-stranded precursors containing alternating carbonyl and benzylic functions as key step. In the two-step sequence, poly(*para*-phenylene)-type single-stranded precursors made in a Suzuki-type cross coupling of AA/BB-type monomers with both benzyl and benzoyl functions had been cyclized in a post-polymerization treatment with KOC(CH$_3$)$_3$ as base.[47] Corresponding oligomers had been also made by Lei Fang and co-workers in a related, elegant approach with an olefin metathesis as ring-closing step that was assumed to be reversible.[48] Following the above outlined, base-mediated cyclization approach between benzylic and arylketone side groups, the first conjugated hydrocarbon ladder
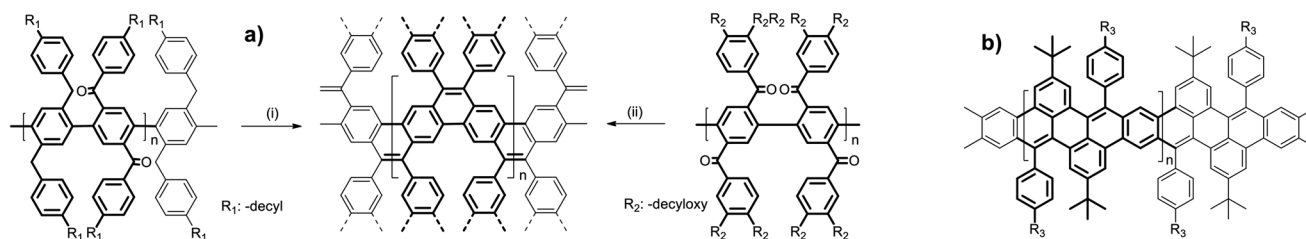
Scheme 2. a) Two synthesis variants toward diarylvinylene-bridged para-phenylene ladder polymers; depicted is the last post-polymerization cyclization step[46,47] (left, a-i) KOC(CH_3)$_3$/DMF, a-ii) in situ generated B_2S_3); b) chemical structure of a fully aromatic ladder polymer, formally with a polyacene skeleton, made in a final post-polymerization dehydration step (right[49]); R$_1$: decyl; R$_2$: hexyloxy; and R$_3$: decyl.

polymer formally comprising a polyacene skeleton was generated (Scheme 2, right).[49] Here, the benzannulation of the polyacene backbone furnished a distinctly increased aromaticity when compared to a hypothetical, unsubstituted [n]yacene ladder; and therefore, to a widened gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Geometry optimizations indicated a certain flexibility of the ladderized backbone with a manifold of different conformations, as manifested in a distinctly increased Stokes loss if compared to MeLPPP. At this point, a short comment on the rigidity of CP chains is appropriate because this is strongly influenced by the connection and substitution patterns of unsaturated repeat units. Two examples are revealing: i) The rigidity of single-stranded poly(1,4-phenylene)s, represented by the persistence length (or Kuhn length) and estimated from light scattering investigations, can be much enhanced by the introduction of ortho-substituents at their aryl–aryl linkages; this will, of course, imply strong interring torsion and obstruct conjugative interaction.[50] ii) The rigidity of double-stranded ladder polymers can significantly vary with the connection mode of their carbon-based frameworks. This becomes obvious when comparing the rigid MeLPPP (Scheme 1) having alternating 5- and 6-membered rings along its double-stranded backbone with relatively flexible aromatic polyacene-type ladders (discussed last, Scheme 2, right). For the latter, this is documented by a distinctly enhanced Stokes loss and an enlarged span of the individual emission maxima for a representative number of individual polymer chains, as derived from single-molecule optical spectroscopy.[49]

8. Nanographenes and Graphene Nanoribbons

Organic electronics employs CPs as molecular components of devices and; is thus, largely defined by the availability of materials, that is, their synthesis and processing. Nevertheless, the discussion of the underlying chemistry cannot be separated from the targeted physical function. CPs stand in competition with small organic molecules (SMs) but also with inorganic materials such as metal oxides or quantum dots. SMs are easier to obtain and purify than CPs, let alone the chance of depositing SMs by sublimation. While the resulting processing issues will be discussed below, it should be mentioned that the rise of fullerenes[51] and carbon nanotubes[52] in the 1990s furnished yet another family of conjugated species, that of carbon allotropes. In the early 2000s, this scenario was further extended by graphene which sometimes seemed to adopt a role as "wonder material".[53] The dimensionality of these "nanocarbons" appeared as a particularly important

Scheme 3. Representative edge structures of GNRs.

