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Synthesis of anthraquinone based electroactive polymers: A critical review

Gul Zarren[a,b], Bushra Nisar[a,b], Farooq Sher[a,c,*]

a. *Department of Chemical and Environmental Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK*

b. Department of Chemistry, Government College Women University, Faisalabad 38000, Pakistan

c. School of Mechanical, Aerospace and Automotive Engineering, Coventry University, Coventry CV1 2JH, UK

Abstract

Conducting polymer or synthetic monomers have revolutionized the world and are at the heart of scientific research having a scope of vast diverse applications in many technological fields. The conducting and redox polymers have been investigated as an energy storage system due to their better sustainability ease of synthesis and environmental compatibility. Due to the conducting properties of quinones, it gains too much importance among the researchers. Keeping in view the importance and sustainability of conducting polymers, for the first time this study compiles the detailed overview of synthetic approaches followed by electrochemical properties investigations and future directions. This study critically examines the synthetic process of simple monomer, substituted monomer and polymers of anthraquinone under the classification of low and high molecular weight anthraquinone based derivatives, its working principles and its electrochemical applications which enable us to explore its novel possible application in automotive, solar cell

* Corresponding author. Tel.: +44 (0) 24 7765 7754

E-mail address: Farooq.Sher@coventry.ac.uk (F. Sher)

devices, aircraft aileron and biomedical equipment's. Irrefutably, we confirm that high molecular weight polymeric anthraquinone compounds are best in comparison to low molecular weight anthraquinone monomers as they have preeminent properties over monomeric systems. Because of the significant properties of anthraquinone, polymeric systems are high demanding and emerged as a hot topic among the researchers these days. In the current scenario, this study is of immense importance, as it identified and discussed the right and sustainable combination, and pave the way to utilize these novel materials in different technologies.

Keywords: Organic polymer; Anthraquinone; Electrochemistry; Energy harvesting and Future direction.

1 Introduction

Polymers which respond to the external electric stimulation exhibit a considerable change in shape or size and are known as electroactive polymers [1]. Due to the simple synthesis methods and processable signals, electroactive material with tailorable moieties is considered as smart material [2]. These novel electroactive materials can endure large forces and show low deformation value as it can bear an ultimate tensile strength of 320% with normal strength of 8 MPa [3]. Recently, polymeric material designed with the latest technology gives a better result in term of its application and revolutionized the world. In the last few years, researchers introduce us with the new technology in the field of robotics and artificial muscles with the help of using electroactive polymers (EAPs) referred to as electro-responsive material [4].

EAP is extensively used as an actuator and being investigated for sensing purpose. As mentioned above, the most important characteristic property of EAP is the enduring feature of large forces and deformation while the conjugated electroactive polymer also manifests low ionization potential, low energy optical transition and high electron affinities [5]. Such type of material commonly characterized as either electric or ionic [6-8]. Both types have a dissimilar performance and different set of characteristics in certain considerations [9, 10]. Until 1977 all polymers were commonly known as electric insulators but the first work on true conducting polymer was done in 1993 which encourage the researchers to think and explore about its possible application and one-pot synthesis methods [11].

From last two decades, the interest flourishes in these electroactive organic polymers not only because of their ease of synthesis but also due to their wide applications in textile dyes, cosmetics, pharmaceutical, energy storage devices and paints industries. Until now, the classes that developed are categorized into these three groups based on their functionalities:

1. Conducting polymers: Conducting polymers are highly conductive with conjugation along the polymer backbone [12] and their conducting behaviour is firmly related to the highly conjugated electronic structure [13].
2. Donor-acceptor complexes: The material which shows a range of electrical conductivity with respect to insulator, conductor and superconductor is known as donor-acceptor complex [14].
3. Redox polymers: This class of polymer comprises of redox active centres, which reduced and oxidized reversibly and electrochemically [15-17].

These three categories have a close relationship. Sometimes their applications and properties are so similar that even it is difficult to distinguish them from one another such as polyacetylene when used with donor-acceptor could increase the conductivity and often referred as donor-acceptor complex polypyrrole and polyaniline. Conducting polymer are sometimes classified as redox polymers and also known as electron exchange polymer/ redox exchangers/ oxidation or reduction polymer by some other authors [5, 18].

In all evolving fields, organic based conducting polymer have been extensively studied due to their potential application in electronics, sensors, artificial muscles, electrochromic devices, capacitors and electromagnetic radiation shielding etc. [19-23], rather than inorganic oxides [24]. In current years, numerous redox-active organic materials for example radical polymers, organosulphur and carbonyl functionality have been studied in different storage system [25]. The redox function in a polymeric system is organic in nature (e.g., hydroquinone/quinone system) [26, 27], while inorganic systems are also used (.e.g., ferrocene, Ru (bipy) $^{2+}$) [28]. The quinonide structures are of high interest due to their usage in various fields.

The quinones system gives semiquinone and hydroquinone by two electron reversible reduction and oxidation Fig. 1. Quinone system exhibits a drawback as the formation of a quinone from semiquinone oxidation cause toxicity while the hydroquinone formation from two electron reduction of quinone through semiquinone leads to the excretion eventually cause cell damage [29]. To deal with these limitations, researchers worked to figure out the compound that can combat these issues. Over the past few years, anthraquinone (member of class quinone) has been widely examined as an electroactive material in Li ion, Na ion [30] and Au electrodes [31] battery systems in the monomeric and polymeric form [32].

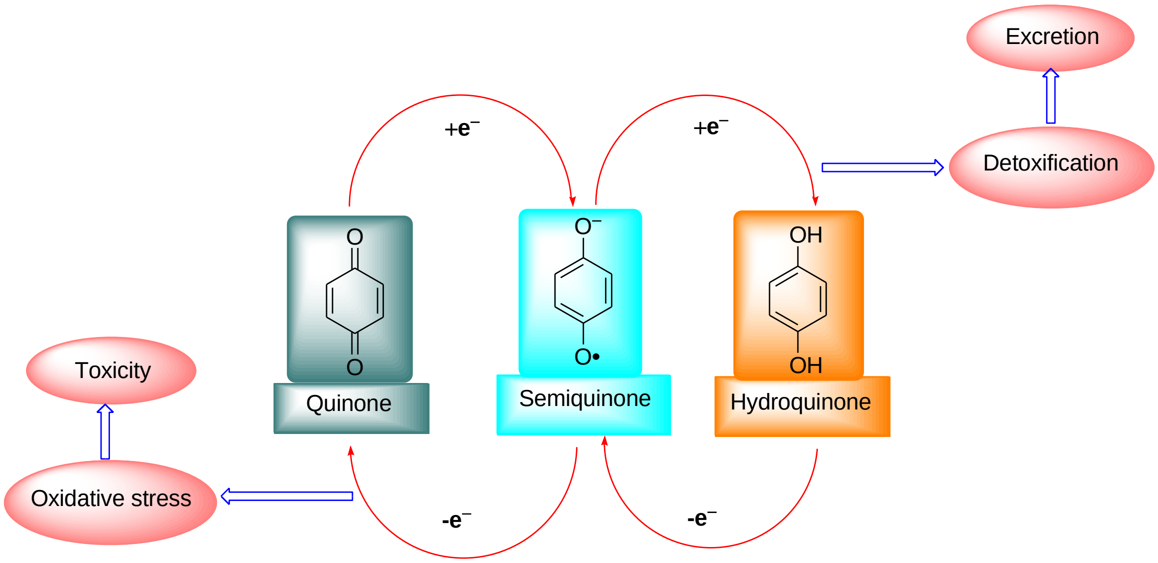


Fig. 1. Quinone redox cycle and its possible effects.

Predominantly, anthraquinones exhibit a faster reaction at heterogeneous rate constant for the electrode reaction (>10^{-2} cm/s) at moderately negative potential (-0.8V) [33]. Anthraquinone also possesses the obvious chemical potential because of the absence of α-hydrogen which mostly incline to the deprivation [34]. Furthermore, anthraquinone derivatives exhibited exceptional performance on electron transfer and electrochromism [35]. The storage of electric energy has significant importance for our developing technology-based society. Current Li [36], Na, and other inorganic ion storage system exhibits many disadvantages such as toxicity, low cycle life, leakage, volatility, polarizability, sustainability, costliness, performance, specific energy, safety and short lifespan [37-39]. Many studies were conducted which focus on plant mediated green chemistry approach having nontoxic and eco-friendly conducting material (quinone and anthraquinone). As an alternative to the traditional energy storage system that causes toxicity and dissolution, organic electroactive polymers combat the issues concerned with the traditional storage system. Quinone functionalize compounds are the promising energy storage material. To fully realize the potential of quinone compound, ancient energy storage components (fossil fuels and coal) [40] must be replaced by green materials. Anthraquinone serves as an efficient energy storage system which could get from the natural sources like Aloe [41] and Rhubarb [42] plants and could be synthesized in organic labs [43]. Different methodologies adopted previously focused on the synthetic methods and applications of anthraquinone derivatives pharmaceutically only in drug formation, drug extraction [44] and electrochemically only in storage battery systems [45] and in dyes industry [46].

In this ever flourishing scientific field, it is difficult to compare even a single organic compound synthesis and its applications as many data are available in the literature and information regarding the species may differ due to the different synthetic approaches and vast applications in different fields. So there is a yawning need to compile the information regarding quinone conducting system to have a quick idea that which is the most appropriate technique to synthesize potentially applicable compound. Herein, the present study aimed to amass the data of anthraquinone based electroactive compounds. Anthraquinone for energy storages systems can be synthesized and modified as a monomer, polymer and copolymer by utilizing three different techniques i.e. by catalytic synthesis, electro-polymerization and free radical polymerization. Therefore, this study comparing the synthetic approaches and electrochemical application of a simple and substituted polymeric system of anthraquinone based low and high molecular weight compounds. Anthraquinone incorporated polymers can be synthesized by different synthetic methods and have a discrete set of advantages over the other.

2 Structure and electrochemistry of anthraquinone

The structure of anthraquinone (AQ) was first evaluated by Sen in 1948 and then was further refined by Murty in 1960. The final refinement of the structure was carried out by Prakash in 1966 and nomenclature by Moss in 1998. Structure of anthraquinone consists of a planar, rigid structure having three conjugated aromatic rings resembling anthracene ring system Fig. 2. The anthracene ring functionalized with the keto function at the 9 and 10 positions [47-49]. This compound anthraquinone was already synthesized with the nitric acid oxidation of anthracene by Laurent [43].

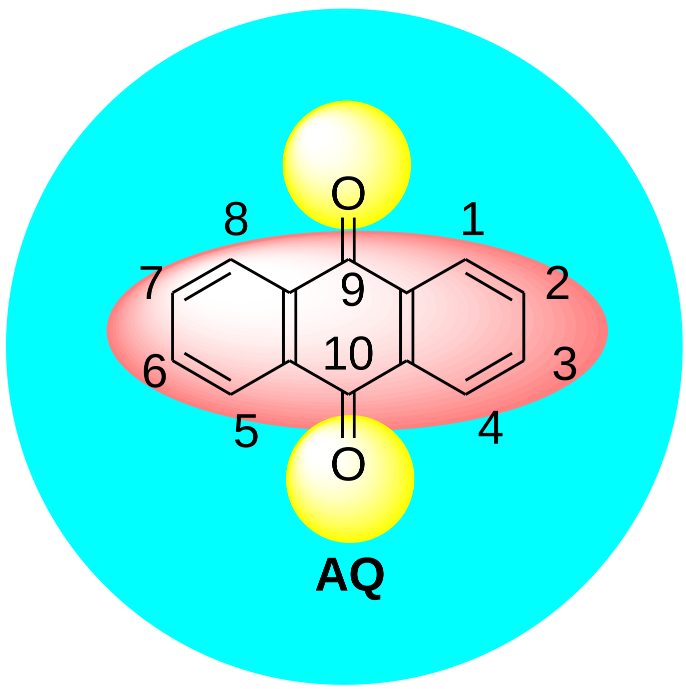


Fig. 2. Structure of anthraquinone.

After the structure elucidation of anthraquinone (AQ), electrochemical investigations of the compound were made by different scientist groups because of their incredible reversible redox reaction ability. The anthraquinone moiety has been used commendably not only in energy storage systems but also in dyes [50], paint [51] and medicinal industries [52, 53]. Yao and coworkers [45] worked on anthraquinone, utilizing its exceptional redox ability in the rechargeable battery system. Anthraquinone having two carbonyl functionality can undergo stepwise two reversible redox reactions at around -1.3 and -1.6V that shows its characteristic of two electron transfer cycle per anthraquinone molecule. This property of two electrons reversible cycle is of keen interest to the scientist for the last 40-50 years. Recently, various anthraquinone derivative with simple to high molecular weight structure was synthesized and investigated. The entire recently reported anthraquinone derivative exhibits remarked life cycle and increase the durability of storage batteries. The resultant of anthraquinone charge/discharge characteristic gives a capacity fade up to 255 mAh/g [54] that signifies the two electron shift reaction of anthraquinone as shown in Fig. 3 and Fig. 4.

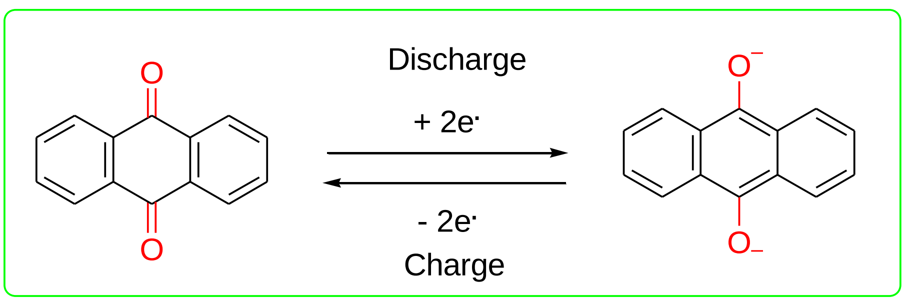


Fig. 3. Electron shift of anthraquinone.

