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)

23 devices, aircraft aileron and biomedical equipment's. Irrefutably, we confirm that high molecular

24 weight polymeric anthraquinone compounds are best in comparison to low molecular weight

25 anthraquinone monomers as they have preeminent properties over monomeric systems. Because

26 of the significant properties of anthraquinone, polymeric systems are high demanding and emerged

27 as a hot topic among the researchers these days. In the current scenario, this study is of immense

28 importance, as it identified and discussed the right and sustainable combination, and pave the way

29 to utilize these novel materials in different technologies.

30

31 **Keywords:** Organic polymer; Anthraquinone; Electrochemistry; Energy harvesting and Future

32 direction.

33

34 1   Introduction

35 Polymers which respond to the external electric stimulation exhibit a considerable change in shape

36 or size and are known as electroactive polymers [1]. Due to the simple synthesis methods and

37 processable signals, electroactive material with tailorable moieties is considered as smart material

38 [2]. These novel electroactive materials can endure large forces and show low deformation value

39 as it can bear an ultimate tensile strength of 320% with normal strength of 8 MPa [3]. Recently,

40 polymeric material designed with the latest technology gives a better result in term of its

41 application and revolutionized the world. In the last few years, researchers introduce us with the

42 new technology in the field of robotics and artificial muscles with the help of using electroactive

43 polymers (EAPs) referred to as electro-responsive material [4].

44

45 EAP is extensively used as an actuator and being investigated for sensing purpose. As mentioned

46 above, the most important characteristic property of EAP is the enduring feature of large forces

47 and deformation while the conjugated electroactive polymer also manifests low ionization

48 potential, low energy optical transition and high electron affinities [5]. Such type of material

49 commonly characterized as either electric or ionic [6-8]. Both types have a dissimilar performance

50 and different set of characteristics in certain considerations [9, 10]. Until 1977 all polymers were

51 commonly known as electric insulators but the first work on true conducting polymer was done in

52 1993 which encourage the researchers to think and explore about its possible application and one-

53 pot synthesis methods [11].

54

55 From last two decades, the interest flourishes in these electroactive organic polymers not only

56 because of their ease of synthesis but also due to their wide applications in textile dyes, cosmetics,

57 pharmaceutical, energy storage devices and paints industries. Until now, the classes that developed

58 are categorized into these three groups based on their functionalities:

59   1. Conducting polymers: Conducting polymers are highly conductive with conjugation along

60   the polymer backbone [12] and their conducting behaviour is firmly related to the highly

61   conjugated electronic structure [13].

62   2. Donor-acceptor complexes: The material which shows a range of electrical conductivity

63   with respect to insulator, conductor and superconductor is known as donor-acceptor

64   complex [14].

65   3. Redox polymers: This class of polymer comprises of redox active centres, which reduced

66   and oxidized reversibly and electrochemically [15-17].

67

68   These three categories have a close relationship. Sometimes their applications and properties are

69   so similar that even it is difficult to distinguish them from one another such as polyacetylene when

70   used with donor-acceptor could increase the conductivity and often referred as donor-acceptor

71   complex polypyrrole and polyaniline. Conducting polymer are sometimes classified as redox

72   polymers and also known as electron exchange polymer/ redox exchangers/ oxidation or reduction

73   polymer by some other authors [5, 18].

74

75   In all evolving fields, organic based conducting polymer have been extensively studied due to their

76   potential application in electronics, sensors, artificial muscles, electrochromic devices, capacitors

77   and electromagnetic radiation shielding etc. [19-23], rather than inorganic oxides [24]. In current

78   years, numerous redox-active organic materials for example radical polymers, organosulphur and

79   carbonyl functionality have been studied in different storage system [25]. The redox function in a

80   polymeric system is organic in nature (e.g., hydroquinone/quinone system) [26, 27], while

81   inorganic systems are also used (.e.g., ferrocene, Ru (bipy) $^{2+}$) [28]. The quinonide structures are

82   of high interest due to their usage in various fields.

83

84   The quinones system gives semiquinone and hydroquinone by two electron reversible reduction

85   and oxidation Fig. 1. Quinone system exhibits a drawback as the formation of a quinone from

86   semiquinone oxidation cause toxicity while the hydroquinone formation from two electron

87   reduction of quinone through semiquinone leads to the excretion eventually cause cell damage

88   [29]. To deal with these limitations, researchers worked to figure out the compound that can

89   combat these issues. Over the past few years, anthraquinone (member of class quinone) has been

90   widely examined as an electroactive material in Li ion, Na ion [30] and Au electrodes [31] battery