design principle because it determined not only the electronic band structure but also the packing in the solid state.[54] While graphene, due to its extremely high charge–carrier mobility,[53b] attracted attention as ideal semiconductor for field-effect transistors, its broader use was hampered by the vanishing band gap, as a result of which a current was always on. An opening of the band gap appeared feasible by geometric confinement as occurring in graphene nanoribbons (GNRs).[55] GNRs are quasi-1D semiconductors and appear as ideal structures to bridge the worlds of classical (1D)-CPs and 2D-graphene.[54] GNRs can be regarded as multi-stranded CPs, suggesting a variety of conjugation modes.[56] Not surprisingly, their structures, in the first place, are determined by their width and lengths, but there is a third feature, namely the edge-type. The armchair, cove, and fjord peripheries are given as examples (**Scheme 3**). The most exciting one from an electronic point of view is the zigzag periphery because it holds promise for edge-localized states, particularly low band gaps; and thus, also for high-spin instead of closed-shell ground states.[57]

Here again, reference to organic chemistry is instructive. Clar, the pioneer of polycyclic aromatic hydrocarbons (PAHs), has described the enormous breadth of their electronic structures since
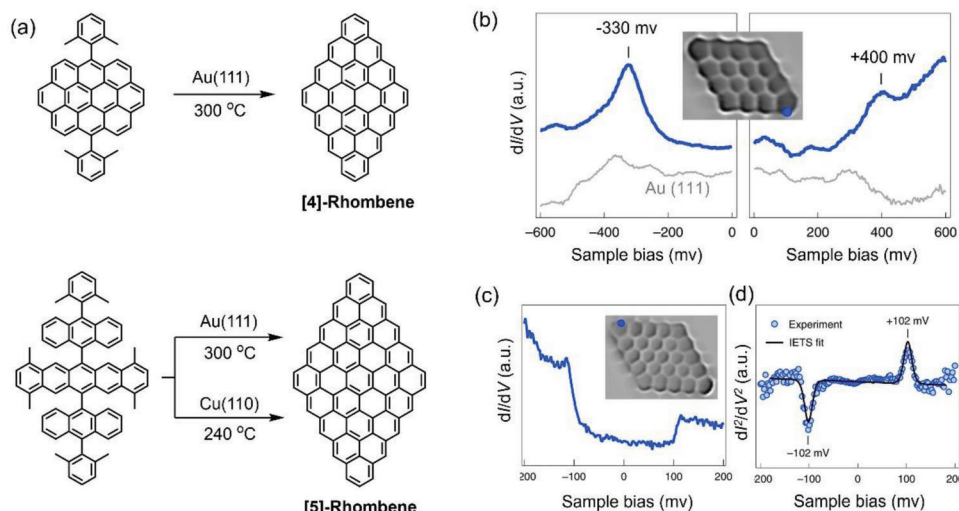
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Figure 3. a) On-surface synthesis of [4]- and [5]-rhombenes. b) dI/dV spectra of [4]-rhombene with HOMO and LUMO resonances at −330 and +400 mV, respectively. c,d) Background-subtracted dI/dV spectrum of [5]-rhombene revealing inelastic excitation steps. Acquisition positions for the respective dI/dV spectra are marked with a blue filled circle in the inset ultrahigh-resolution STM images in (b,c). (b–d): Reproduced with permission.[66] Copyright 2021, Springer Nature.

the mid of the last century.[58] What intrigued us, was increasing the size of PAHs toward the nanoscale en route to so-called nanographenes (NGs) and on to GNRs.