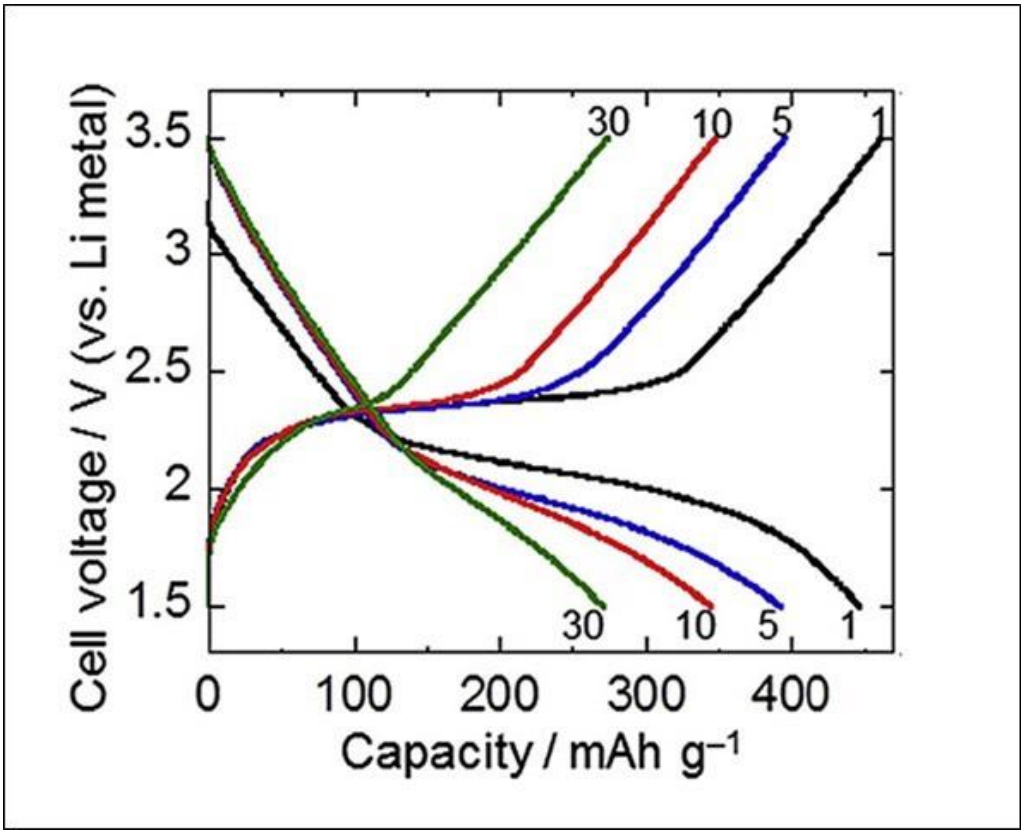


Fig. 4. Graph exhibiting the charge/discharge behaviour of AQ at the scan rate of 0.2C. Charge/discharge curves of AQ for 1st, 5th, 10th and 30th cycles shows capacity fade up to 255 mAh/g [54].

Be contrary to the anthraquinone, its high molecular weight analogues pentacenetetrone showed higher initial discharge and prominent cycle stability due to the extended π system and delocalization of electrons. Nevertheless, the cycle life, durability, stability and capacity of anthraquinone could effectively increase by extended delocalization or by different methods. To overcome the shortcomings of anthraquinone, different approaches were made by simple substitution, derivatization or by polymerization.

3 Synthesis of low molecular weight anthraquinone derivative

Up till now from the discovery of first organic anthraquinone polymer, numerous developments have been taken place in this field. Most of the reports published in the last few years aim to remould anthraquinone to achieve better processibility and sustainability. A great concern about the synthesis and characterization of EAPs has been observed. Herein, we describe an overview of the work of some researchers on EAPs based on anthraquinone, its derivatives and a substituted anthraquinone for rechargeable batteries.

Song et al. (2015) [55] polymerized the 1, 4-dichloroanthraquinone (1,4-DCAQ) to get (**2**) and isomer P15AQ as shown in Fig. 5 This polymer based on simple structures shows unprecedented implementation and better performance to achieve effective cycle stability. Due to the high solubility of (**2**) in $CHCl_3$, it could be used effectively in flexible, high-performance and green energy-storage devices. While Zhou *et al*. (2015) [56] analyzed the Ketjenblack carbon supported polyanthraquinone (P26AQ) (**4**) synthesized according to the method shown in Fig. 5, in aprotic electrolytes as a pseudo-supercapacitor electrode material. The quinone molecules on the carbonated support mainly polymerized by this method could increase the conductivity, reduce the possibility of proton donation and enhance the performance. The electrochemical studies divulge that these composite materials have good cycling stability, large energy or power density and high specific capacitance.

Poly-AQS (**6**) as an active material for rechargeable batteries instead of using simple polyanthraquinoe (PAQ) made according to the Phillips method by polycondensation as shown in Fig. 5. The analysis of cathode active material in ether and ester electrolyte shows better cyclability and sustainability because of attached sulphide group in any solvent but in term of energy density, it provides not a better alternative because of its lower discharge voltage [57].

By following the method of song et al. Xu *et al*. (2012) [58] synthesized isomer of PAQS that is P15AQS and P18AQS. The analysis of the performance and electrochemical behaviour of these anthraquinone derivatives was done. These organic cathode materials due to their different site and less steric hindrance of substitution on anthraquinone give remarkable effect on the performance of batteries system and higher capacity and rate capability. By replacing Li (smaller) ions with Na (larger) ions, the redox reaction of anthraquinonoid group could easily be done. Deng *et al*. (2013) [30] prepared Na-ion battery based on PAQS (by following the scheme of Song et al.) [57] as an organic redox active anode and polytriphenylamine (PTPAn) cathode. The above synthesized battery system proposed a high energy density storage system but have a drawback that the excessive amount of electrolytic solvent is required for the fast conducting reaction. Instead of using Na and Li, Bitenc and coworkers [59] use Mg powdered metal anode. They produced PAQS (**6**) as redox active cathode by the same scheme used by song and coworkers. In different electrolyte systems, the rate capability of PAQS assessed the best performance in terms of capacity, but show no major development in long-term cycling with respect to the other two electrolytes used.

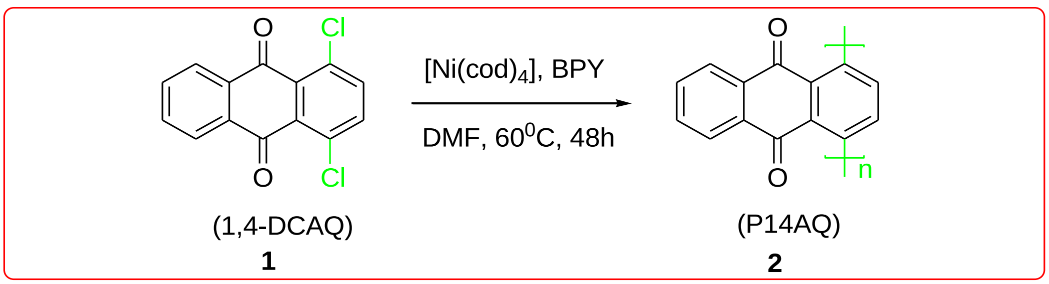
In 2016 Pan and co-workers [60] work on 14PAQ, 26PAQ and PAQS and evaluated their electrochemical properties for rechargeable Mg-ion batteries. The comprehensive study on these three compounds tells that Mg-ion battery of 14PAQ rather than 26PAQ and PAQS give a very small capacity fading during cycle life and give best cycle stability. To attain the better cycle stability the carbonyl group is replaced with thio-carbonyl group to synthesize the monothioanthraquinone polymer as described in Fig. 5. The analyses with the positive active electrode in a mixture of solvents shows the better cycle-life stability of monothioanthraquinone

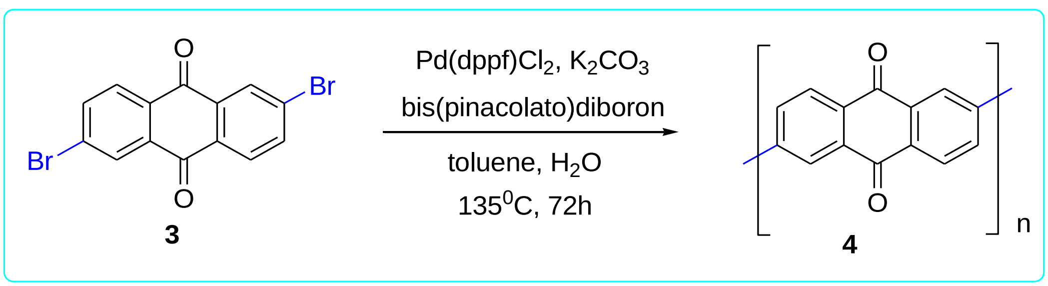
(MTAQ) (**8**) than anthraquinone (AQ) but MTAQ (**8**) have a disadvantage as the specific capacity decreases after 5 cycles due to the dissolution of active material [32].

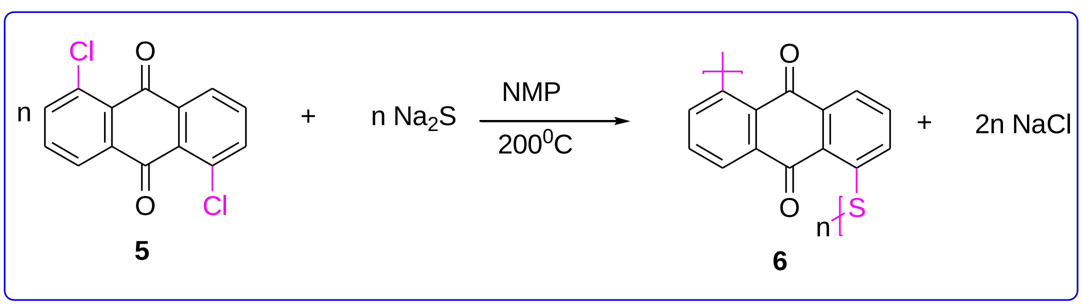
A conducting polymer such as poly-diaminoanthraquinone (Poly-DAAQ) having amino substituted anthraquinone was studied as a capacitor Fig. 5. The study shows two reversible redox reactions for continuous cycles in non-aqueous media. The spectroscopy proposed that the two sets of redox reaction observed is due to the quinone group and p-conjugated system. The study reveals that Poly-DAAQ could be used as a capacitor and in rechargeable battery systems can serve as polymer cathode [61]. The unique polymer poly (5-amino-1,4-dihydroxy anthraquinone) (**12**) synthesized according to Fig. 5 by a facile oxidation process for lithium batteries as the cathode material and characterized by different electrochemical methods. The study reveals that PADAQ shows an amended cycle performance and a high rate capacity compared to its monomer amino dihydroxyanthraquinone ADAQ but for discharge depth of (**12**) was sensitive and its cycle performance is poor when discharged to 1.0 V [62].

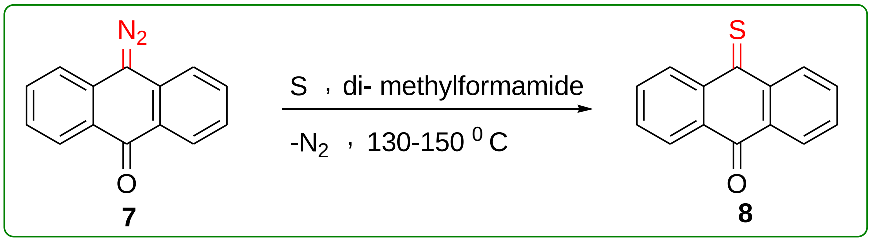
Wang and their workmate [63] examined anthraquinone derivative (**13**) Fig. 5 by nucleophilic aromatic substitution of triethylene glycol derivative into 1,5-dichloroanthraquinon. This modified anthraquinone (AQ) molecule form a different redox current flow battery with the increased solubility and stability for its imminent large-scale applications. While Choi and their colleague [34] synthesize poly (2-vinylanthraquinone) (**18**) by substituting vinyl derivative to anthraquinone to increase the formula weight Fig. 5. They analyzed it as anode active material in the aqueous electrolyte. They concluded that PVAQ is not only insoluble in aqueous electrolyte but also have stable cell capacity even after 300 cycles compared to that of conjugated, non-conjugated and polysulfide analogue.

The successful examination of novel bio-based battery material via pGD-AQ (**22**) (collecting from the biodiesel processing unit as a bio-based polymer) and redox-active anthraquinone unit utilizing as a positive electrode for Li-ion battery (synthesized according to Fig. 5) shows high capacity and greater cycle-life stability due to the incorporation of anthraquinone in polyglycidol (**22**) [64].





