Electron transfer in polyaromatic hydrocarbons and molecular carbon nanostructures

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Abstract

Planar and curved polycyclic aromatic hydrocarbons (PAHs) represent an interesting class of compounds with physical chemical properties particularly appealing, as good organic semiconductors and molecular model of larger carbon nanostructures. Investigation of the heterogeneous electron transfer in these systems lets to probe their electronic properties and the reactivity of the corresponding generated carbanions and carbocations that can form new bonds, thus leading to different carbon systems. A particular focus is on the intrinsically high reactivity of carbocations which induces a series of reactions building up new carbon-carbon bonds, thus allowing to enlarge the initial molecular unit into a nanostructure. This represents a new and convenient way to exploit the electrochemically triggered reactivity into the synthesis of carbon nanostructured materials.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large class of π-conjugated molecules with more than two condensed aromatic rings. PAHs can be classified as planar, e.g.

triphenylene, pyrene, or curved with a bowl-like shape[1], as corannulene and sumanene[2,3], or helically-shaped[4]. In recent years, PAHs have raised an increasing interest in the materials chemistry field due to the tuning of their electronic properties obtained through improved synthetic methodologies (e.g., different molecular topologies, functional groups), making the PAH-based materials as a new class of organic semiconductors for optoelectronic devices. Furthermore, PAHs can be seen as precursors for the bottom-up synthesis of more extended molecular carbon nanostructures, as C_{60}[5,6] and planar and/or curved nanographenes[7,8], by cyclodehydrogenative carbon-carbon bond formation. The cyclodehydrogenation of PAH precursors has been successfully exploited by organic chemists for the synthesis of a large number of expanded PAHs, through the well-known Scholl reaction. The Scholl reaction is typically performed in solution in presence of Lewis acids[9] or oxidants and Brønsted acids[10,11] but, recently, different approaches which leaded to extended PAH have been reported, as surface-assisted[12] or electrochemically induced cyclodehydrogenation[13,14].

In this review, we will summarize recent works regarding the chemical and electrochemical electron transfer (ET) focussing on PAHs and molecular carbon nanostructures. Understanding the electron transfer processes and the electronic properties of PAHs (Section 2) is fundamental for their possible applicability. This is followed by the chemical reactivity of the related PAH radical anions and cations discussed in Section 3 and finally, in Section 4, some intriguing applications of PAHs will be briefly presented, closely related to the energy conversion and storage (e.g., super capacitators and electrode material for batteries), and the field of organic electronic devices. In our view, PAHs with their electrochemical behaviour can be exploited to provide new materials and an innovative synthetic route towards more extended conjugated nanostructures.

Section 1 Overview of the electron transfer

Electron transfer (ET) is an elementary step which involves the transfer of typically one-electron. The products of single ET (SET) of a neutral organic molecules are the radical-ions. ET can occur in solution by a redox reaction between two molecular species, a donor and an acceptor, or at the heterogeneous interface by an electrochemical reaction between a molecular species and an electrode. The theoretical framework for SET was developed by Marcus et. al in 1950 for the homogeneous "redox" ET[15–17] and successively further expanded[18,19] for the heterogeneous ET[20–24]. Several chemical reductants and oxidants have been reported in literature[25], alkali, e.g. Li, Na, and alkaline earth metal, e.g. Mg, Ca, are the most popular inorganic reducing agent. Transition metal complexes can also be used as electron donor or acceptor depending on the metal oxidation state. Among organic electron donors[26], aromatic amines are well recognized donor. Recently, Rohrbach et. al[27] have reported a catalytic benzimidazolium salt with a redox oxidation potential $E_{1/2}$ = -1.86V (vs. SCE). Typical examples of organic electron oxidizers are 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)[28] and hypervalent iodine[29].

In electrochemistry, by applying a suitable potential to the electrode we can induce a ET reaction at the interface generating a radical cation or radical anion. An organic species can undergo ET directly at the electrode or mediated (indirect) by a redox mediator (Fig. 1a), which must be stable in the oxidized/reduced state and the redox ET must be kinetically and thermodynamically favourable. In the very last years, organic electrosynthesis has re-emerged as a powerful and environmentally friendly strategy for the synthesis of many molecules. The generation and use of radical-ions, that are comprehensibly more reactive than the neutral molecule, is of paramount importance and they have been extensively used in many organic reaction[30], e.g. C-H activation, oxidative cyclodehydrogenation, intra- and

intermolecular coupling. Recently, Röse et al.[31] reported an electrocatalytic oxidation of terphenyl precursor by using DDQ as a redox mediator for the Scholl reaction resulting in triphenylenes derivatives (Fig. 1b). Similarly, Ma et. al[32] reported the synthesis of extended PAH-C96 by electrocatalytic use of DDQ. DDQ was reduced to $DDQH_2$ by the homogeneous redox process with the precursor and it was, in turn, subsequently oxidized at the anode closing the catalytic cycle. DDQ mediator provided a lower oxidation potential with respect to the direct oxidation of the oligophenyl precursor and resulted in a complete conversion to PAH-C96.