Thereby, two features have been of key importance. One relates to synthesis, namely, the formation of twisted polyphenylenes by, for example, aryl–aryl-coupling,[59] Diels–Alder cycloaddition,[60] cyclotrimerization of diarylacetylenes,[61] or electrocyclic ring closure of ethinyl substituted biphenyl moieties,[62] followed by the flattening, one might say graphitization, by cyclodehydrogenation of these soluble precursors via the Scholl reaction.[63] This is classical solution chemistry which can then be logically extended toward making GNR polymers. The second feature relates to nanoscience. Scanning tunneling microscopy (STM) has allowed to visualize NGs in real space with atomic resolution after immobilization on conducting surfaces, and scanning tunneling spectroscopy (STS) even enabled their electronic characterization.[64] Thus, recording their current–potential curves and correlating these with the energies of frontier orbitals has been an early step toward nanoelectronics.
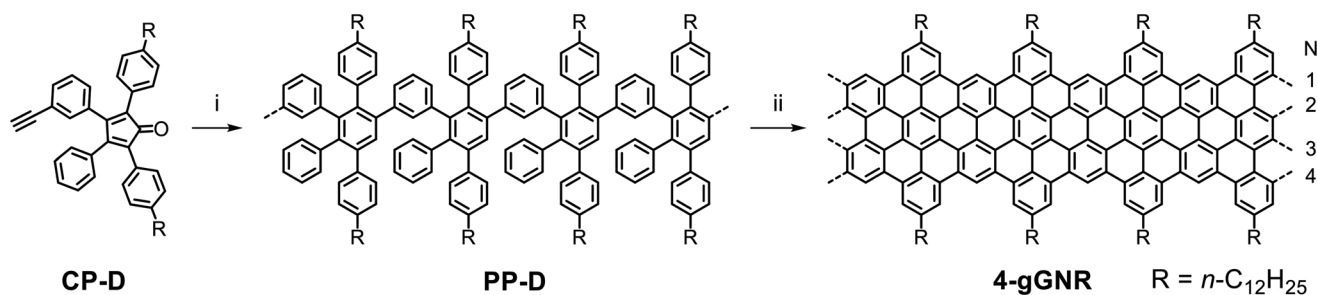
The topology of NGs, that is the mode of fusion of the hexagons, is decisive for the electronic structure.[65] Together with the group of Roman Fasel, we have introduced a whole new family of NGs comprising several hundred carbons, but a particularly exciting case of NGs are [4]- and [5]-rhombenes (**Figure 3**a) whose synthesis by on-surface reactions using the catalytic effect of metals will be mentioned below.[66] STS reveals that they possess extremely small HOMO–LUMO gaps and, if large enough, a magnetic ground state (Figure 3b–d). More importantly, there is a pronounced magnetic exchange coupling of the spins which is well above the famous Landauer limit of minimum energy dissipation.

When proceeding to polymeric GNRs, the connectivity of the polyphenylene precursors is crucial because all their benzene units must fit into one plane upon cyclodehydrogenation.[67] The other issue, of course, is to achieve high-molecular weight precur-

sors. As expected from the linear PPPs, monomeric oligophenylene precursors were thereby chemically functionalized and subjected to polycondensation reactions according to a Yamamoto or Suzuki protocol.[59] The loss of functional groups upon the coupling of bulky oligomer units; however, seriously limited the achievable molecular weights due to the mismatch of stoichiometries. Therefore, we realized the growth of, for example, the precursor polyphenylene PP-D (**Scheme 4**) by the repetitive Diels–Alder cycloaddition of the AB-type monomer CP-D (Scheme 4) which contained, both, a diene and dienophile function.[68] Each growth step was irreversible because it was accompanied by the extrusion of carbon monoxide and there was no "failure" as caused by the loss of functional groups. Dynamic light scattering proved that polymer lengths as high as 600 nm could be achieved, whereby the extensive alkyl substitution allowed film deposition from solution even for the final, chemically dehydrogenated gulf-edged 4-gGNR (Scheme 4, "4" is the ribbon width defined by the smallest number N of carbon atoms across the ribbon).

Not surprisingly, variation of the monomeric starting compounds allowed one to vary not only the widths of the ribbon and the nature of the edges but also the attachment of functional substituents. Chromophores enabled modulation of optical properties while stable free radicals led to partial transfer of spin density onto the GNR core as shown by cases such as GNR-CP and NIT-GNR (**Scheme 5**a,b).[69]

Having discussed the introduction of chiral alkyl side chains with stereogenic centers into CPs and its impact on circularly polarized emission, the discussion of graphene molecules would not be complete without considering "planar" chirality as well. NGs can be forced out of planarity and, in case of suitable substitution, made chiral by incorporation of 5- or 7-membered rings.[71] This structural modification is also important for adding spins to graphene molecules because non-hexagonal rings can be regarded as defects within the lattice, whose engineering will also furnish spins.[72] The most famous approach

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Scheme 4. The synthetic route toward 4-gGNR: i) Ph$_2$O, reflux, 96% and ii) FeCl$_3$, 99%.[68] The width is defined by the number (N) of carbon atoms across the ribbon.

toward chirality comprises helicenes and, similar to the flat NGs, much work has been dedicated to increase the size of the polycycles in attempts at achieving larger dissymmetry factors for circularly polarized emission.[73] Cyclodehydrogenation of suitable precursors has again been instrumental and even furnished "double" helicenes,[73b] but other protocols such as a [2+2+2]cyclotrimerization have been employed as well.[74] One readily concludes from Scheme 3, that cove-and-fjord-edges also induce non-planarity as a result of steric hindrance.[70,75] In the case of FGNR (Scheme 5c), it is the bulk of tert–butyl groups which prevents the final C–C-bond formation upon cyclodehydrogenation of the precursor polyphenylene; and thus, brings about an up-down shape of the ribbon.[70] Corrugation is an important feature in graphene itself, but here an up–down behavior is determined by molecular synthesis. Nevertheless, the actual configuration is difficult to control in a polymer. Therefore, oligomeric model compounds with multiple helicene units have been synthesized as well, whose crystal structures nicely document the prevailing configuration. This is another convincing case of the "oligomer approach," where defined model compounds help to unravel the complex behavior of the polymer.