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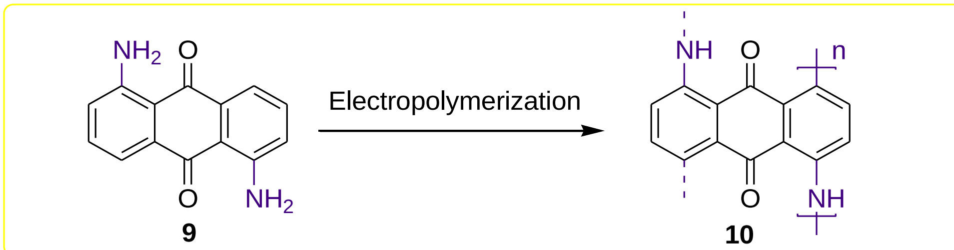
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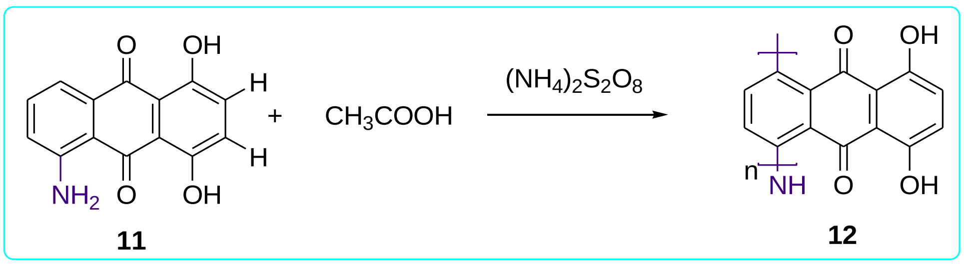
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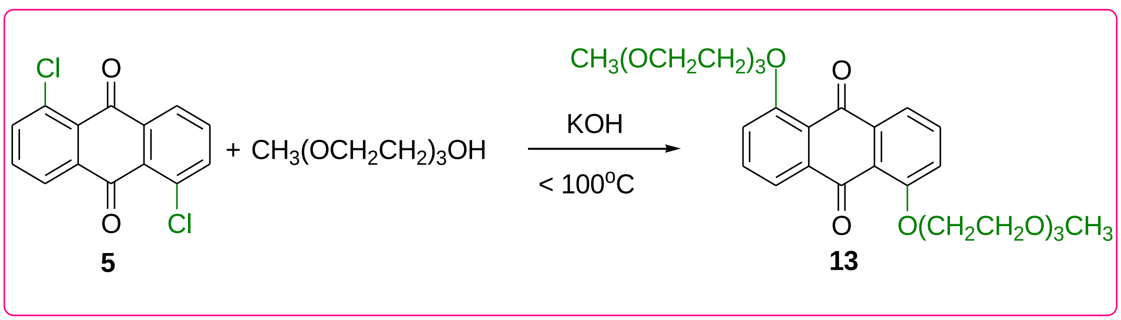
Cl O
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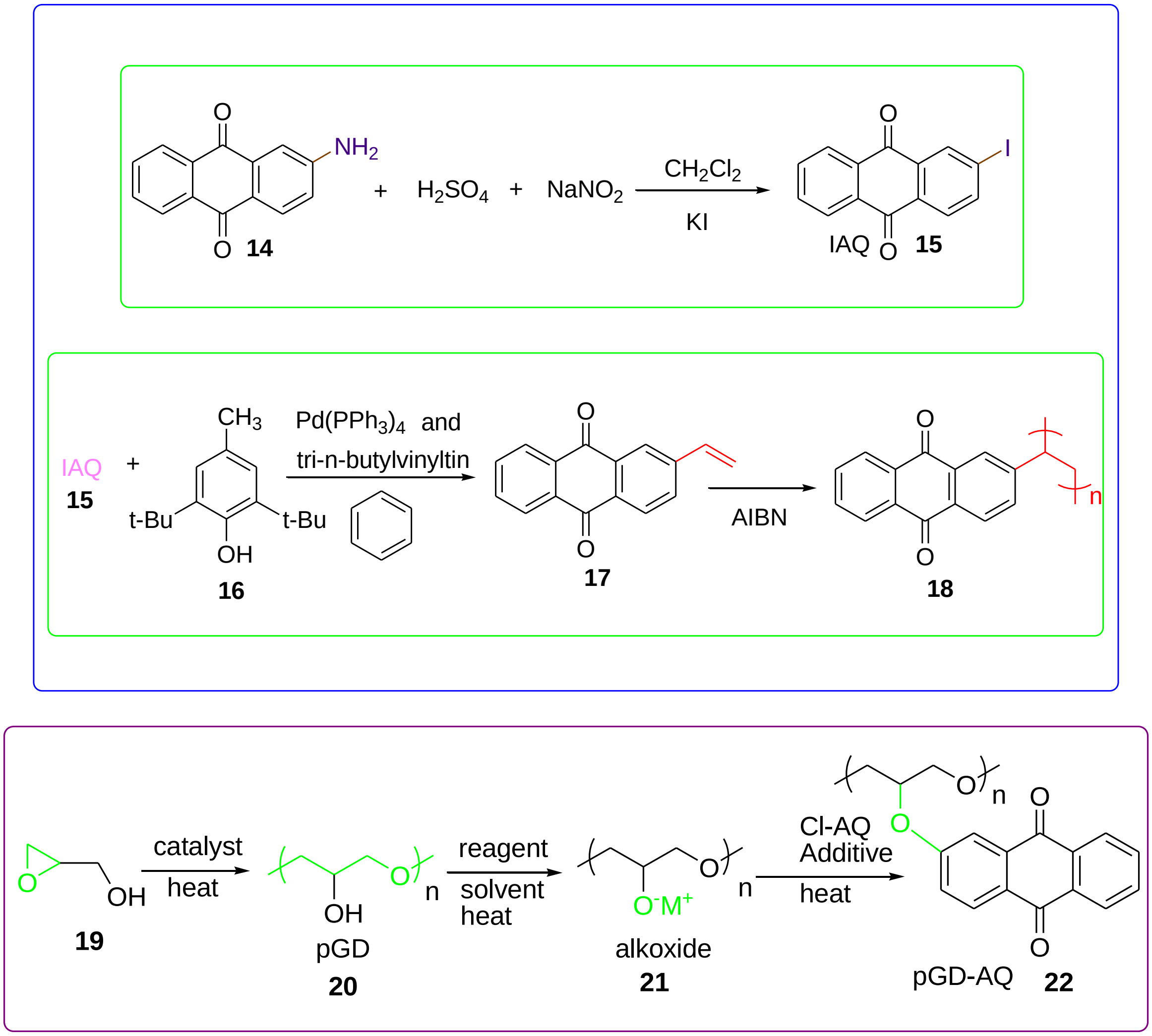


Fig. 5. Synthetic routes to anthraquinonoid derivatives poly-1,4-anthraquinone (P14AQ), poly-2,6-anthraquinone (P26AQ), polyanthraquinone sulphide (PAQS), monothioanthraquinone (MTAQ), poly-diaminoanthraquinone (Poly-DAAQ), poly-5-amino-1,4-dihydroxy anthraquinone (Poly-ADAQ), polyvinylanthraquinone (PVAQ) and polyglycidol substituted anthraquinone (pGD-AQ) (**1-22**).

Currently, Hernandez and coworkers [65] give a new approach toward a green future and examined the new polymeric redox-active poly (ionic liquids) (**24**). They incorporated the redox active counterions, anthraquinone and nitroxide into the poly (ionic liquids) which enhances the application of these materials in energy storage systems. Polyionic liquids synthesized by simple ions exchange reactions. Among the reported compounds, the schematic procedure mentioned here in Fig. 6 show remarkable properties. The electrochemical study shows that these materials have specific property to be used in energy storage systems. The homopolymer having 100% of anthraquinone units exhibits a very good capacity and stable life cycle when used as the electrode in lithium batteries.

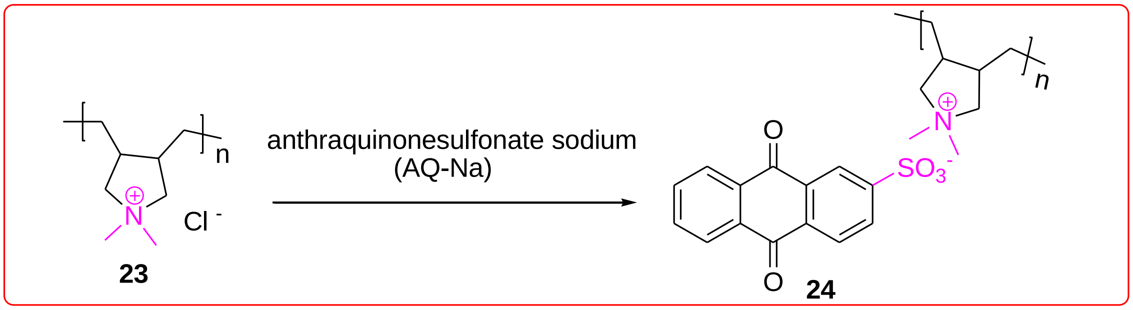


Fig. 6. Ionic anthraquinonoid polymer.

4 Synthesis of high molecular weight anthraquinone derivative

Literature reports a number of syntheses in which there is an incorporation of high molecular weight substituted rings. These substituted rings contain anthraquinone either as a central core or as a pendant group. Due to the incorporated anthraquinone, these materials also show electrochemical properties, some of them are discussed here in this review. Oyaizu [33] explored the new redox active polymer that is anthraquinone-functionalized polystyrene (**28**), synthesized according to Fig. 7, which at negative potentials shows a reversible charge storage capability. The ester linkage here allows the swelling of the polymer that describes its good affinity to the electrolyte solution. For charge storage application the pendent group, successively reduce anion and dianion and proved to be used as organic anode-active materials.

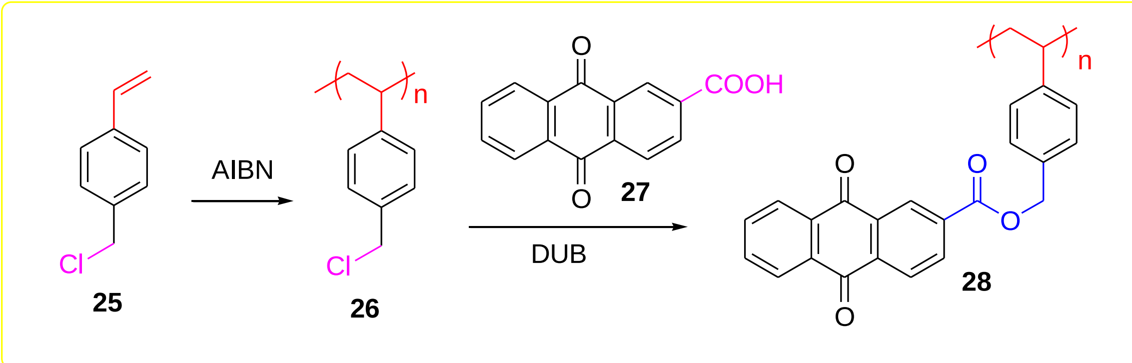


Fig. 7. Anthraquinone reaction with the polystyrene derivative **25-28**.

The carbonyl group of AQ by substituting N-cyanoimine group gives N, N´dicyanoanthraquinone diamine (DCAQI) (**29**, **32**) (synthesized according to Fig. 8). The analyses of poly- DCAQI (**30**, **33**) in dimethylforamide (DMF) electrolyte shows the stronger electron accepting properties of N-cyanoimine group leads to higher reduction potentials compare to that of AQ. But the difficulty in this compound utilization is the partial hydrolysis of cyanoimine group which ultimately give higher reduction signal value of -1.26V [28]. Instead of using dicyano, a new tetracyano group replace the carbonyl functionality and give tetracyano anthraquinone derivative (**36**). Poly-TCAQ (**37**) as mentioned in Fig. 8 synthesized in four simple steps. Poly-TCAQ exhibits a high material activity of 97%, the excellent columbic efficiency of 99% and high rechargeability with only 12% loss [66].

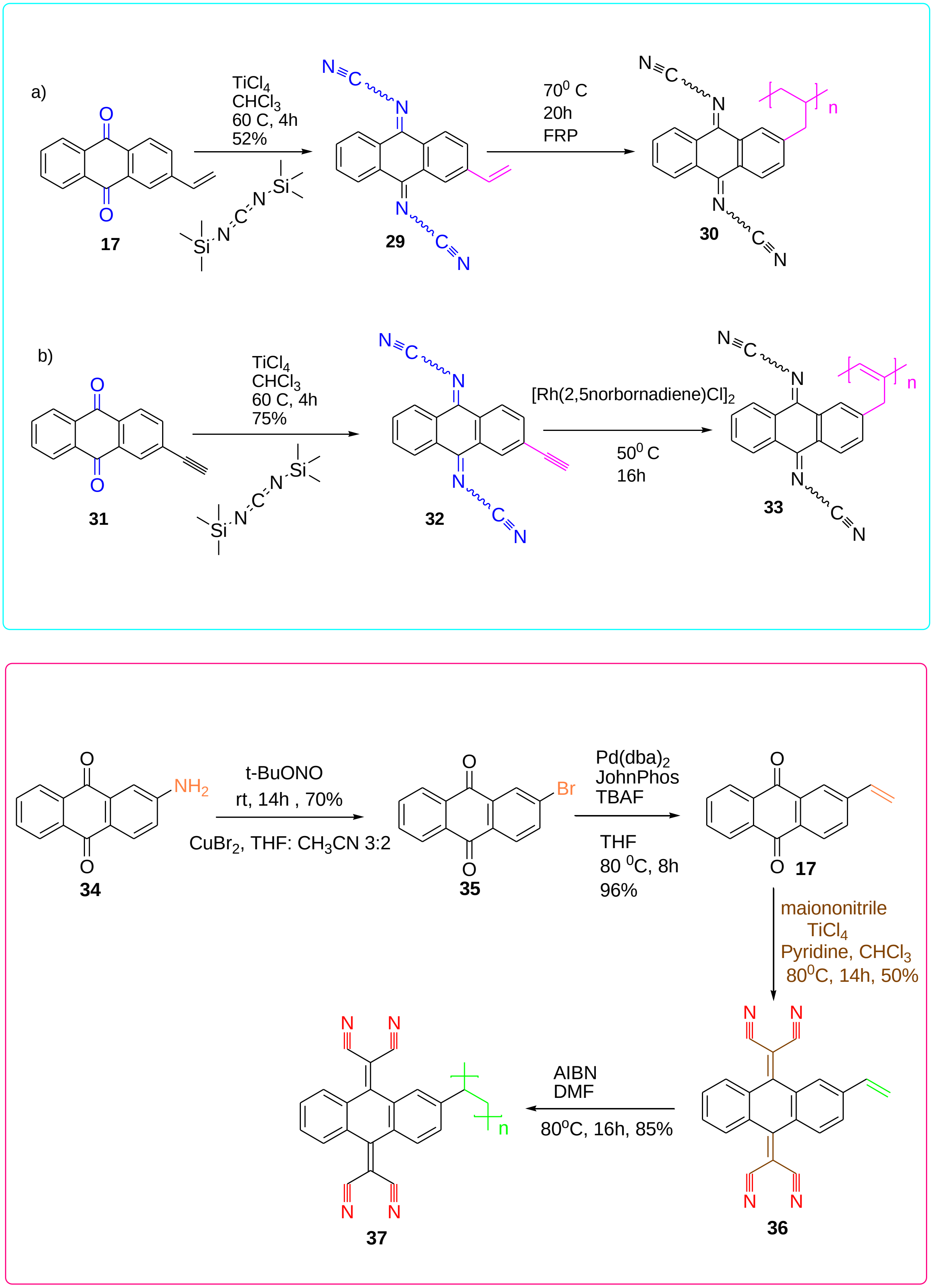


Fig. 8. Synthetic route to Poly-DCAQI (**17**, **29-33**) and Poly-TCAQ (**34-37**).