Section 2 Electron transfer in PAH and carbon nanostructures

Electrochemical reduction of small planar PAHs, e.g. naphthalene, phenanthrene, pyrene, perylene and coronene, are well-known processes. Generally, reduction half-wave potential ($E_{1/2}$) of small PAHs correlates linearly with the lowest unoccupied molecular orbital (LUMO) energy, which decreases as the molecules become more and more π-conjugated. Wang et al.[33] reported the reduction of a series of small PAHs by cyclic voltammetry observing chemically reversible electrochemical reduction processes for each PAHs (Fig.1c and Fig.1d). Similarly, Bachman et al.[34], investigated the oxidation of a series of small PAHs, showing that $E_{1/2}$ scales linearly with the highest occupied molecular orbital (HOMO) energy. However, some of the polyaromatic species as pyrene and few other PAHs show an oxidation followed up by a chemical reaction (Fig.1e and Fig.1f) and, in some cases, a film formation occurs on the electrode as a consequence of such electrochemical behaviour. A very similar electrochemical trend holds also for the non-planar polyaromatic hydrocarbons. Corannulene ($C_{20}H_{10}$), archetype of curved polyaromatic hydrocarbons with a molecular structure recalling C_{60}, is the smallest bucky-bowl PAH and its electrochemical characterization was firstly reported soon after its synthesis in 1967 by Lawton et al.[35] However, only the radical anion and dianion of corannulene were reported and any attempt to observe the radical cation failed.

Bruno et al.[36,37] further investigated the electrochemistry of corannulene, observing, for the first time, a third electrochemical reduction process. Despite in conventional solvents the reduction of corannulene to tri-anion is outside the solvent electrochemical stability window, the third reduction process was observed only in presence of small size electrolyte cations and ultra-dry conditions. In fact, the authors were able to stabilize the corannulene tri-anion and have the halfwave potential ($E_{1/2}$) falling within the experimental potential window by establishing a strong ion-pairing of the higher reduced species with the electrolyte cations[36,38,39]. Moreover, for this species, the fourth reduction process was reported by chemical reduction by Scott et al.[40]; it was established on the basis of theoretical and experimental arguments that the redox potential of the outer-sphere ET is well outside the explorable potential window of a large selection of either common or unconventional electrolyte/solvent systems used in electrochemistry[36]. Corannulene oxidation to radical cation was far less reported in literature described by several authors as a chemically irreversible oxidation, causing an electrode fouling after the initial cycle[35]. Very recently, Bruno et al. further investigated the chemical reactivity of the corannulene radical cation and shed light on the fouling process at the electrode[37]. (Further discussed in section 3.2) Several derivates of corannulene have been reported as well, e.g., containing fused planar groups attached to the corannulene core[41,42]. Extended PAHs and carbon nanostructure may undergo multiple stepwise ET processes, moreover extended π-conjugated molecules are typically easier to oxidize and reduce. The generated radical ions are also less reactive with the increase of the π-conjugation since extended π-system improves the delocalization of the charge. A recent review by Ueda et al. summarizes the electrochemistry of expanded PAHs[43], i.e. nanographenes, radicaloids and macrocycles, with chemically reversible multi-redox electron transfer.

Section 3 Chemical stability of radical anion and cation

In many cases the first processes are reversible but the successive ones, or those occurring at high potentials, can be affected by chemical reactions. Thus, herein some general aspects of polycyclic radical ions and their chemical stability will be discussed. Moreover, how radical-ions reactivity can be exploited for the synthesis of new molecules and materials will be shortly analysed.

3.1 Radical anions. Radical anions ($R^{\bullet-}$) of PAHs are ionic species with an odd number of electrons which result by the chemical or electrochemical reduction of a neutral molecule. Further reductions to dianion (R^{2-}) and higher charged species have been reported as well[44], typically the added electrons occupy the LUMOs at lower energy. Generally, a radical-anion of PAH shows a high chemical stability in conventional organic solvent. This is particularly true for extended PAH, where the more extended π-system of PAHs better delocalizes the negative charge, thus increasing $R^{\bullet-}$ chemical stability. Solvent and electrolyte could also affect the redox properties, in some instances due to ion-pair formation, as mentioned and discussed above[36,38,39]. Nonetheless, concerning the stability of $R^{\bullet-}$, it can react as a nucleophile, even with the solvent itself or the supporting electrolyte. Several chemical reactions of PAH anions have been reported in literature[44]. The Birch reaction, involving PAH anions as intermediates, has long been known, where carbon sp^2 of PAHs is reduced and protonated to sp^3 in the presence of a proton donor (BH). Alternatively, in the presence of electrophiles, like CO_2, PAH radical-anions can undergo electrophilic addition to the corresponding carboxylic acids. Interestingly, Scott et al. reported an anionic cyclodehydrogenation reaction of 1,1'-binapthyl to perylene, where the former is chemically reduced to dianion by metal potassium[45]. A similar approach was used by Matsuda et. al. to synthesize more π-extended PAHs[46].