The above GNR syntheses are, in a sense, "conventional" because they are executed in solution. Access toward GNRs has, on the other hand, immensely profited from another synthetic protocol already mentioned above.[79] As shown by Grill and Hecht, UHV-deposition of dihalo fluorene on metal surfaces followed by thermally induced carbon–halogen cleavage and polymerization of the resulting diradicals gave rise to polyfluorenes which could be visualized by STM.[80] Toward GNRs, an oligophenylene "monomer" made from twisted benzene units was polymerized as before, followed by a dehydrogenation and flattening upon further heating. Again, the choice of the starting compound was crucial. In our initial case of on-surface GNR synthesis, we made a seven C-atom-wide armchair GNR by starting from 10,10"-dibromo-9,9"-bianthryl (DBBA, **Scheme 6**a).[76] The product is denoted as 7-AGNR (Scheme 6a) whereby "A" stands for armchair. Introduction of the suitably functionalized 3",6"-dibromo-1,1":2",1""-terphenyl (DBT, Scheme 6b) and 3,9-dibromoperylene (DBP, Scheme 6c) provided the wider polymer 9-AGNR (Scheme 6b)[77] and the narrower 5-AGNR (Scheme 6c),[78] respectively. This variation is important as the width of the ribbon determines the electronic band gap; and thus, also their function as semiconductors.[81] So far, however, all these GNRs comprise armchair edges. The reactions employed could be described as aryl–aryl coupling cat-

alyzed by the metal. Interestingly, such a C–H activation was extended to alkyl–aryl and even alkyl–alkyl couplings. A particularly remarkable alkyl–alkyl connection was the oxidative 3 + 3-cyclodimerization of isopropyl groups to yield new benzene moieties: thus, when starting from 2,7-diisopropylpyrene (DIPP, **Figure 4**a), the alternating copolymer poly(2,7-pyrenylene-1,4-phenylene) was obtained (Figure 4a).[82] A somewhat related case was the synthesis of the zig-zag edged 6-ZGNR (Figure 4b) by polymerization and subsequent cyclodehydrogenation of the complex monomer 2,12-dibromo-14-(3",5"-dimethyl-[1,1'-biphenyl]-4-yl)benzo[m]tetraphene (DBDMBPBT, Figure 4b).[64b] Here, the transformation of the precursor polymer into 6-ZGNR implied an oxidative methyl–aryl coupling. An exciting follow-up experiment was the characterization of 6-ZGNR by STS which disclosed the occurrence of edge-localized electronic states with energy splittings (Figure 4c).