Foremost to bipolar compounds, the carbonyl functional group modified with three different moieties that ~~is~~ are Thione (**42**), dicaynomethylene (**43**) and N-caynoimine (**44**). The scrutinization of these redox active compound, which polymerizes with the vinyl group through free radical polymerization method Fig. show limited reversibility. Due to the limited reversibility and side reactions, these compounds could be used after further optimization in organic batteries [67].

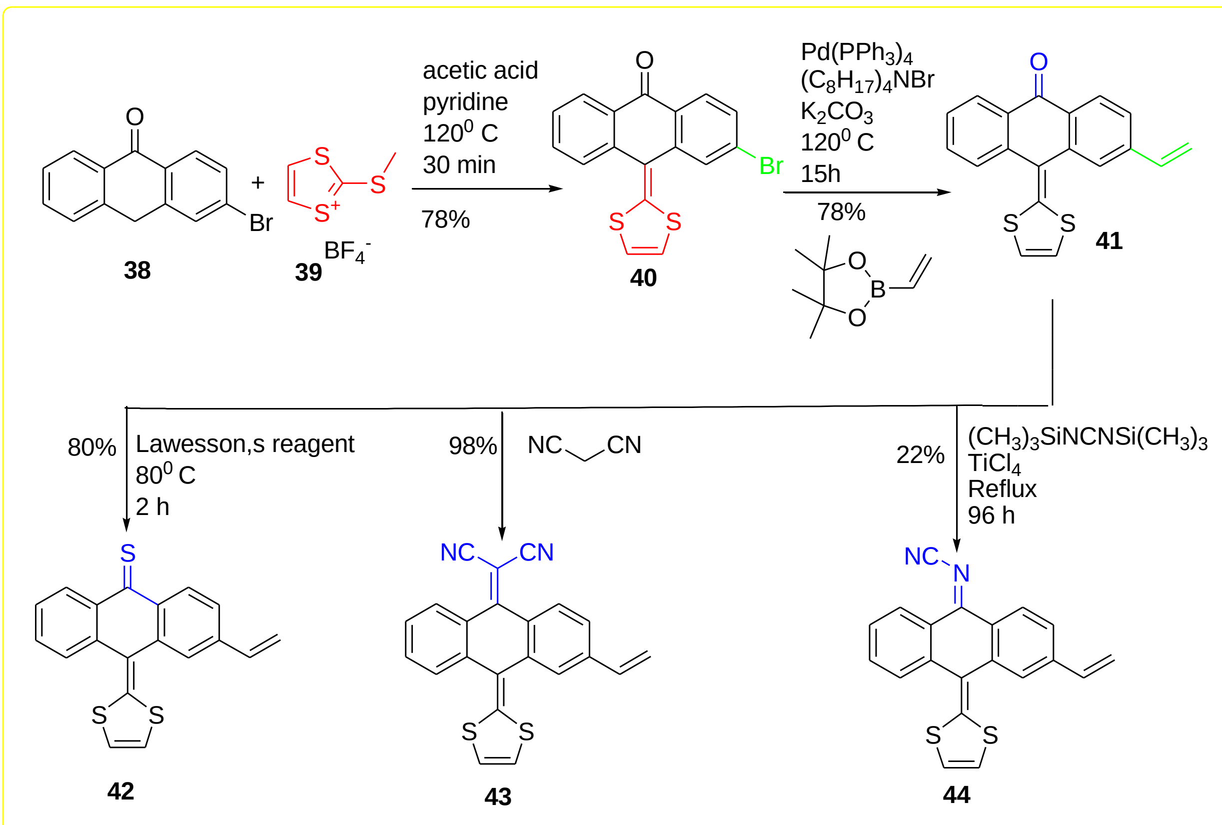


Fig. 9. Thione (**42**), dicyanomethylene (**43**) and N-cyanoimine (**44**) functionalized anthraquinone derivative.

Seidel and their workmates synthesized, designed and characterized the fourteen novel products of 9,10-anthraquinone and 9,10-dimethoxy anthracene from which the synthesis of two are mentioned in Fig. 10. The corresponding compounds due to the π conjugated thiophene ended side groups linked with the anthracene core at 1 and 5 position give somewhat stable compounds [68].

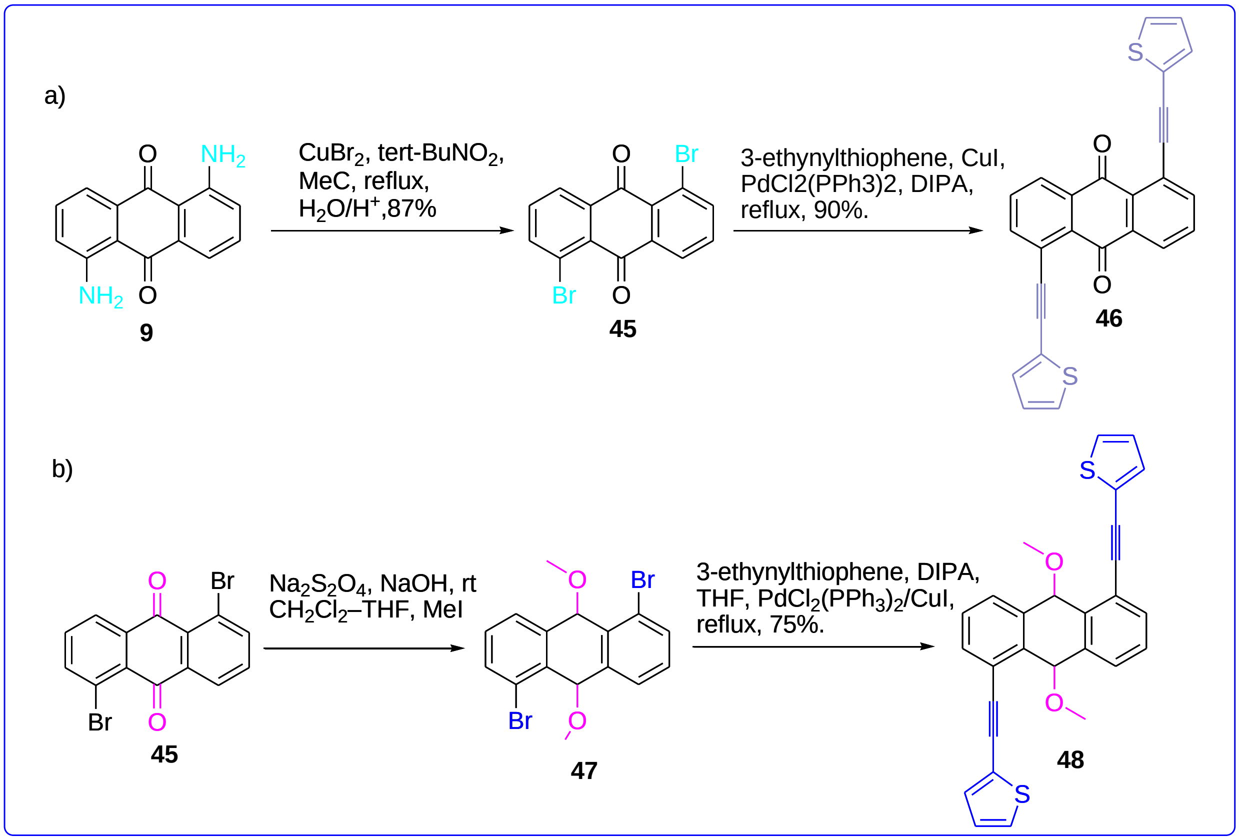


Fig. 10. Anthraquinone having thiophene terminated groups **45-48**.

The substitution of tetrathiafulvalene (TTF) moiety at the place of the carbonyl group in AQ gives compound (**49**) shown in Fig. 11. The synthesis of this yellow powdered compound provides a satisfactory result as cathode active material in the aqueous electrolyte [69]. Though, Diaz and coworkers [70] report the dimer compound by Witting-Horner reaction consisting of two exTTF units connecting through the vinyl group (**50**) Fig. 11. Principally, this anthraquinone derivative shows different electrochemical behaviour than that of compound (**49**) previously reported. Resultantly, in spite of the connection between two exTTF units, both units behave independently with no significant electronic communication.

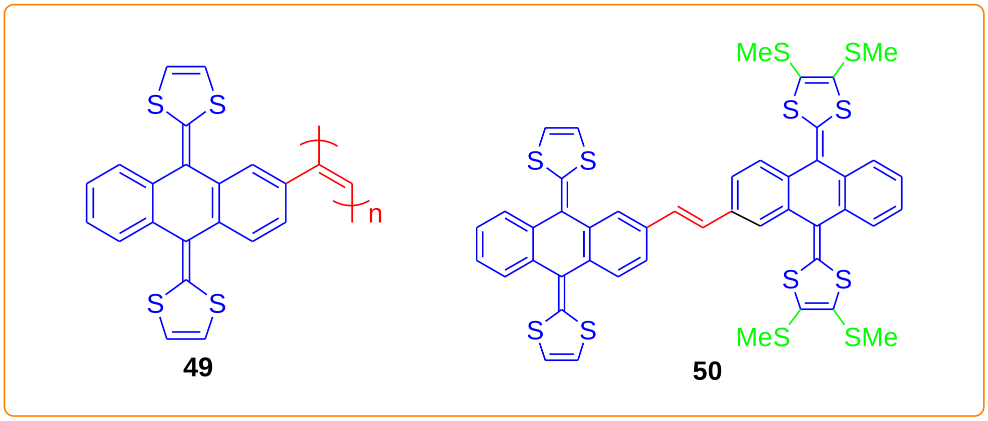


Fig. 11. Structures of anthraquinone containing exTTF moieties [69, 70].

Back in 2015, some researchers inspected two polyimides (PI) having anthraquinone group as a connection unit. Two polyimides were prepared by the imidization polymerization of two different compounds that are PMDA (**51**) and NTCDA (**52**) with anthraquinone derivative Fig. 12. Because the products (**54**, **55**) of these syntheses can endure reversible four electron shift so it could be used as a cathode for Na secondary battery system [71].

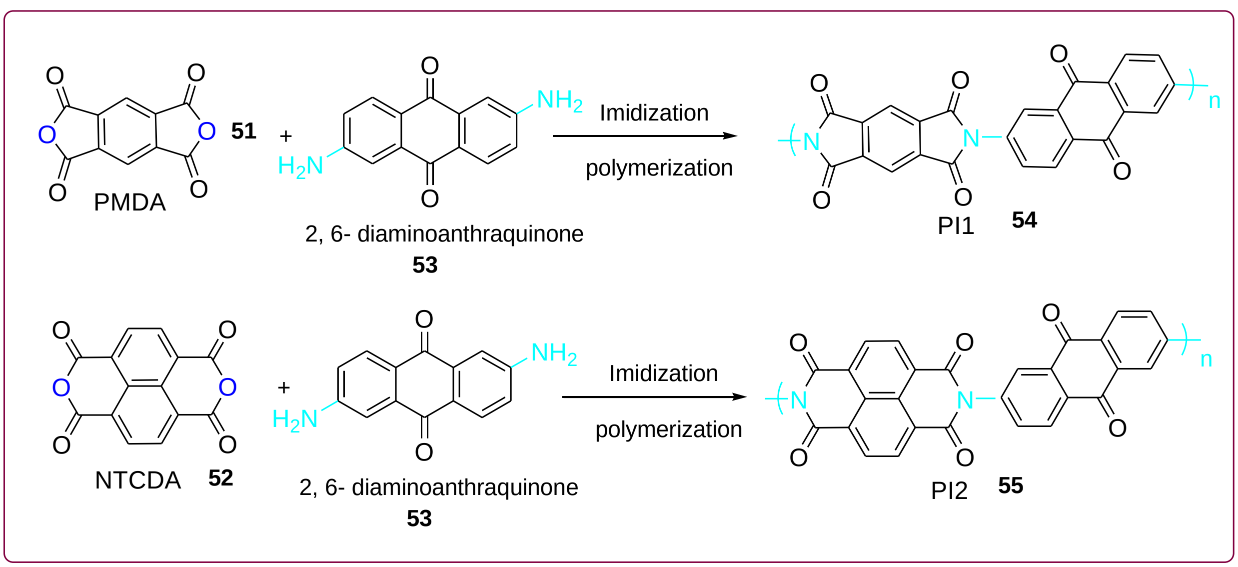


Fig. 12. Synthesis of anthraquinone derivative having polyimide side groups **51** and **52**.