3.2 Radical cations. Radical cation ($R^{\bullet+}$) species, with an odd number of electrons obtained by one electron abstracted from the HOMO, are generally less investigated than their anionic counterparts, mostly because the stability of $R^{\bullet+}$ at room temperature is severely limited by their high reactivity. $R^{\bullet+}$ has been reported to easily undergo deprotonation, rearrangement, bond dissociation and nucleophilic attack[47]. Many factors affect the chemical stability of $R^{\bullet+}$, thus ultimately influencing its reactivity, such as temperature, solvent, electrolyte, charge distribution effect of the π-system[48], protection of reactive positions[49], functionalization with electron-donating and withdrawing groups, and finally, the presence of a nucleophile. Solvent with low nucleophilicity, like CH_2Cl_2 and liquid-SO_2, and non-nucleophilic counterions, such as $[AsF_6]^-$, $[SbF_6]^-$, $[SbCl_6]^-$, $[Nb_2F_{11}]^-$ [50,51], and tetrakis(fluorophenyl)borate anions as $[B(C_6F_5)_4]^-$ and $[B(C_6H_3(3,5-CF_3)_2)_4]^-$ [52,53] have been reported to allow the observation of very reactive cations. For example, Bruno et. al reported the electrochemical oxidation of corannulene to dication[37] ($C_{20}H_{10}^{2+}$) in liquid-SO_2/Bu_4NAsF_6 and CH_2Cl_2/Bu_4NAsF_6. It would be worth mentioning also the rather high reactivity of C_{60} carbocations, although fullerene does not belong to the PAH family but it can be regarded structurally related to curved polyaromatics (e.g., corannulene). The electrochemical investigation of C_{60} up to the C_{60}^{3+} redox state[54] showed a reactivity of cations[55] comparable to that of planar and curved PAH oxidized species. With a similar approach, Riccò et al. exploited a strong chemical oxidant, AsF_5, in order to crystallize a highly reactive fullerenium salt, $C_{60}(AsF_6)_2$, with a non-nucleophilic anion in liquid-SO_2. The X-ray analysis of the resulting salt shows that a polymerization process occurred between the C_{60}^{2+} units[51], with the formation of new C-C bonds.

Despite the instability of π-radical carbocations, their reactivity have been exploited, in recent years, for new synthetic approaches. $R^{\bullet+}$ has been reported to play an important role in many reactions[47], i.e. C-H activation, oxidative coupling[56,57],

functionalization and cyclodehydrogenation[10,11,32]. $RH^{\bullet+}$s are typically more acidic than their neutral molecules, although for radical cations without benzylic or allylic position the nucleophilic attack is the preferred reaction pathway[47]. Intermolecular oxidative coupling of aryl species has been reported as well, both homocoupling and cross-coupling are possible, even though the latter requires more controlled reaction conditions in order to limit the homocoupling reaction. Oxidative aromatic coupling has been performed by several chemical oxidants[56,57], e.g. $CuCl_2$, $FeCl_3$, and by electrochemistry either directly at the electrode, as investigated by Schäfer[58,59] and by Waldvogel[60,14] by using a boron-doped diamond electrode or a molybdenum anode, or indirectly by redox mediators[61]. Recently, electrochemical oxidative coupling of PAHs has been proposed for the synthesis of new materials which are generated by a sequential stepwise coupling of $R^{\bullet+}$ that finally leads to an insoluble film on the electrode surface. Planar PAHs, like triphenylene[62] and pyrene[34], and bucky-bowl one, like corannulene[37], have been reported to generate a conductive film on the electrode by coupling of their radical-cations. The mechanism that induces the generation of PAH film is similar to the already established electro-polymerization mechanism of thiophene, carbazole and other heteroaromatic molecules[63]. In particular, oxidation of PAHs generates radical cations that in the proximity of the electrode undergo a rapid chemical reaction (coupling) with other $R^{\bullet+}$ (radical-radical coupling) or with the neutral parent molecule (parent-son coupling) to form a cationic dimer, which subsequently undergoes a deprotonation step. Successively, coupling of other $R^{\bullet+}$ with dimer or trimer generates oligomers which typically become less soluble as the size increases and ultimately deposits on the electrode surface.