9. Beyond Molecular Design

We have so far focused on principles of molecular design and the occurrence of structural defects in CP synthesis which might well hamper device performance. Issues of precision synthesis include regioselectivity of bond formation as occurring in the oxidative polymerization of electron-rich aromatic molecules but also of stereoisomerism as resulting from the configuration of double bonds and the conformations of chains. On the other hand, rigid CPs tend to aggregate in solution which sets limits for solubility and solution-processing. Optoelectronic devices rely on the solid state of thin films[83] and, when processes such as charge–carrier transport come into play, as in field-effect transistors, supramolecular order is desirable to obtain high mobility for the charge transport. While we know a lot about molecular control of properties, a corresponding supramolecular control is much more difficult to achieve because it is based on a subtle interplay of weak intermolecular forces. Formation of thin films is further complicated because substrate–adsorbate interactions and kinetic effects such as the rate of solvent evaporation can be decisive. From the point of view of atom economy, monolayers of polymers are appealing, even more so because the charge transport is believed to occur close to the substrate surface. Indeed, such field effect transistors (FETs) could be fabricated and built into integrated circuits whereby the deposition was preceded by an ordered assembly in solution.[84]
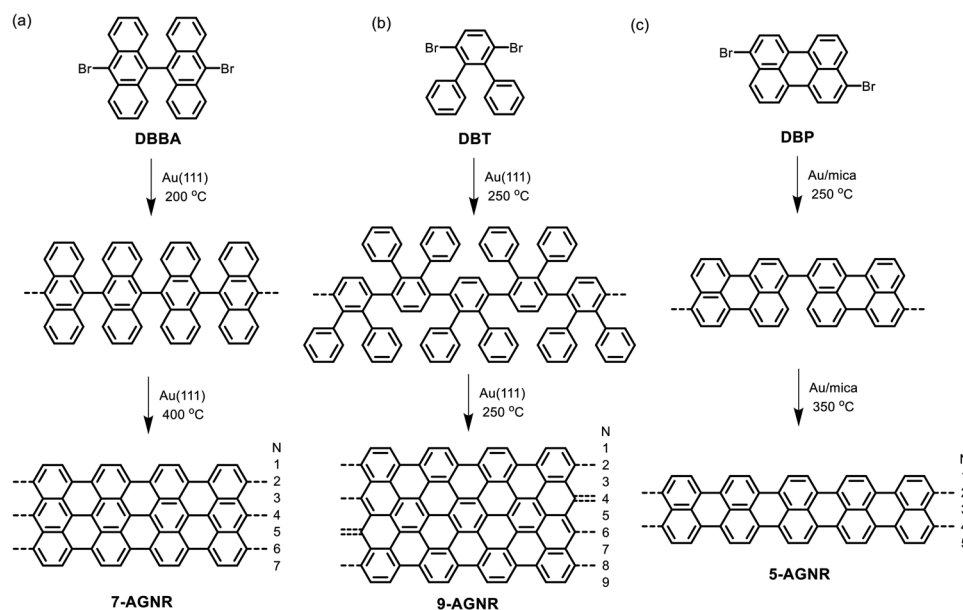
Processing goes into the opposite direction if single polymers are needed for nanodevice fabrication. This is particularly severe
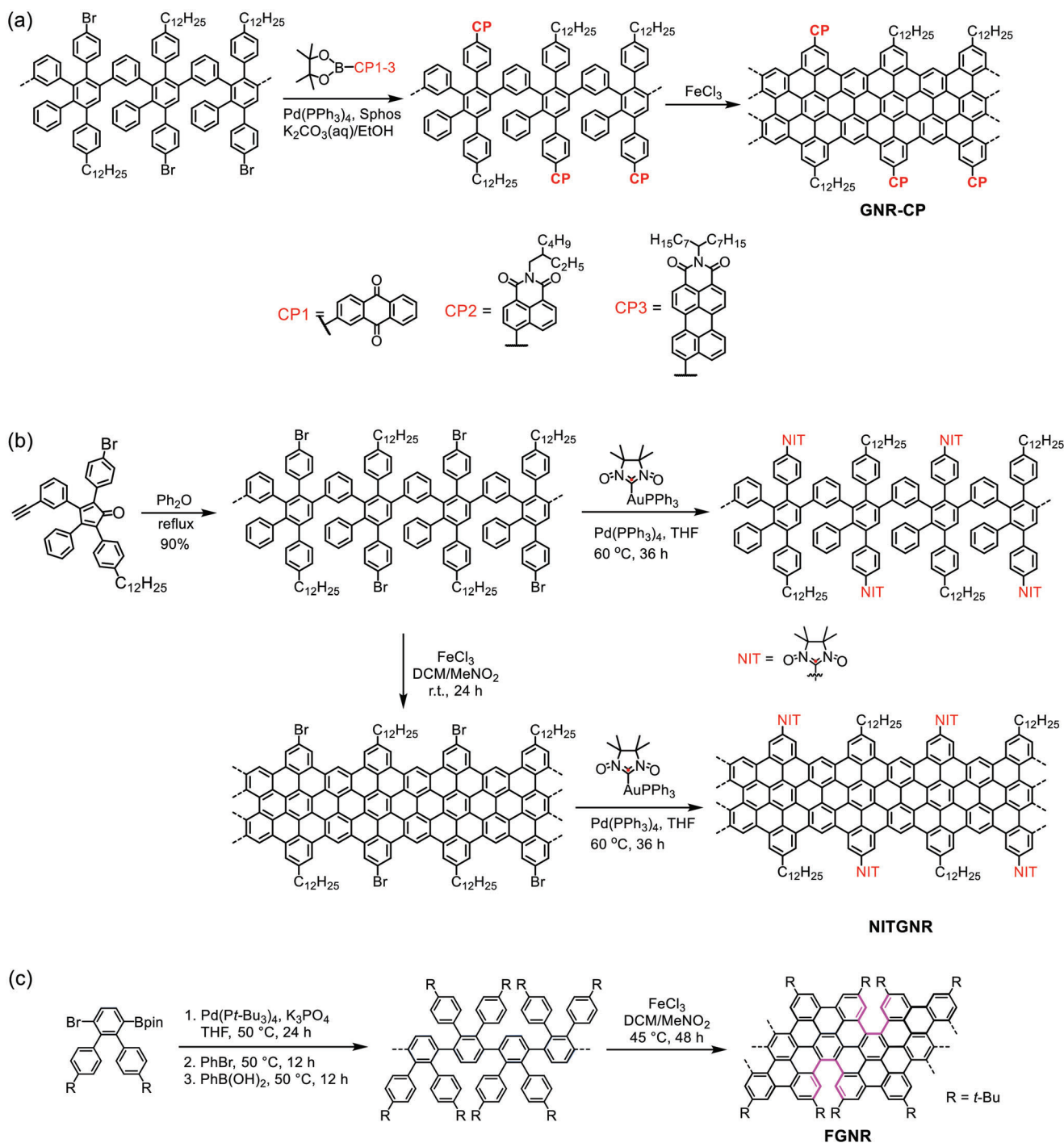
Scheme 5. Synthetic routes toward a) GNR-CP,[69a] b) NITGNR,[69b] and c) FGNR.[70] CP stands for chromophores. NIT stands for nitronyl nitroxide radicals.