Wang *et al*. (2010) [35] came out with a hybrid material having five membered cyclic rings with central pyrrole ring from where the anthraquinone attached and produce SNS-1AQ and SNS-2AQ (**56**-**57**). After the synthesis and electro polymerization of these moieties, they got polymer films. As shown in Fig. 13 the conjugation of anthraquinone extends to a high degree through these five membered conjugated rings due to which the products could effectively provide stable electrochromic and redox couple behaviour.

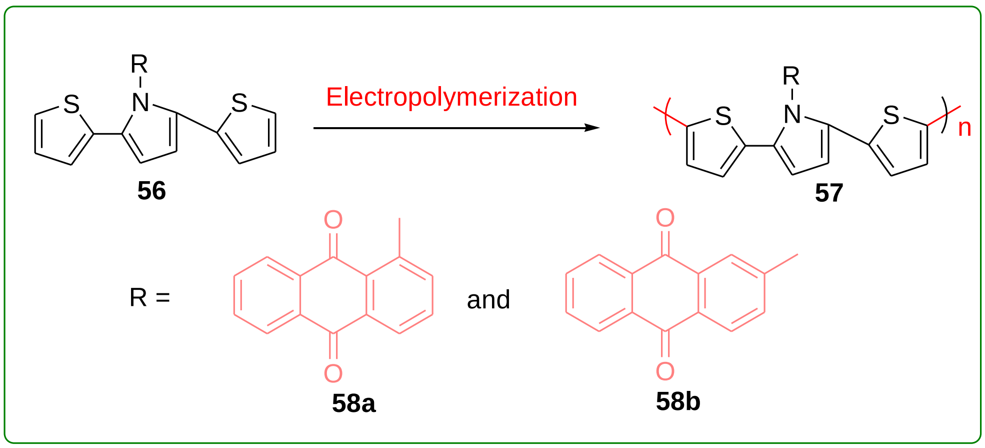


Fig. 13. Composite of polymer films with SNS-1AQ (**57-58a**) and SNS-2AQ (**57-58b**) moieties.

Recently in 2017, the azide functionalized anthraquinone derivative is synthesized in one-step by using nitrene and natural graphite; reduced graphene oxide RGO is formed which on reaction with azide substituted anthraquinone derivative give amended reduced graphene oxide anthraquinone (RGO-AQ).This product is basically considered as cathode active material. The results demonstrated the prominent differences in capacity and performance of these newly synthesized RGO-AQ (**63**) [71, 72].

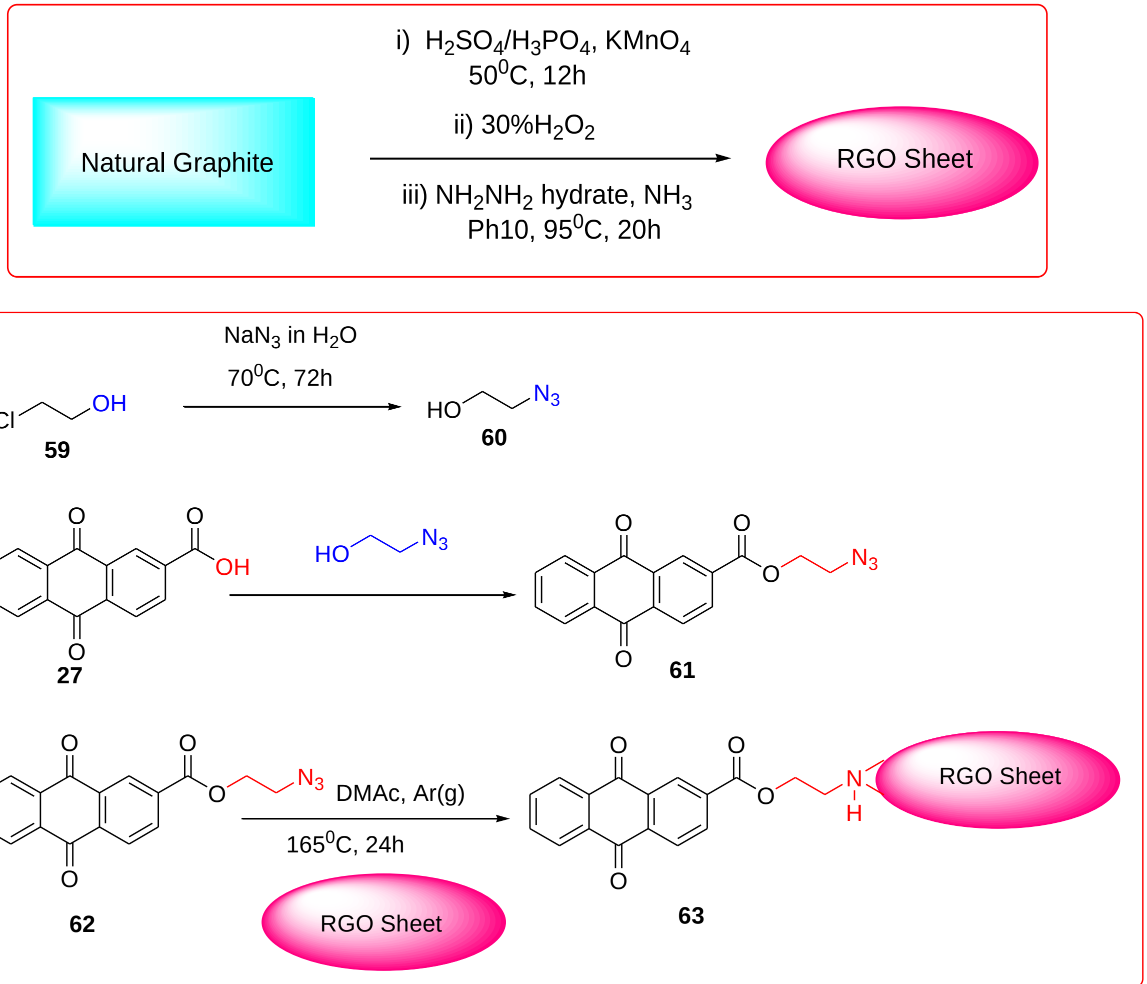


Fig. 14. Synthetic route to anthraquinone functionalized RGO sheets (**59-63**).

Recently a redox active polymer having anthraquinone moieties and cyclic structures in the backbone is synthesized by the lead (Pd) catalysed cyclopolymerization of dienes as shown in Fig. 15. Cyclic voltammetry of monomer and polymer (**67**) supported by carbon paper were performed which allow high electrochemical stability and reversible electrochemical property [73].

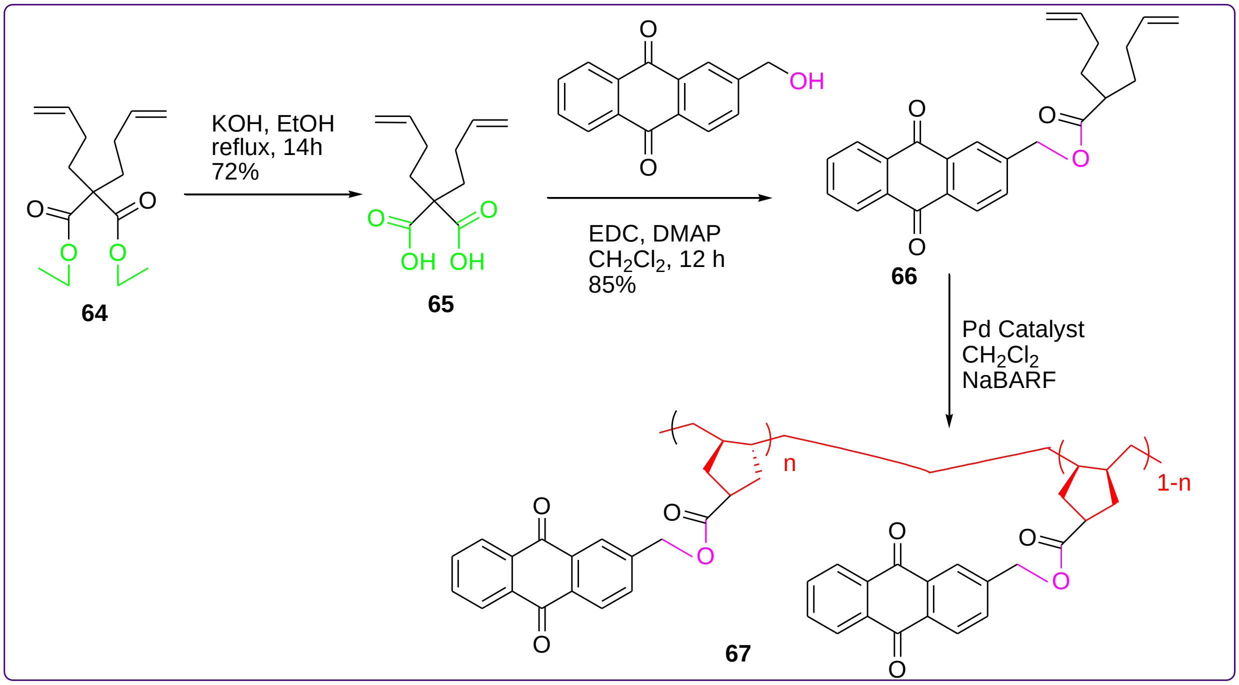


Fig. 15. Schematic representation of the polymer having a cyclic structure in the backbone (**64-67**).

Palaniappan and Manisankar [74] examined the effect of using copolymers rather than simple carbonyl polymers on sensing and electrocatalytic applications. They worked with aniline (**68**) and amino anthraquinone (**34**) in single step reaction and electropolymerized the product (Fig. 16). The result of this analysis permits the preparation of the copolymer having a maximum conductivity and stability up to pH 7 useful for fuel cell application.

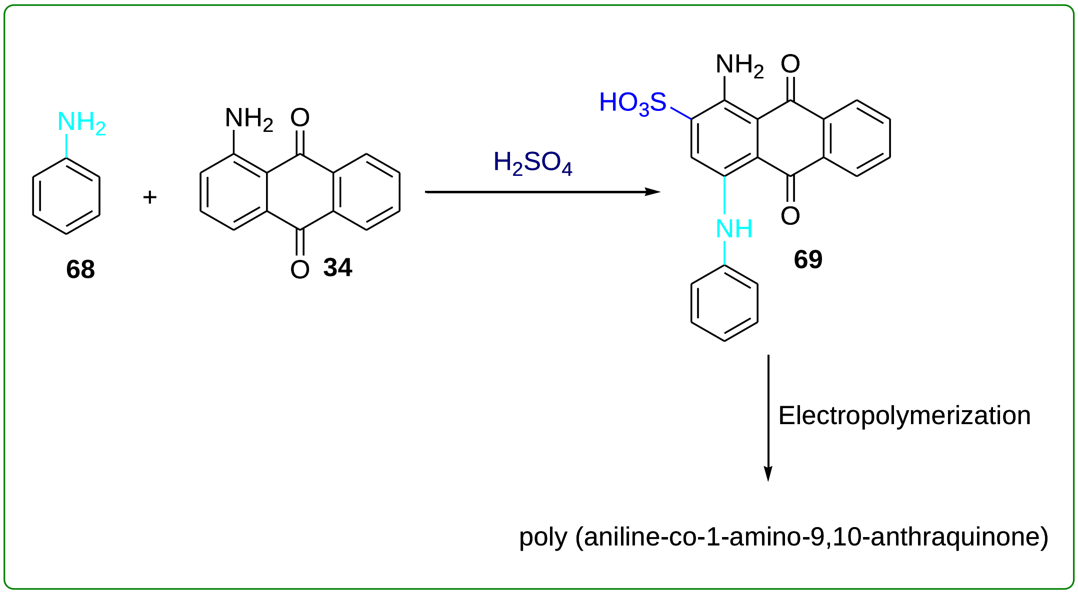


Fig. 16. The reaction of aniline with amino anthraquinone (**68**, **34** and **69**).

Whereas, for the first time the ionic moieties in the polymer containing anthraquinone imide (AQI) was introduced which then homopolymerized and copolymerized with structure (**73**) shown in **Fig. 17**. This unique infrared electrochromic polyelectrolyte system exhibits two reversible redox cycle and a prompt response time of one second. Without an electrolyte layer, this new kind of polymer can be amenable for electric based chromic devices [75].