Cyclic voltammetry is a powerful tool to monitor the electro-polymerization process[64]. In fact, the oxidation wave appears chemically irreversible with a number of exchanged electron close to 2[63], moreover, by performing multiple

cycles a stepwise increase of the current is observed and new redox processes start to appear in the voltammetric patterns (Fig. 2). Such processes are typically related to the doping/de-doping processes of the electrolyte ions inside the film[32,34]. Furthermore, as observed in some works concerning the organic semiconductors and their electrochemical synthesis, as also reported by Bruno et al.[37], the oligomerization process leads to an apparent narrowing of the solvent potential window at negative values[37]. The authors proposed that the proton released in the proximity of the electrode during the oligomerization process, coordinated by two CH_2Cl_2 molecules would in fact undergo a reduction process at a potential of -2.19V vs SCE (calculated by DFT-B3LYP/cc-pVTZ), thus limiting the potential window at negative potentials.

Radical-cation may also play an important role as intermediate in the cyclodehydrogenation reaction, also known as Scholl reaction. Even though the reaction mechanism is not completely clarified, following Rathore works,[11] $R^{\bullet+}$ can act as an electrophile which reacts at the electron-rich position of the other aromatic ring, forming a new C-C bond followed by a deprotonation step to restore the aromaticity. Electrochemical intramolecular cyclodehydrogenation has been recently reported as well, Ma et al. reported the synthesis of hexa-peri-hexabenzocoronene (HBC) from the electrochemical oxidation of hexaphenylbenzene[13,65][a] in CH_2Cl_2/Bu_4NPF_6 on ITO electrode. Similarly to the oxidative coupling discussed above, cyclic voltammetry shows an irreversible oxidation wave and an increasing current during multiple cycling with new processes appearing in the CV curve associated to cyclodehydrogenation (Fig. 2b). The authors

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[a] Note: In the same period, research on the electrochemically induced cyclodehydrogenation was independently carried out also at the University of Bologna. The cyclodehydrogenation of o-terphenyl to triphenylene and hexaphenylbenzene to hexa-peri-hexabenzocoronene were reported in CH_2Cl_2/Bu_4NPF_6 on Pt, Au and ITO electrodes. Unpublished results were reported in: E. Ussano, G. Valenti, F. Paolucci, M. Marcaccio. An electrochemical pathway to generate self-assembled nanographenes and graphene-like films. Abstract of meeting *ChemOnTubes*, March 30th-April 3rd 2014, Riva del Garda, Italy.

also observed the formation of a conductive film on the ITO electrode, which was attributed to the self-assembling of HBC molecules in fiber-like structures, due to the lower solubility of HBC molecules and intermolecular π-π interactions, even with a graphene monolayer surface influencing the crystal growth orientation[66]. Recently, following the same procedure, Ma et al. also reported the electrochemical synthesis of more expanded PAH[32]. Also, Bruno et al. under strictly aprotic conditions in dichloromethane observed an electrochemically induced intramolecular and intermolecular cyclodehydrogenation mechanism (Fig. 3) during the oxidative oligomerization of corannulene[37] (Fig. 4) that leads to a polycorannulene film made of wavy sheet nanostructures (Fig. 4d). Despite the electrochemically deposited film of polycorannulene is mainly composed of an amorphous phase, some lamellar crystals were observed in the TEM images (Fig. 4c) with a large inter-layer distance (from FFT analysis 10.2 ± 0.2 Å); such a value, higher than graphene interlayer separation in graphite and other carbon nanostructures, is due to the corannulene bowl-shape and favourable concave-convex interactions also mediated by intercalated solvent molecules.

Section 4 Applications

The PAHs discussed above and the examples of materials obtained through electrochemically induced processes make these carbon-based systems very attractive from an application point of view. Among the various employments PAHs have attracted interest for the electrochemical energy storage technologies, e.g., organic redox flow battery (ORFB), anode for Li-ion batteries, cathode materials for Al-ion batteries[67,68] and pseudocapacitive electrodes[34] owing to their low cost, stability and low molecular weight. Wang et al. reported the use of small PAHs and their radical-anions[33] as anolytes for ORFB that potentially could reach very high power density[69], due to their very negative reduction potential and high chemical

stability. However, some technological aspects still remain challenging for the development of commercial ORFB, like suitable separating membranes[70]. In the framework of nonplanar π-structures, Petrukhina's group have investigated the ability of corannulene to reversibly store multiple electrons, with an electron capacity (5C/e⁻) superior to the pristine graphite (6C/e⁻) and C_{60}-fullerene (10C/e⁻). Furthermore, corannulene anions (up to $C_{20}H_{10}^{4-}$) have been observed to generate sandwich complexes with Li^+ and other alkali ion, which potentially, could be exploited as anode material in Li-ion batteries[71,72].