in case of graphene nanoribbons where, not surprisingly in view of the stacking of graphene, multilayered aggregates are quite common. Thus, similar to the debundling of carbon nanotubes, shear-force delamination could be used before heterostructures of GNRs with other semiconductors such as molybdenum sulfide were formed.[85] A similar problem occurred in quantum experiments such as the construction of ultra-clean single-electron FETs. Separate ribbons from solution could only be deposited after drastically boosting the solubility of GNRs because alkyl substitution alone was not sufficient for this purpose. Instead, anthracene units were connected to the GNR cores via alkanediyl spacers and subjected to a further Diels–Alder cycloaddition with alkyl maleimides; thus; furnishing a highly irregular, flexible substitution type.[86]

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Scheme 6. Schematic synthetic routes to a) 7-AGNR,[76] b) 9-AGNR,[77] and c) 5-AGNR.[78] The width is defined by the number (*N*) of carbon atoms across the ribbon.

This is the right occasion to discuss the pros and cons of CPs versus conjugated small molecules (SMs) and their corresponding deposition techniques. First, controlling color of absorption and emission or establishing different electron demand: what has above been described as being readily possible by the design of CPs,[87] is well-documented for SMs as well which have the additional advantage of easier structure proof and purification.[88] Second, small molecules are deposited by evaporation under vacuum, while polymers require solution processing also comprising a variety of printing methods. The former process allows straightforward multilayer fabrication whereas the latter is complicated by the need of orthogonal solubilities of different components. Cross-linking of polymers is often required to shut down solubility before formation of the next layer.[89] However, such cross-linking steps frequently cause a significant reduction of device performance.[90] Alternatively, thermally cleavable side chains can be used to modulate polymer solubility as demonstrated for a couple of polythiophene derivatives, which can lead to an improvement in device performance at the same time.[91] Third, the limited effective conjugation length of CPs suggests that their optical or electrochemical characteristics would be more easily achieved by defined oligomeric congeners. A key advantage of CPs is, indeed, the possible control over the solid-state morphology, especially in amorphous CPs for optics and optoelectronics applications, by avoiding the formation of (micro)crystallites which would hamper the performance of such devices as OLEDs and solid-state lasers due to scattering of light. A troublesome shortcoming of polymers, and especially CPs, is the inherent immiscibility with most other polymers. Polymer blends tend to phase separate and the resulting multiphase arrangement is often of limited morphological stability. Even doping CPs with small molecule-based dopants as i) as oxidizing/reducing agents, that means *p*-/*n*-dopants, and as ii) SM acceptor components of bulk-heterojunction-type organic solar cells, or as iii) chiral dopants, often cause significant distortions of the polymer morphology, especially for semicrystalline CPs.[92]

10. Outlook

After all, there remains the question of current trends and hot developments in the field of conjugated polymer syntheses and applications. First, there are the fields of flexible or stretchable electronics and the rapidly growing domain of bioelectronics, all based on devices with organic materials as active layers, for example, for bio-based sensor applications or body–device interfaces.[93]

Flexible and stretchable semiconducting polymers as active components of OFETs can be generated by introducing soft aliphatic or oligosiloxane segments into the main chain of CPs. Such (co)polymers must be designed in a way that the electronic properties are influenced as little as possible while achieving the desired elastomeric behavior. Here, a nanophase separation of hard and soft segments is advantageous because it allows for a spatial "decoupling" of semiconducting and elastomeric properties. Target applications will be diagnostic and therapeutic medical aids with integrated electronic components, which come with catchwords such as artificial skin or brain–computer interfaces.[94]