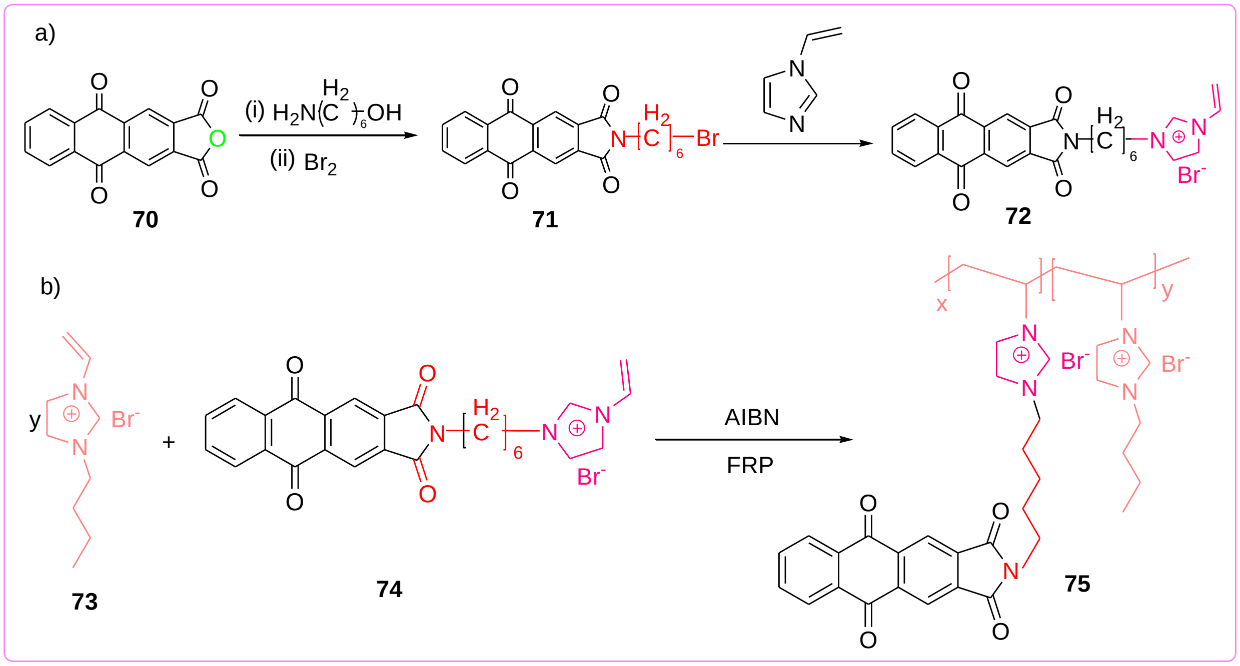


Fig. 17. Homo and copolymerized derivative of anthraquinone (**70-75**).

The anthraquinone as a central core with carbazole or triphenylamine side groups having two ester linkage was synthesized Fig. 18. The electrochemically generated polymer films of the triphenylamine (TPA), biscarbazole unit and anthraquinone shows two reversible oxidation redox couples and two quasi-reversible one-electron reductions respectively and exhibits strong colour changes upon electro-reduction / oxidation [76].

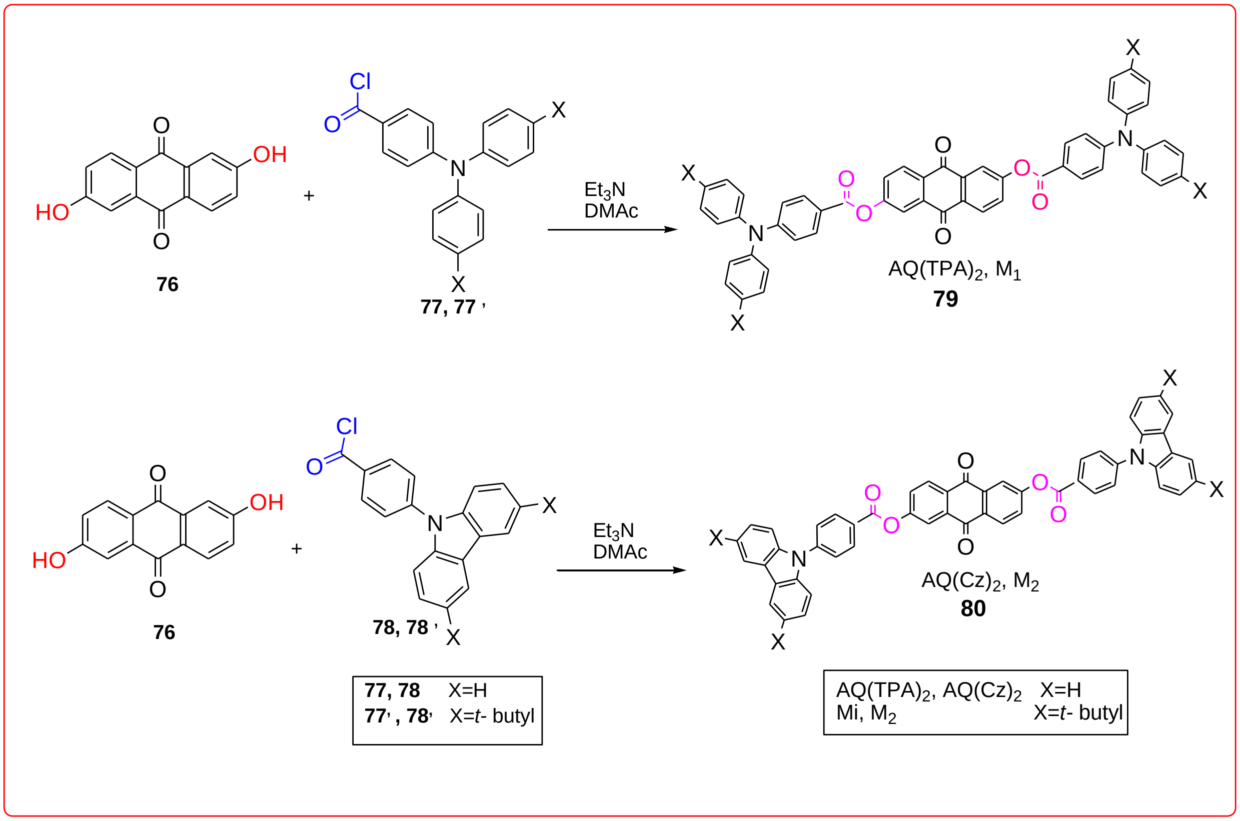


Fig. 18. General reaction of 2, 6-hydroxyanthraqunone (**76**) with carbazole (**78**) or triphenylamine (**77**) groups.

However, some researcher reconnoitred the high molecular weight redox active poly (dianthraquinone -substituted norbornene **83**), synthesized according to Fig. 19, working as an anode for high-power organic batteries. Due to the incorporation of nor-bornene the two sites of AQ indicate the swift electron self-exchange reaction, high redox capacity and stable cyclability up to 500 cycles [77].

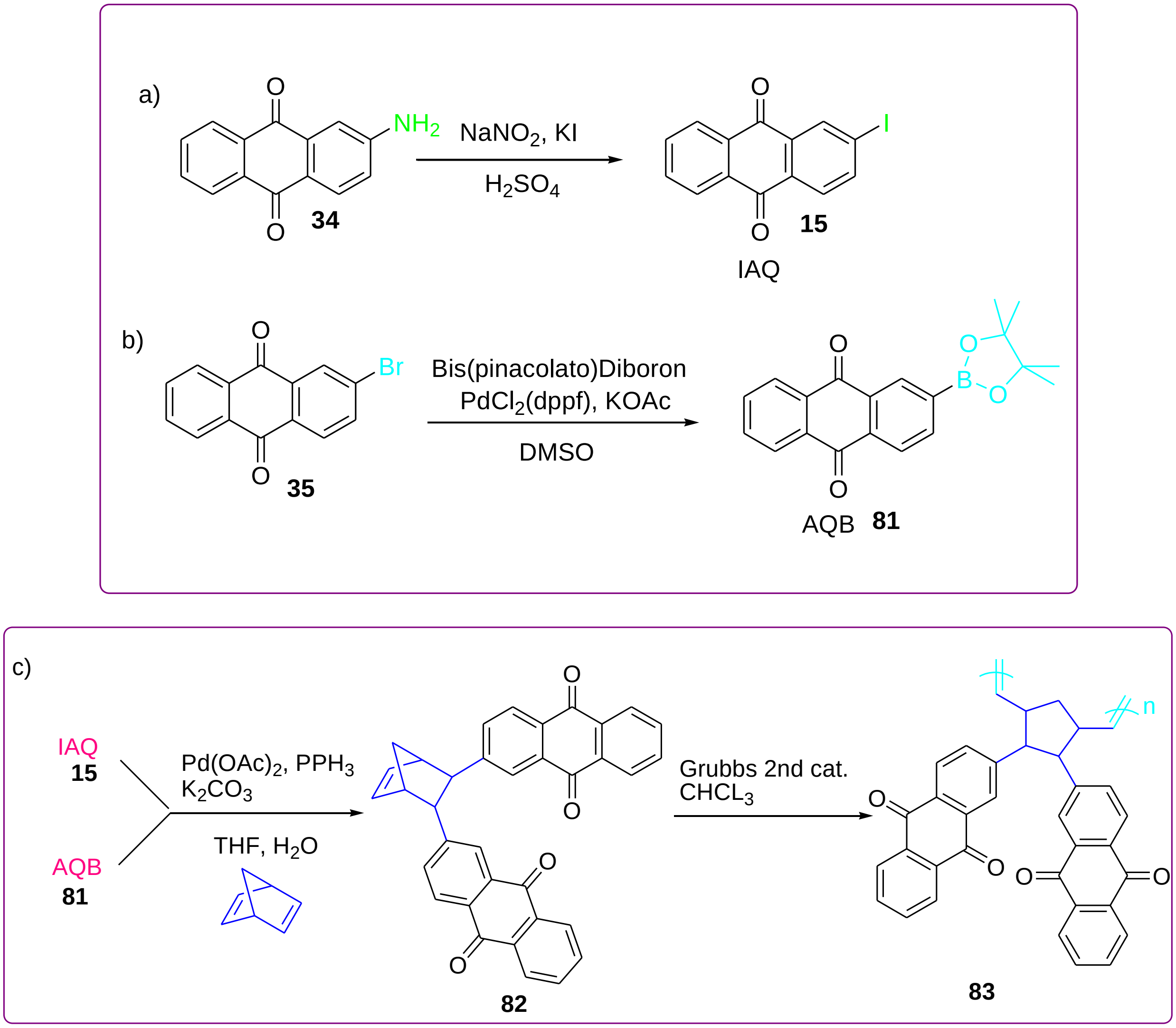
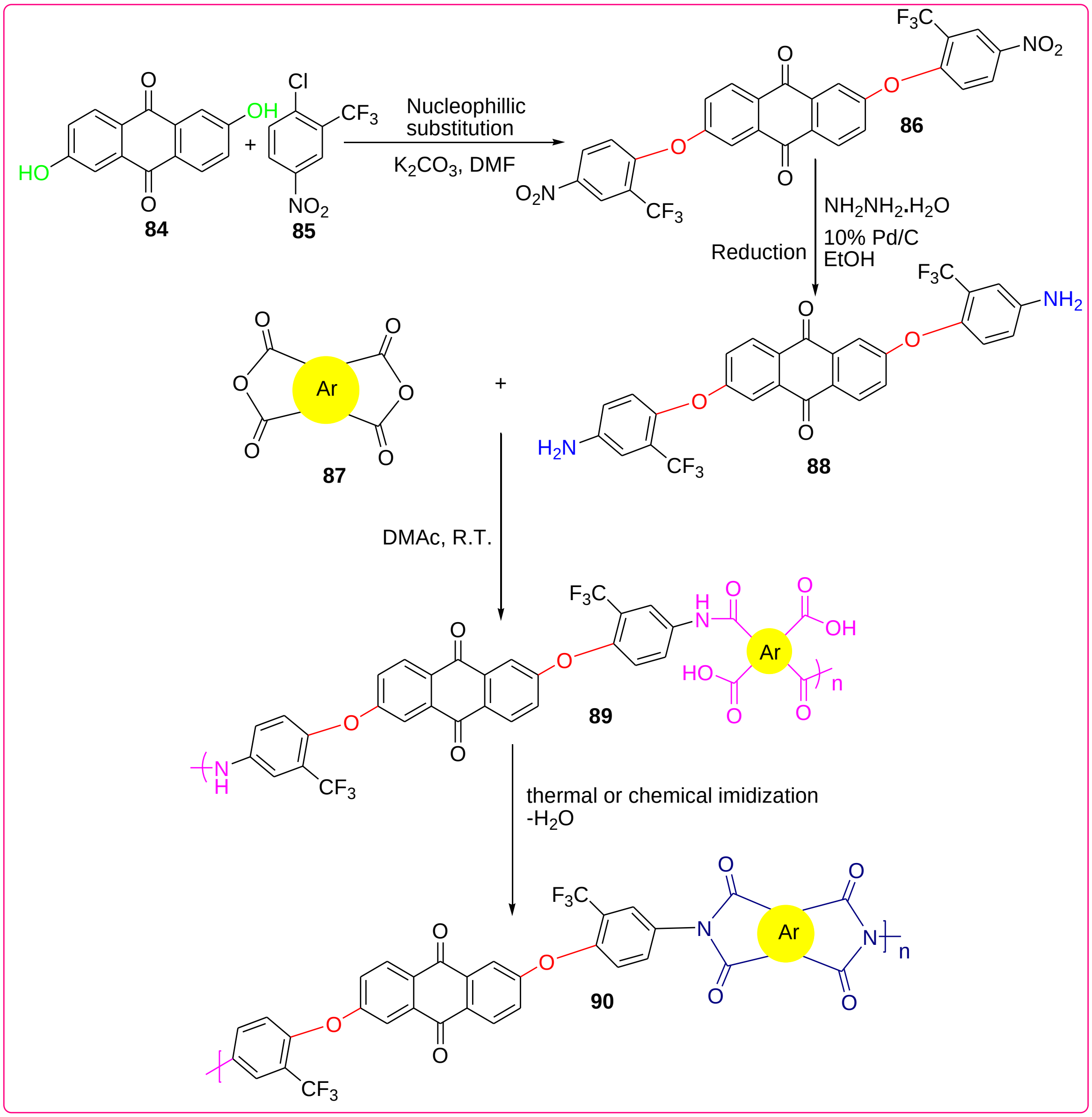


Fig. 19. Synthesis of high molecular weight norbornene substituted anthraquinone (**34**, **15**, **35** and **81-83**).