Other fields of application deal with the nature of PAHs; they can be considered as molecular subunits of graphene or nanographene systems, that have the ability to arrange into ordered columnar mesophases with high charge carrier mobilities along the major axis, depending on their size and shape. Also, taking into account their optical and electronic properties makes these systems suitable as organic semiconducting materials to be exploited both to design single-molecule device on a surface and optoelectronic devices like field-effect transistors or light emitting systems[63,73,74].

Conclusions

In conclusion, the electron transfer in planar and curved polyaromatic systems and related carbon nanostructures can generate carbanions and carbocations that are stabilized by the π-delocalization of the charge over the molecular framework. Often, especially for the carbocations, it is observed an intrinsically high reactivity that brings to a series of reactions, which leads to the formation of new carbon-carbon bonds, thus allowing to widen the initial unit into a larger nanostructure. Such carbocation reactivity has mostly been exploited through the use of chemical oxidants. Only recently the use of electrochemistry has emerging as a highly precise

and convenient method to perform this kind of reactions and not only considered as a characterization tool. Thus, the electrochemical approach can provide new synthetic routes based on the radical-ion chemistry for building up organic devices based on polyaromatic molecules.
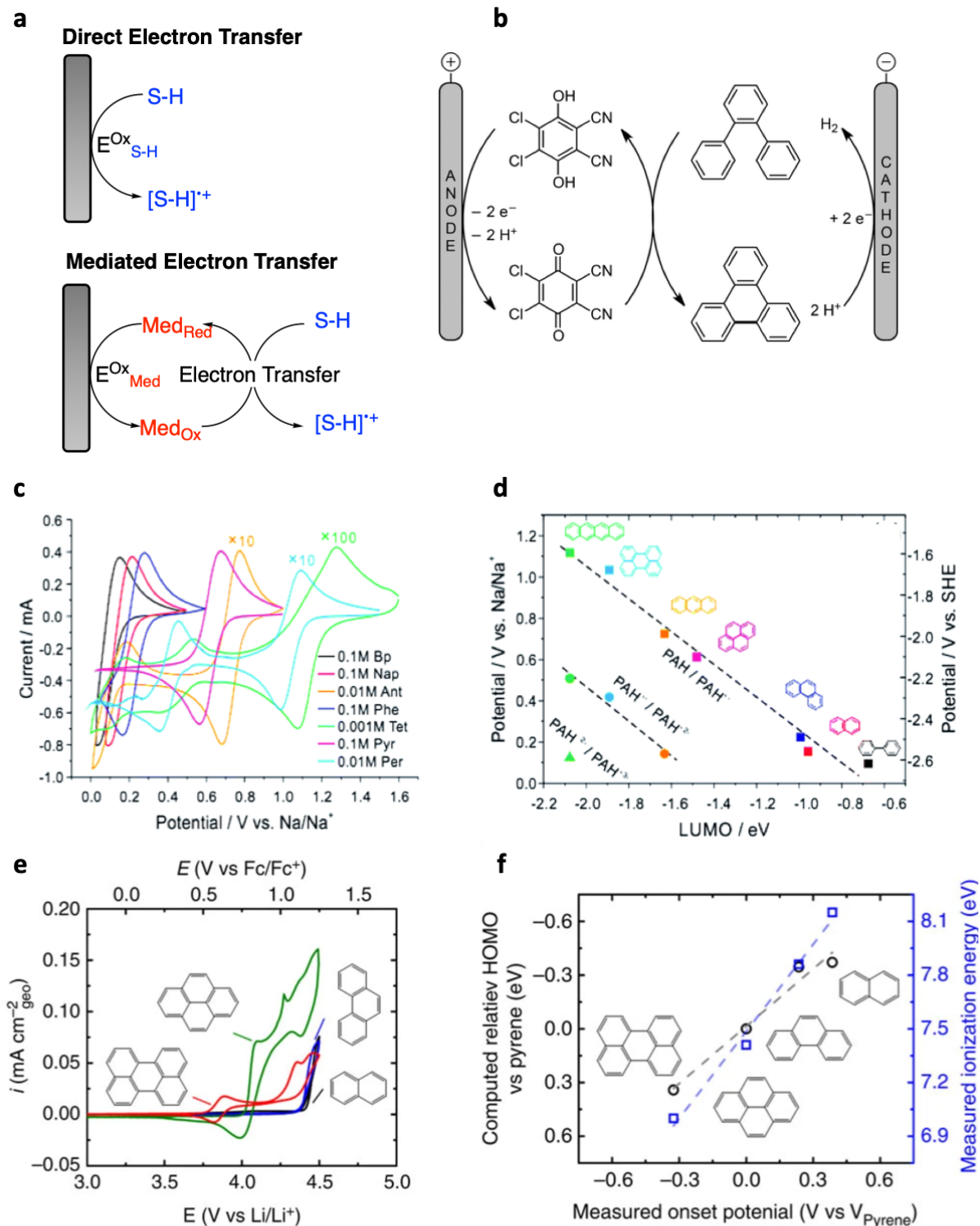
Figures