CPs that are used for bioelectronic applications often possess mixed ionic and electronic conductivity, in most cases realized by attaching hydrophilic, cation-stabilizing oligoethyleneglycol side chains onto CPs. In many cases, electron-rich CPs with a polythiophene backbone have been used. Related hydrophilically substituted donor–acceptor copolymers also came into the focus of interest in order to achieve *p*-type as well as *n*-type conducting behavior. Bioelectronic devices made from these materials are mainly operated in aqueous environments and often use the
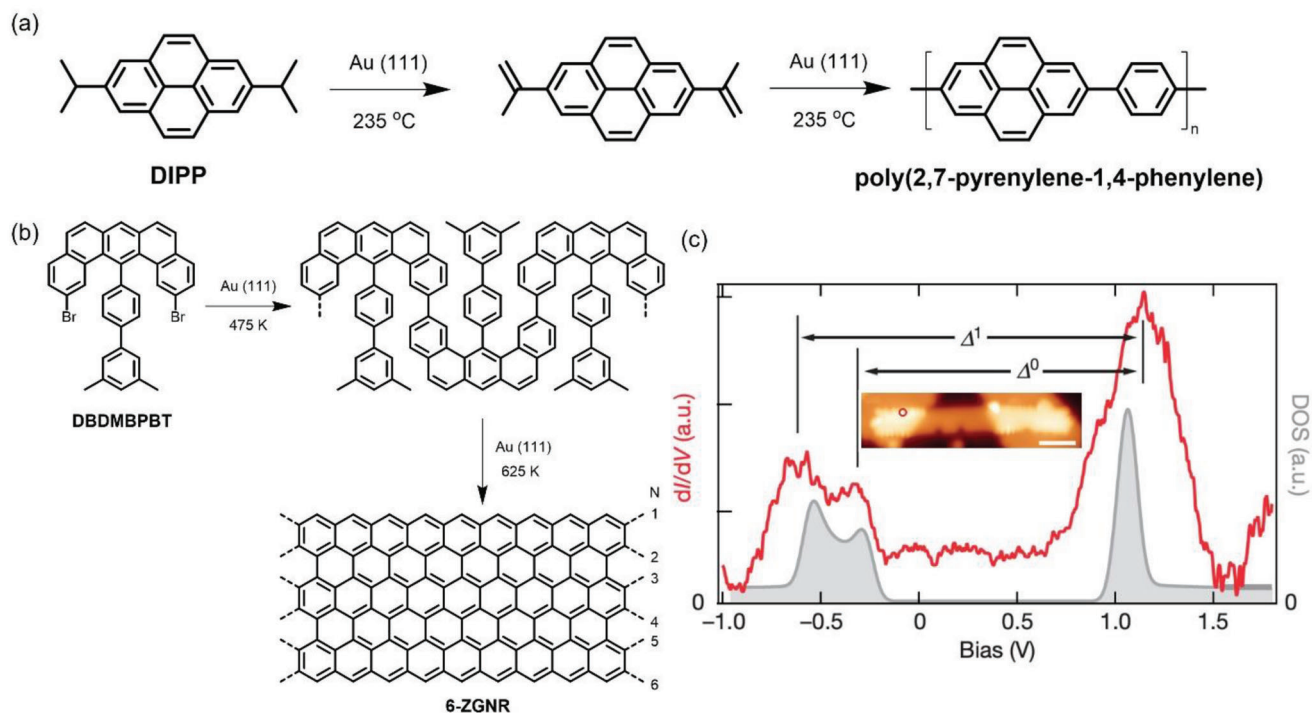
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Figure 4. a) On-surface synthetic route to the copolymer poly(2,7-pyrenylene-1,4-phenylene).[82] b) Surface-assisted synthesis of zigzag-edged 6-ZGNR. c) Differential conductance (dI/dV) spectrum (red) taken at the zigzag edge marked by the red circle in the inset STM topography image of 6-ZGNR bridging between two NaCl monolayer islands, and the quasiparticle density of states (DOS; gray). (c): Reproduced with permission.[64b] Copyright 2010, Springer Nature.

design principle of organic electrochemical transistors (OECTs), fabricated as electrolyte- or water-gated devices with a large application potential in biosensing or in bioelectronic interfaces.[95] In this context, CP-based devices are being developed that exhibit a type of short- and long-term "neuroplasiticity;" thus, mimicking typical conditioning behavior and providing an attractive future potential for applications in artificial neural networks (ANNs).[96] For bioelectronics functions, the generation of flexible neural interfaces, for example, realized in soft electrode arrays based on PEDOT:PSS micropillars,[97] defines an important step toward their reliable interaction with living cells. Similar "neuromorphic" behavior has been described for two-terminal devices with oligoethyleneglycol-substituted polyfluorenes in their active layer. This device configuration has initially been applied in light-emitting electrochemical cells (LECs)[98] but is also holding promise for many related uses.