Hsiao and Lin [78] worked on the synthesis of polyetherimides (**90**) with CF_3 substituted diethylamine which is formed according to the synthetic route described in Fig. 20. Due to the enhanced covered volume due to the bulky group CF_3, all fluorinated polyether imide exhibited optical transparency, improved solubility and film-forming capability.



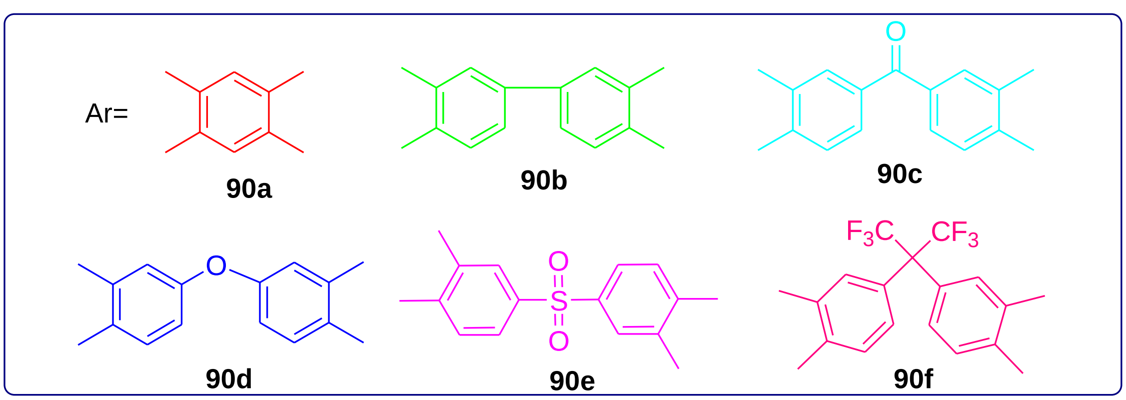
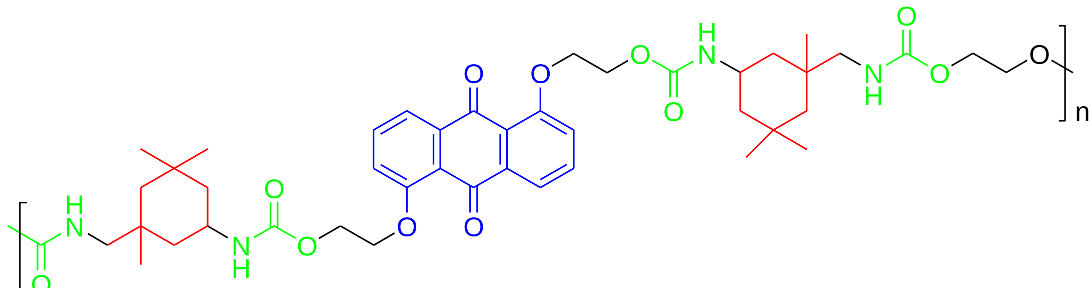


Fig. 20. Diagrammatic representation to the formation of CF_3 substituted anthraquinone incorporated polyetherimide (**84-90**).

Recently, anthraquinone incorporated polyurethane Fig. 21 was evaluated for their electrochromic and electrical memory applications. The result shows that these are the promising materials in electrochromic and artificial intelligence as anthraquinone in polymeric backbone gives a good electron withdrawing characteristic which imparts high influence on resistive switching [79].



94

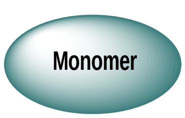
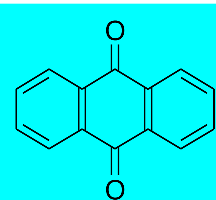
Fig. 21. Structure of newly synthesized anthraquinone incorporated polyurethane **94**.

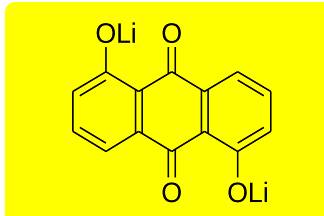
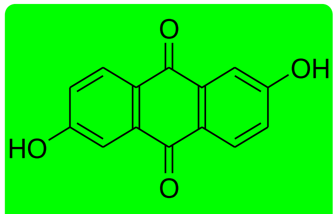
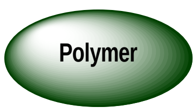
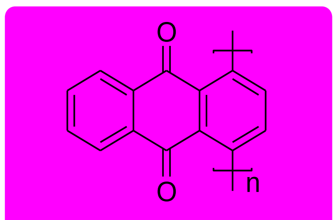
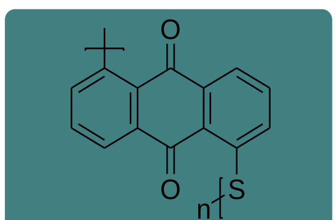
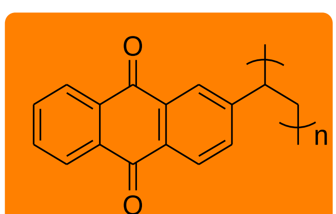
5 Electrochemical applications

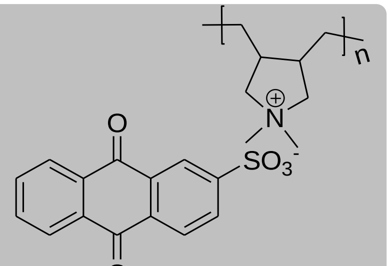
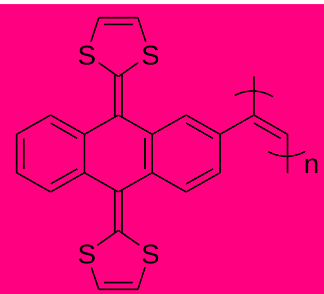
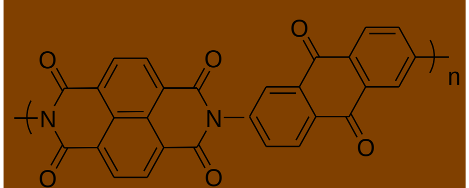
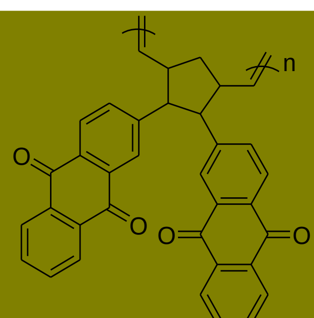
Due to the dissolution of an electrode made up of monomeric anthraquinone **91-93** [80-82] in the electrolyte, chemists polymerizes anthraquinone derivative to solve this problem. Polymerization of varying degree in active material not only solve the solubility issues but also increases cell life, stability and capacity [83-85]. In literature, we found many examples of monomers and polymers containing anthraquinone, some of them are given in Table 1. Poly-1,4 anthraquinone **2** [55] shows a significantly enhanced capacity of 260 $mAhg^{-1}$ and long lifetime up to 100 cycles. While in comparison to **2**, polyanthraquinone sulphide **6** [57] cannot be able to provide a better cyclability in Mg ion batteries and face the capacity fading issues. Although, by the incorporation of the polymerizable vinyl group with anthraquinone **18** [34] resolves the issue of capacity fading and have a long lasting life time up to 300 cycles. While the substitution of exTTF moiety instead of the carbonyl group in AQ **49** [69] gives a stable system even up to 1000 cycles and reasonable capacity of 105 mAhg^{-1}.

Recently a new system generated by the incorporated redox active counter ions i.e. anthraquinone and nitroxide into the poly (ionic liquids) **24**, enhances the utilization of these materials as redox active material in various energy storage technologies. This system **24** [65] gives a stable lifecycle and good capacity. Although, cyclic voltammetry of **55** [71] revealed that this polyimide (PI2) as a cathode active material for sodium secondary batteries endure a reversible four-electron transfer because of cycle stability and good capacity. While the data of poly-dianthraquinone substituted norbornene **83** [77] illustrates the swift electron self-exchange reaction, a high redox capacity and stable cyclability up to 500 cycles which is due to the incorporation of nor-bronene and the two redox active sites (i.e. AQ) per repeating unit.

Table 1. Comparison between the electrochemical properties of anthraquionone derivative.

Entry	Category	Structural formula	Capacity (mAhg^{-1})	Life-time (Cycle)	Current (C)
1		 **91**	212	50	0.1C

2		 **92**	120	50	0.1C
3		 **93**	100	100	0.1C
4		 **2**	260	100	0.2C
5		 **6**	30	100	0.5C
6		 **18**	>200	300	15C

7	 **24**	130	100	1C
8	 **49**	105	1000	120C
9	 PI2 **55**	192	150	3.2C
10	 **83**	212	500	1.2C

6 Future prospective

Organic based electroactive material plays an important role in the ever-growing field of science and technology. Owing to their interesting properties, these smart materials at present have a vast range of applications that include sensors, optical, energy storage and electrochromic devices. However, these materials face many issues, like capacity fading, low cell cycle reversibility, the short lifespan of battery and production of toxic materials. In future, these limitations can be overawed by modifying the moieties and functionalities of anthraquinone and by replacing traditional components with greener, nontoxic and organic material. Still, there is a need to think about the right combination of compounds to exercise these materials in automotive industries, biomedical engineering, aircraft and dye-based photography that is not explored yet. Further research is required in future to synthesize the different derivatives containing anthraquinone moieties, most importantly to check the electroactive properties in biomedical equipments, automotive and electric vehicles.

7 Conclusions

Among quinone, anthraquinone is the most promising compound due to its eco-friendly nature, process ability, sustainability, high electrochemical application and flexibility in term of its use as an anode as well as a cathode. Owing to its important features, great concern on its synthesis and potent applications brought it in front of scientific research. The structural and electrochemical behaviour of AQ shows reversible two-electron redox system. Having high cycle reversibility and untoxicity, several synthetic approaches are developed either by converting anthraquinone to polymers or by coupling it with a different compound. Among the low molecular weight anthraquinone polymers, polyionic liquids emerged as a potential compound as it is synthesized by simple one step ion exchange reaction and exhibits good capacity, less fading and stable cell cycle. Though, among high molecular weight anthraquinone polymer, catalytically polymerize norbornene substituted dianthraquinone, due to incorporation of two molecules of anthraquinone, give high cycle stability up to 500 cycles which gives a long battery life cycle. However, the synthetic pathway is time consuming and needs attention to figure out more facile pathway to synthesize this compound, while, polyimide synthesis provides the one pot synthetic pathway that gives reversible comparable capacity and excellent cyclability with four electron transfer system. Based on these critical analyses we conclude that in comparison to simple and substituted anthraquinone, synthetic polymers of anthraquinone are most important as it gives high cycle stability, facile synthetic approach, less dissolution and comparable storage cell capacity. Hence, commercially anthraquinone derivatives would be very important in the energy storage system, automotive, biomedical, aircraft, pharmaceutical, electrochromic, paints, dyes industries and could be very helpful in flourishing these industries in near future.

References

1. Zhang, J., D. Zhu, and M. Matsuo, Synthesis and characterization of polyacene quinone radical polymers with high-dielectric constant. Polymer, 2008. 49(25): p. 5424-5430.
2. Carpi, F. and D. De Rossi, Colours from electroactive polymers: Electrochromic, electroluminescent and laser devices based on organic materials. Optics & Laser Technology, 2006. 38(4-6): p. 292-305.
3. Qiu, Y., Z. Lu, and Q. Pei, Refreshable Tactile Display Based on a Bistable Electroactive Polymer and a Stretchable Serpentine Joule Heating Electrode. ACS applied materials & interfaces, 2018. 10(29): p. 24807-24815.
4. Bar-Cohen, Y. EAP as artificial muscles: progress and challenges. in Smart Structures and Materials 2004: Electroactive Polymer Actuators and Devices (EAPAD). 2004. International Society for Optics and Photonics.
5. Chen, F., Synthesis and characterisation of some electroactive polymers. 1992, Dublin City University.
6. Bar-Cohen, Y. and S.P. Leary. Electroactive polymers (EAP) charaterization methods. in Smart Structures and Materials 2000: Electroactive Polymer Actuators and Devices (EAPAD). 2000. International Society for Optics and Photonics.
7. Alici, G., et al., Response characterization of electroactive polymers as mechanical sensors. IEEE/ASME Transactions on Mechatronics, 2008. 13(2): p. 187-196.
8. Price, A.D., Fabrication, Modelling and Application of Conductive Polymer Composites. 2012.
9. Jean-Mistral, C., S. Basrour, and J. Chaillout, Comparison of electroactive polymers for energy scavenging applications. Smart Materials and Structures, 2010. 19(8): p. 085012.
10. Lallart, M., et al., Actuation abilities of multiphasic electroactive polymeric systems. Journal of Applied Physics, 2012. 112(9): p. 094108.
11. Wagner, M., Synthesis, characterization and chemical sensor application of conducting polymers. 2013.
12. Skotheim, T.A., Handbook of conducting polymers. 1997: CRC press.
13. Guarino, V., et al., Electro-active polymers (EAPs): a promising route to design bio-organic/bioinspired platforms with on demand functionalities. Polymers, 2016. 8(5): p. 185.
14. Simionescu, C. and M. Grigoras, Macromolecular donor—acceptor complexes. Progress in polymer science, 1991. 16(6): p. 907-976.
15. Abruña, H.D., Coordination chemistry in two dimensions: chemically modified electrodes. Coordination Chemistry Reviews, 1988. 86: p. 135-189.
16. Gracia, R. and D. Mecerreyes, Polymers with redox properties: materials for batteries, biosensors and more. Polymer Chemistry, 2013. 4(7): p. 2206-2214.
17. Kamogawa, H., Y.H.C. Giza, and H.G. Cassidy, Electron transfer polymers. XXIII. Interactions of the quinhydrone type in polyvinylhydroquinone solutions. Journal of Polymer Science Part A: General Papers, 1964. 2(10): p. 4647-4659.