Figure 1 a) Scheme of direct and mediated electron transfer. Adapted from Ref. [30] with permission from the American Chemical Society. b) Example of Redox mediated electron transfer by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) for the

cyclodehydrogenation of terphenylene to triphenylene. Reproduced from Ref. [31] with permission from Wiley-VCH. c) Reduction processes of biphenyl, naphthalene, anthracene, phenanthrene, tetracene, pyrene and perylene in NaPF$_6$/dimethoxyethane, reference electrode Na/Na$^+$ (E^0 = -2.71 V vs. SHE). d) Linear correlation of reduction halfwave potential $E_{1/2}$ and LUMO energy. Reproduced from Ref. [33] with permission from the Royal Society of Chemistry. e) Oxidation processes of naphthalene, phenanthrene, pyrene and perylene in a mixture of ethylene carbonate, dimethyl carbonate (3:7 vol. ratio) and 1M LiPF$_6$, reference electrode Li/Li$^+$ (E^0= -3.25V vs. Fc/Fc$^+$). f) Linear correlation of oxidation potentials E_{onset} and HOMO energy. Reproduced from Ref. [34] with permission from Springer Nature.
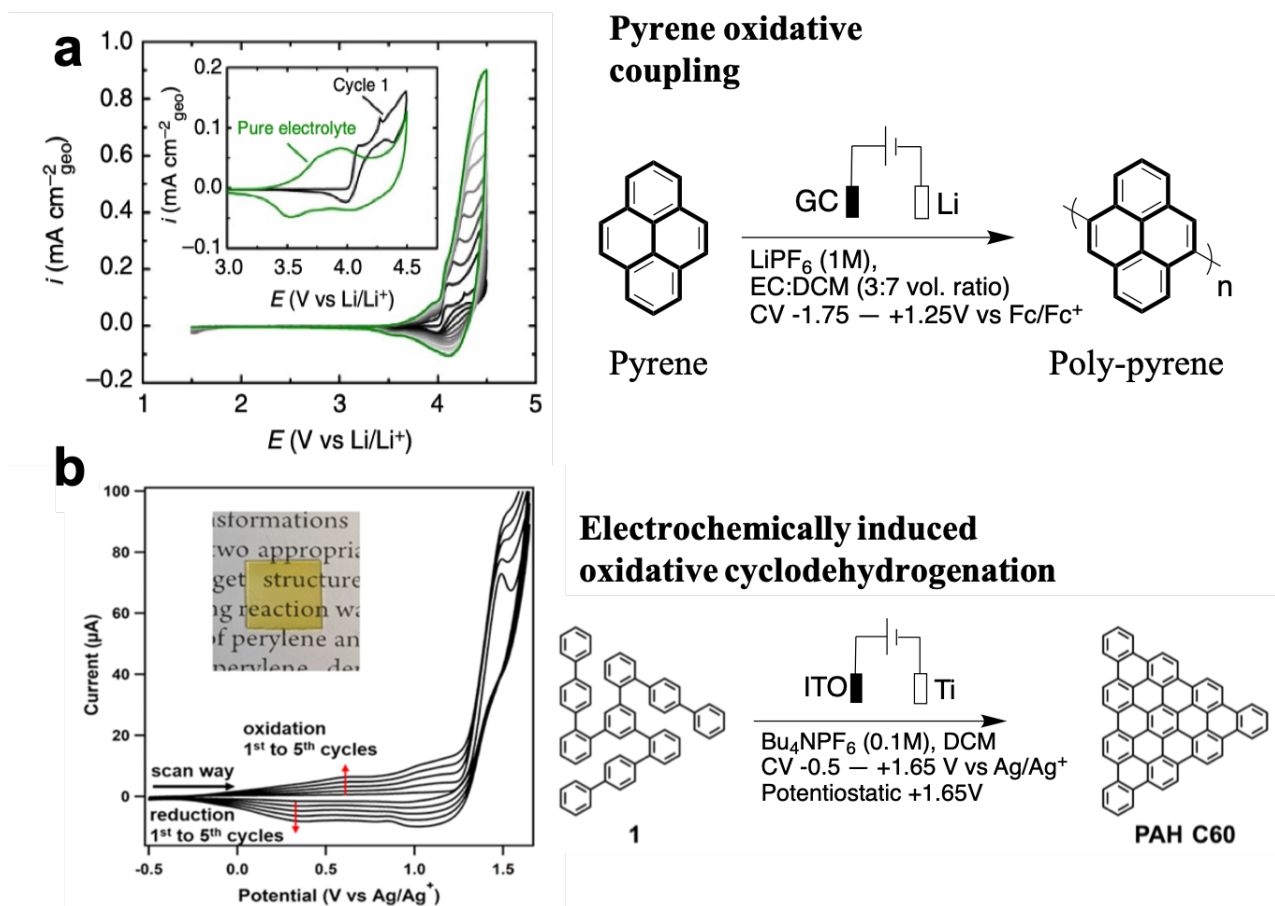
Figure 2 a) Cyclic voltammetry of pyrene in a mixture of ethylene carbonate and dimethyl carbonate (3:7 vol. ratio) and 1M LiPF$_6$, reference electrode Li/Li$^+$ (E^0= -3.25V vs. Fc/Fc$^+$) and its experimental conditions. Adapted from Ref. [34] with permission from Springer Nature. b) Cyclic voltammetry of 1,3,5-tris(2'-(4''-phenyl)biphenyl)benzene (**1**) in 0.1M Bu$_4$NPF$_6$/CH$_2$Cl$_2$, reference electrode Ag/Ag$^+$ and its experimental conditions. Adapted with permission from J. Am. Chem. Soc. 2021, 143, 7, 2682–2687. Copyright 2021 American Chemical society.
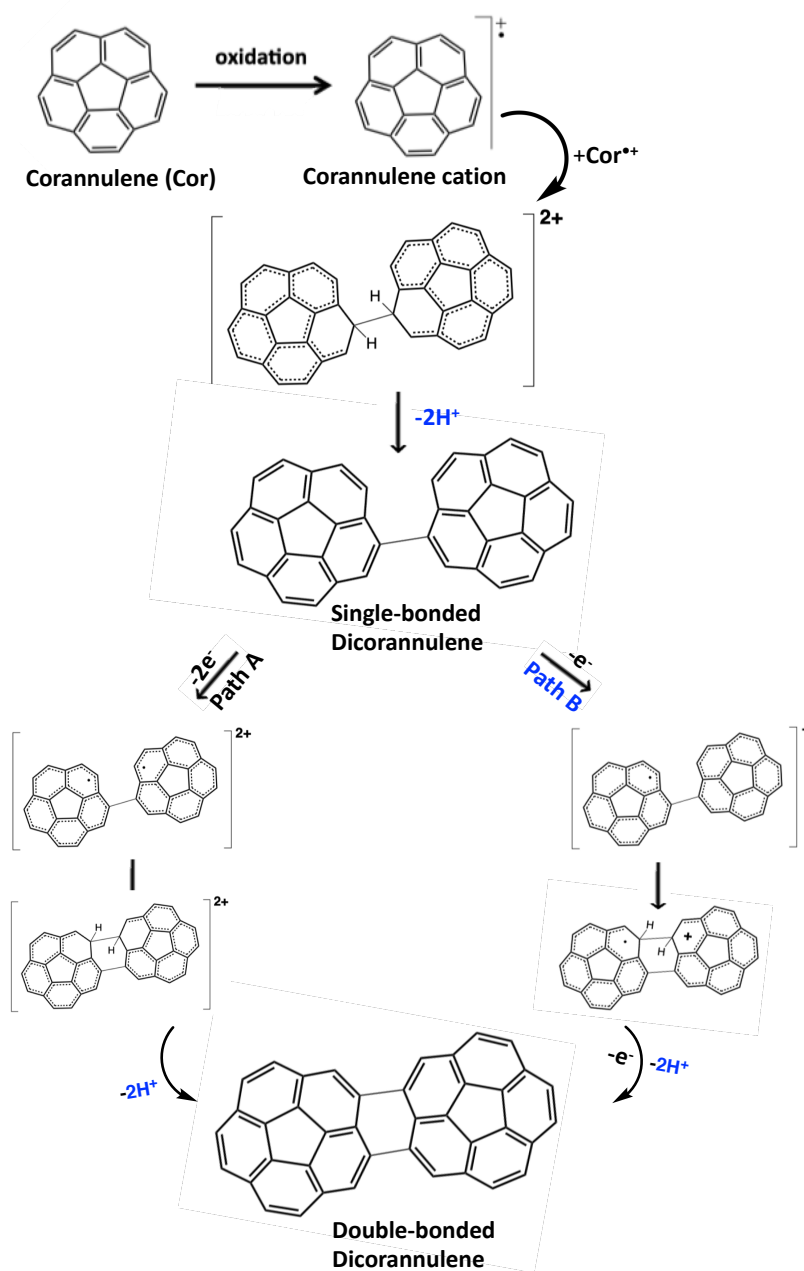
Figure 3 Proposed mechanism of corannulene for the electrochemically induced oxidative coupling and subsequent intramolecular cyclodehydrogenation to dicorannulene as first steps for the oligomerization process. Adapted from Ref. [37] with permission from the Royal Society of Chemistry.