Conjugated polyelectrolytes (CPEs), mainly CPs with ionic side chains, that can contain cationic, anionic, or zwitterionic functions, are another topic of growing interest, including low bandgap CPEs[99] and potential device applications in biosensors or as bio-probes.[100] A special facet is the formation of so-called coacervates, dense and fluid polyelectrolyte–polyelectrolyte complexes, as mixtures of oppositely charged CPEs, with identical or different backbones. For binary coacervate blends containing CPs with different, either electron-rich or electron-deficient backbones, energy- or charge-transfer phenomena have been studied with an envisaged application potential in fluid CP materials.[101]

There is also a visible revival in research activities on doped-CPs, mostly for realizing high doping levels, also for *n*-type semi-conducting CPs.[102] This can mainly be accomplished by the development of improved doping and processing procedures. During the last years, a potential use in thermoelectric devices came into the focus as the currently most attractive function of doped CPs. For thermoelectric devices, a stable and resistant doping of CPs leading to high electrical conductivities will be of primary importance.[92a,103] An interesting debate has recently developed around novel oxidative doping procedures of CPs with strong Lewis acids such as $B(C_6F_5)_3$. As $B(C_6F_5)_3$ is not an oxidizing agent itself, the mode of doping has remained unclear but new results indicate that such doping procedures are coupled to a partial decomposition of the respective CPs under doping.[104]

The fascinating idea of miniaturized or even single-molecule devices has seen some disputes as there are issues of stability and of interfacing. In any case, CPs and their oligomeric models, in particular when suitably end-functionalized, remain of undiminished importance. A related topic is the detection of exotic quantum states which will open up technologies far beyond the established cases of optoelectronic devices. While the use of LPPP-type materials in quantum optical devices has already been discussed,[44] FETs have been built from single GNRs displaying ultrahigh on/off-current ratios; thus, overcoming a major drawback of graphene with its vanishing band gap.[105] More recently, transistors could be fabricated which displayed a clean single-electron feature due to a pronounced Franck–Condon blockade.[69b] One of the hottest topics of solid-state physics is the construction of topological insulators, so far, mostly from 3D inorganic materials. Topological end states could now be demonstrated by STS for qusai-1D GNRs. This finding might

prompt two remarks: this experiment was only possible based on the synthesis of GNRs with atomically precise zigzag and armchair edges and its theoretical basis was taken from the famous Su–Schrieffer–Heeger model for describing the electronic states of polyacetylene with which this walking tour along CP synthesis began.[64a,106] Nevertheless, the field of GNRs still faces ample chemical challenges of which the creation of spins and magnetic ground states has already been mentioned. Adding the spin-degree of freedom to ribbon-type CPs is synthetically demanding, whether by defect engineering or by constructing zigzag edges (see above) but on the other hand extremely rewarding. Convincing evidence for this claim comes from the detection of high spin-correlation times which is known as a key requirement for error correction in quantum computing.[107] Another relevant feature is the "chiral induced spin selectivity" according to which an electron transfer through a chiral molecule is dependent upon the electron spin.[108] The use of an electron spin as a "chiral reagent" is expected to have important consequences in quite different fields from spintronics to the generation of enantiomeric excesses, and CPs will certainly be part of this.

Whether targeting electrical conductor or semiconductor behavior, light absorption and emission, lasing and non-linear optical properties or the response to external stimuli; the past, present, and future of research into CPs has faced, both persistent fundamental questions and more fashionable topics. There are still many attractive targets and challenges: be it the long-runner stable blue OLED emitters, the strong coupling regime in CP films embedded between suitable mirrors for future quantum optical devices, or topological insulators for potential applications in quantum technology. The vivacity of CPs appears undiminished. With an emphasis on function, CPs will always ask for interdisciplinary approaches whose breadth will be further extended by excursions into biomedicine, nanoelectronics, and quantum technologies, as introduced during our short tour. Further motivation for CP research will originate from growing societal needs in sustainable energy technologies or circular economy. In addition, there is hope that artificial intelligence will help us to close gaps of knowledge and allow us to progress much more rapidly than before.

Conflict of Interest

The authors declare no conflict of interest.

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Klaus Müllen was director at the Max Planck Institute for Polymer Research. His research interests range from new polymer-forming reactions to the chemistry and physics of single molecules. His group has introduced unconventional polymer structures such as graphene nanoribbons, polyphenylene dendrimers or biosynthetic hybrids and studied their materials properties. They published more than 2100 papers. From 2008–2009 he served as president of the German Chemical Society (GDCh). From 2013–2014 he was president of the German Association for the Advancement of Science and Medicine. In 2010 he won an ERC Advanced Grant for his work on nanographenes. He was associate editor of the *Journal of the American Chemical Society*.

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