18. Inzelt, G., Conducting polymers: a new era in electrochemistry. 2012: Springer Science & Business Media.
19. Son, E.J., et al., Quinone and its derivatives for energy harvesting and storage materials. Journal of Materials Chemistry A, 2016. 4(29): p. 11179-11202.
20. Esteves, C.H.A., et al., Identification of Tobacco Types and Cigarette Brands Using an Electronic Nose Based on Conductive Polymer/Porphyrin Composite Sensors. ACS omega, 2018. 3(6): p. 6476-6482.
21. Ha, D., Z. Fang, and N.B. Zhitenev, Paper in electronic and optoelectronic devices. Advanced Electronic Materials, 2018. 4(5): p. 1700593.
22. Fannir, A., et al., Linear Artificial Muscle Based on Ionic Electroactive Polymer: A Rational Design for Open-Air and Vacuum Actuation. Advanced Materials Technologies, 2019. 4(2): p. 1800519.
23. Takalloo, S.E., H. Seifi, and J.D. Madden. Design of ultra-thin high frequency trilayer conducting polymer micro-actuators for tactile feedback interfaces. in Electroactive Polymer Actuators and Devices (EAPAD) 2017. 2017. International Society for Optics and Photonics.
24. Gazotti Jr, W.A., et al., A Solid-State Electrochromic Device Based on Two Optically Complementary Conducting Polymers. Advanced Materials, 1998. 10(1): p. 60-64.
25. Sharma, P., et al., Perylene-polyimide-Based organic electrode materials for rechargeable lithium batteries. The Journal of Physical Chemistry Letters, 2013. 4(19): p. 3192-3197.
26. Karlsson, C., Conducting Redox Polymers for Electrical Energy Storage: Backbone-Substituent Interactions in Quinone Polypyrrole Model Systems. 2014, Acta Universitatis Upsaliensis.
27. Waterlot, C., D. Couturier, and B. Hasiak, Synthesis of new electron transfer polymers for the reduction of dissolved oxygen in water. Journal of applied polymer science, 2001. 80(2): p. 223-229.
28. Schmidt, D., et al., Poly (DCAQI): Synthesis and characterization of a new redox-active polymer. Journal of Polymer Science Part A: Polymer Chemistry, 2016. 54(13): p. 1998-2003.
29. Brunmark, A. and E. Cadenas, Redox and addition chemistry of quinoid compounds and its biological implications. Free Radical Biology and Medicine, 1989. 7(4): p. 435-477.
30. Deng, W., et al., A low cost, all-organic Na-ion battery based on polymeric cathode and anode. Scientific reports, 2013. 3: p. 2671.
31. Milczarek, G. and O. Inganäs, Renewable cathode materials from biopolymer/conjugated polymer interpenetrating networks. Science, 2012. 335(6075): p. 1468-1471.
32. Iordache, A., et al., Monothioanthraquinone as an organic active material for greener lithium batteries. Journal of Power Sources, 2014. 267: p. 553-559.
33. Oyaizu, K., W. Choi, and H. Nishide, Functionalization of poly (4-chloromethylstyrene) with anthraquinone pendants for organic anode-active materials. Polymers for Advanced Technologies, 2011. 22(8): p. 1242-1247.

34. Choi, W., et al., Aqueous electrochemistry of poly (vinylanthraquinone) for anode-active materials in high-density and rechargeable polymer/air batteries. Journal of the American Chemical Society, 2011. 133(49): p. 19839-19843.
35. Wang, G., et al., Synthesis and spectroelectrochemical properties of two new dithienylpyrroles bearing anthraquinone units and their polymer films. Electrochimica Acta, 2010. 55(23): p. 6933-6940.
36. Tian, R., et al., Drastically enhanced high-rate performance of carbon-coated LiFePO4 nanorods using a green chemical vapor deposition (CVD) method for lithium ion battery: a selective carbon coating process. ACS applied materials & interfaces, 2015. 7(21): p. 11377-11386.
37. Liang, J., F. Li, and H.-M. Cheng, On energy: Batteries beyond lithium ion. 2017, Elsevier.
38. Canepa, P., et al., Odyssey of multivalent cathode materials: open questions and future challenges. Chemical reviews, 2017. 117(5): p. 4287-4341.
39. Geng, P., et al., Transition metal sulfides based on graphene for electrochemical energy storage. Advanced Energy Materials, 2018. 8(15): p. 1703259.
40. Abas, N., A. Kalair, and N. Khan, Review of fossil fuels and future energy technologies. Futures, 2015. 69: p. 31-49.
41. Radha, M.H. and N.P. Laxmipriya, Evaluation of biological properties and clinical effectiveness of Aloe vera: A systematic review. Journal of traditional and complementary medicine, 2015. 5(1): p. 21-26.
42. Pandith, S.A., et al., Evaluation of anthraquinones from Himalayan rhubarb (Rheum emodi Wall. ex Meissn.) as antiproliferative agents. South African Journal of Botany, 2014. 95: p. 1-8.
43. Laurent, A., Ueber verschiedene Verbindungen des Anthracen's. Justus Liebigs Ann Chem, 1840. 34(3): p. 287-296.
44. Malik, E.M. and C.E. Müller, Anthraquinones as pharmacological tools and drugs. Medicinal research reviews, 2016. 36(4): p. 705-748.
45. Yao, M., et al., Crystalline polycyclic quinone derivatives as organic positive-electrode materials for use in rechargeable lithium batteries. Materials Science and Engineering: B, 2012. 177(6): p. 483-487.
46. Salabert, J., R.M. Sebastián, and A. Vallribera, Anthraquinone dyes for superhydrophobic cotton. Chemical Communications, 2015. 51(75): p. 14251-14254.
47. Moss, G., Nomenclature of fused and bridged fused ring systems (IUPAC Recommendations 1998). Pure and applied chemistry, 1998. 70(1): p. 143-216.
48. Prakash, A., Refinement of the crystal structure of anthraquinone. Acta Crystallographica, 1967. 22(3): p. 439-440.
49. Murty, B., The space group of anthraquinone. Acta Crystallographica, 1955. 8(2): p. 113-114.
50. Ding, Y., et al., Molecular and excited state properties of photostable anthraquinone blue dyes for hydrophobic fibers. Journal of Molecular Structure, 2019. 1181: p. 109-117.

51. Cui, Z., et al., New Type of Eco-Friendly Polymeric Dye by Covalently Bonding Anthraquinone into Polyphenylsulfone. Macromolecular Materials and Engineering, 2019: p. 1800692.
52. Jing, Y., et al., Two novel anthraquinones with cytotoxicity from Hedyotis caudatifolia. Phytochemistry Letters, 2019. 29: p. 134-137.
53. Feijen, E.A., et al., Derivation of anthracycline and anthraquinone equivalence ratios to doxorubicin for late-onset cardiotoxicity. JAMA oncology, 2019.
54. Takeda, T., et al., Electron-deficient anthraquinone derivatives as cathodic material for lithium ion batteries. Journal of Power Sources, 2016. 328: p. 228-234.
55. Song, Z., et al., Polyanthraquinone as a reliable organic electrode for stable and fast lithium storage. Angewandte Chemie, 2015. 127(47): p. 14153-14157.
56. Zhou, Y., et al., Polyanthraquinone-based nanostructured electrode material capable of high-performance pseudocapacitive energy storage in aprotic electrolyte. Nano Energy, 2015. 15: p. 654-661.
57. Song, Z., H. Zhan, and Y. Zhou, Anthraquinone based polymer as high performance cathode material for rechargeable lithium batteries. Chemical communications, 2009(4): p. 448-450.
58. Xu, W., et al., Factors affecting the battery performance of anthraquinone-based organic cathode materials. Journal of Materials Chemistry, 2012. 22(9): p. 4032-4039.
59. Bitenc, J., et al., Anthraquinone-Based Polymer as Cathode in Rechargeable Magnesium Batteries. ChemSusChem, 2015. 8(24): p. 4128-4132.
60. Pan, B., et al., Polyanthraquinone-Based Organic Cathode for High-Performance Rechargeable Magnesium-Ion Batteries. Advanced Energy Materials, 2016. 6(14): p. 1600140.
61. Naoi, K., S. Suematsu, and A. Manago, Electrochemistry of poly (1, 5-diaminoanthraquinone) and its application in electrochemical capacitor materials. Journal of The Electrochemical Society, 2000. 147(2): p. 420-426.
62. Zhao, L., et al., A novel polyquinone cathode material for rechargeable lithium batteries. Journal of Power Sources, 2013. 233: p. 23-27.
63. Wang, W., et al., Anthraquinone with tailored structure for a nonaqueous metal–organic redox flow battery. Chemical communications, 2012. 48(53): p. 6669-6671.
64. Tsuzaki, A., et al., A New Bio-based Battery Material: Effect of Rate of Anthraquinone Skeleton Incorporation into Polyglycidol on Battery Performance. Energy Procedia, 2016. 89: p. 207-212.
65. Hernández, G., et al., Redox-active poly (ionic liquid) s as active materials for energy storage applications. Journal of Materials Chemistry A, 2017. 5(31): p. 16231-16240.
66. Häupler, B., et al., PolyTCAQ in organic batteries: enhanced capacity at constant cell potential using two-electron-redox-reactions. Journal of Materials Chemistry A, 2014. 2(24): p. 8999-9001.

67. Schmidt, D., et al., Synthesis and characterization of new redox-active polymers based on 10-(1, 3-dithiol-2-ylidene) anthracen-9 (10H)-one derivatives. Polymer, 2015. 68: p. 321-327.
68. Seidel, N., et al., Synthesis and properties of new 9, 10-anthraquinone derived compounds for molecular electronics. New Journal of Chemistry, 2013. 37(3): p. 601-610.
69. Häupler, B., et al., Aqueous zinc-organic polymer battery with a high rate performance and long lifetime. NPG Asia Materials, 2016. 8(7): p. e283.
70. Díaz, M.C., et al., Synthesis and electron-donor ability of the first conjugated π-extended tetrathiafulvalene dimers. The Journal of organic chemistry, 2004. 69(13): p. 4492-4499.
71. Xu, F., J. Xia, and W. Shi, Anthraquinone-based polyimide cathodes for sodium secondary batteries. Electrochemistry Communications, 2015. 60: p. 117-120.
72. Sertkol, S.B., et al., An anthraquinone-functionalized reduced graphene oxide as electrode material for rechargeable batteries. Carbon, 2017. 116: p. 154-166.
73. Motokuni, K., et al., Synthesis and electrochemical properties of novel redox-active polymers with anthraquinone moieties by Pd-catalyzed cyclopolymerization of dienes. Journal of Polymer Science Part A: Polymer Chemistry, 2016. 54(14): p. 2184-2190.
74. Palaniappan, S. and P. Manisankar, Electrochemical synthesis and characterization of poly (aniline-co-1-amino-9, 10-anthraquinone), a nanosized conducting copolymer. Journal of polymer research, 2011. 18(2): p. 311-317.
75. Zheng, Y., et al., Synthesis and characterization of a novel kind of near-infrared electrochromic polymers containing an anthraquinone imide group and ionic moieties. Journal of Materials Chemistry, 2009. 19(44): p. 8470-8477.
76. Hsiao, S.H. and J.Y. Lin, Electrosynthesis of ambipolar electrochromic polymer films from anthraquinone–triarylamine hybrids. Journal of Polymer Science Part A: Polymer Chemistry, 2016. 54(5): p. 644-655.
77. Kawai, T., K. Oyaizu, and H. Nishide, High-density and robust charge storage with poly (anthraquinone-substituted norbornene) for organic electrode-active materials in polymer–air secondary batteries. Macromolecules, 2015. 48(8): p. 2429-2434.
78. Hsiao, S.-H. and J.-Y. Lin, Synthesis and electrochromic properties of novel aromatic fluorinated poly (ether-imide) s bearing anthraquinone units. Journal of Fluorine Chemistry, 2015. 178: p. 115-130.
79. Li, Y., et al., Anthraquinone-functionalized polyurethane designed for polymer electrochromic and electrical memory applications. Journal of materials science, 2018. 53(22): p. 15600-15613.
80. Zeng, R.-h., et al., Synthesis and properties of a lithium-organic coordination compound as lithium-inserted material for lithium ion batteries. Electrochemistry communications, 2010. 12(9): p. 1253-1256.
81. Bu, P., et al., Effects of carbon black on the electrochemical performance of lithium-organic coordination compound batteries. Int. J. Electrochem. Sci, 2012. 7: p. 4617-4624.
82. Lin, K., et al., Alkaline quinone flow battery. Science, 2015. 349(6255): p. 1529-1532.

83. Cao, J., et al., A new redox-active conjugated polymer containing anthraquinone pendants as anode material for aqueous all-organic hybrid-flow battery. Journal of Power Sources, 2019. 423: p. 316-322.
84. Juvenal, F., et al., Ultrafast Photo-Induced Electron Transfers in Platinum (II)-Anthraquinone Diimine Polymers/PCBM Films. The Journal of Physical Chemistry C, 2019.
85. Tang, W., et al., Highly Stable and High Rate-performance Na-ion Batteries by Using Polyanionic Anthraquinone as the Organic Cathode. ChemSusChem, 2019.