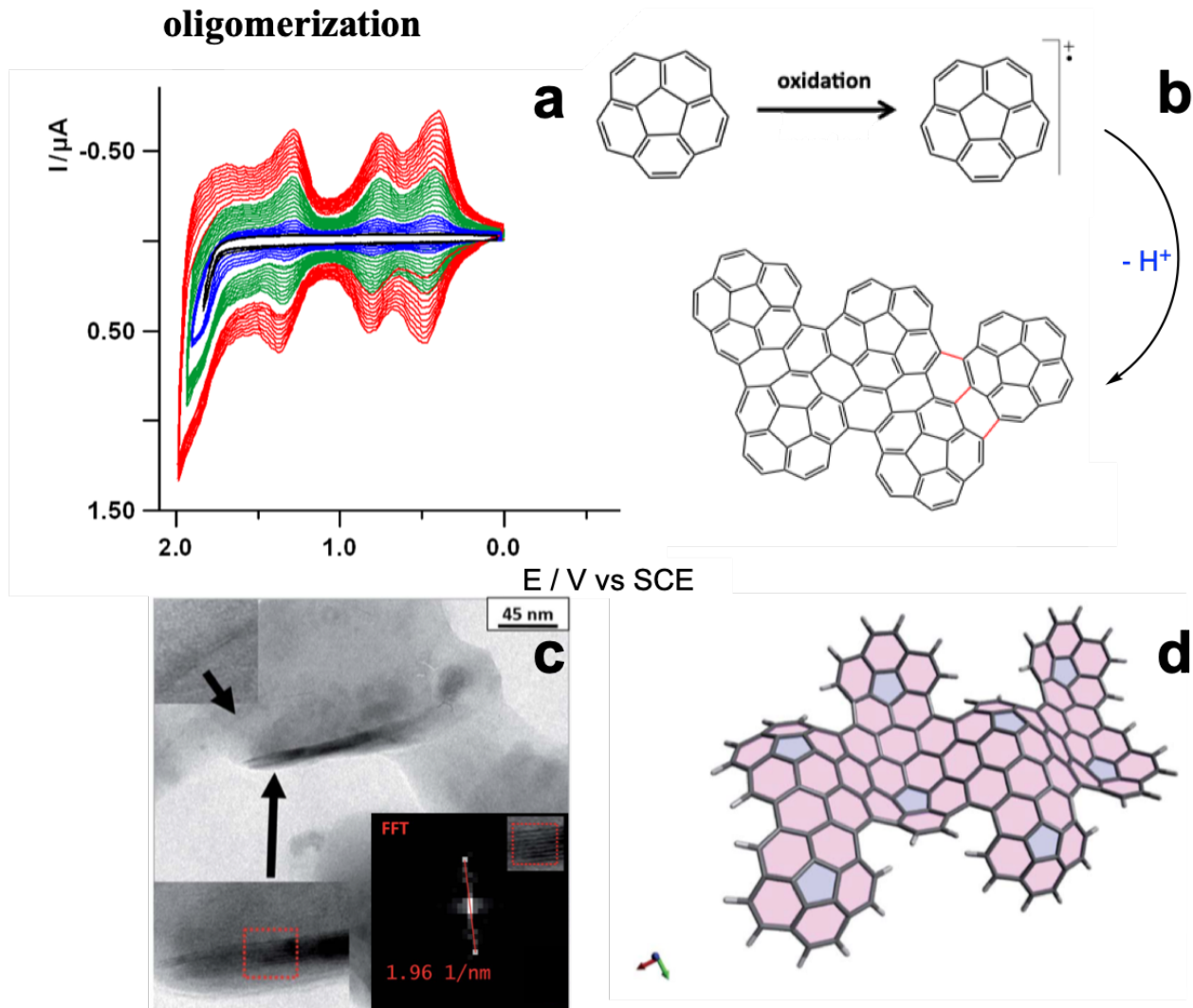**Figure 4** a) Cyclic voltammetry of 1mM corannulene in 0.08M Bu_4NPF_6/CH_2Cl_2, WE Pt disk diameter 125μm; reference electrode SCE; multiple set of scans with slightly higher reversing potentials. b) Simplified sketch of the proposed intermolecular cyclodehydrogenative oligomerization of corannulene. c) Bright-field TEM image of suspended polycorannulene and FFT analysis of the dashed red square. d) DFT-optimized structure of the condensed corannulene octa-oligomer. Adapted from Ref. [37] with permission from the Royal Society of Chemistry.

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