91   systems in the monomeric and polymeric form [32].
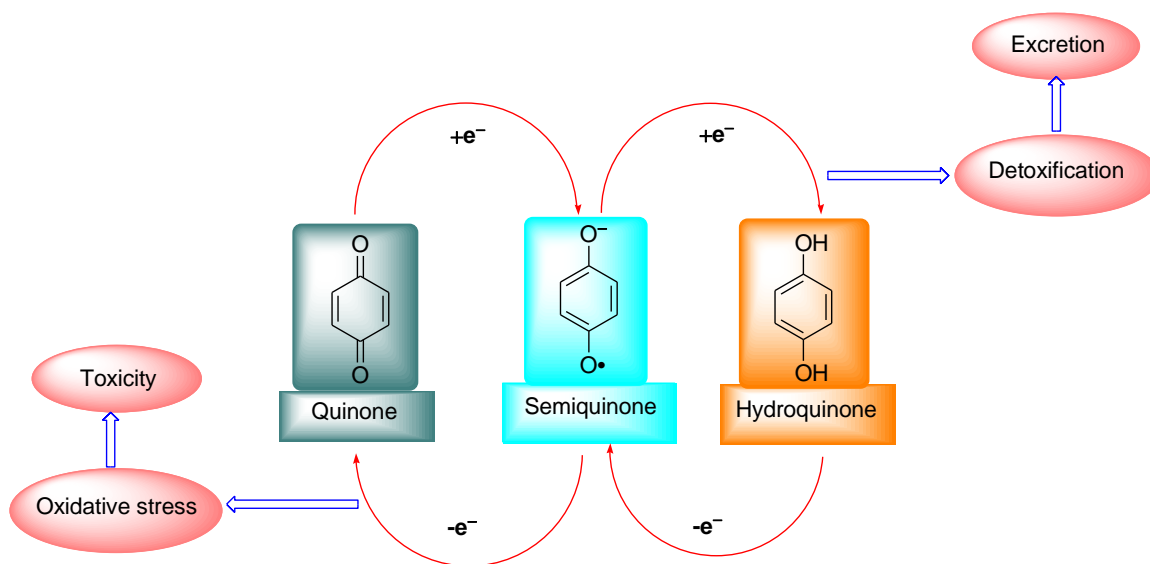
92

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

94

95   Predominantly, anthraquinones exhibit a faster reaction at heterogeneous rate constant for the

96   electrode reaction ($>10^{-2}$ cm/s) at moderately negative potential (-0.8V) [33]. Anthraquinone also

97   possesses the obvious chemical potential because of the absence of α-hydrogen which mostly

98   incline to the deprivation [34]. Furthermore, anthraquinone derivatives exhibited exceptional

99   performance on electron transfer and electrochromism [35]. The storage of electric energy has

100   significant importance for our developing technology-based society. Current Li [36], Na, and other

101   inorganic ion storage system exhibits many disadvantages such as toxicity, low cycle life, leakage,

102   volatility, polarizability, sustainability, costliness, performance, specific energy, safety and short

103   lifespan [37-39]. Many studies were conducted which focus on plant mediated green chemistry

104   approach having nontoxic and eco-friendly conducting material (quinone and anthraquinone). As

105   an alternative to the traditional energy storage system that causes toxicity and dissolution, organic

106 electroactive polymers combat the issues concerned with the traditional storage system. Quinone

107 functionalize compounds are the promising energy storage material. To fully realize the potential

108 of quinone compound, ancient energy storage components (fossil fuels and coal) [40] must be

109 replaced by green materials. Anthraquinone serves as an efficient energy storage system which

110 could get from the natural sources like Aloe [41] and Rhubarb [42] plants and could be synthesized

111 in organic labs [43]. Different methodologies adopted previously focused on the synthetic methods

112 and applications of anthraquinone derivatives pharmaceutically only in drug formation, drug

113 extraction [44] and electrochemically only in storage battery systems [45] and in dyes industry

114 [46].

115

116 In this ever flourishing scientific field, it is difficult to compare even a single organic compound

117 synthesis and its applications as many data are available in the literature and information regarding

118 the species may differ due to the different synthetic approaches and vast applications in different

119 fields. So there is a yawning need to compile the information regarding quinone conducting system

120 to have a quick idea that which is the most appropriate technique to synthesize potentially

121 applicable compound. Herein, the present study aimed to amass the data of anthraquinone based

122 electroactive compounds. Anthraquinone for energy storages systems can be synthesized and

123 modified as a monomer, polymer and copolymer by utilizing three different techniques i.e. by

124 catalytic synthesis, electro-polymerization and free radical polymerization. Therefore, this study

125 comparing the synthetic approaches and electrochemical application of a simple and substituted

126 polymeric system of anthraquinone based low and high molecular weight compounds.

127 Anthraquinone incorporated polymers can be synthesized by different synthetic methods and have

128 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].
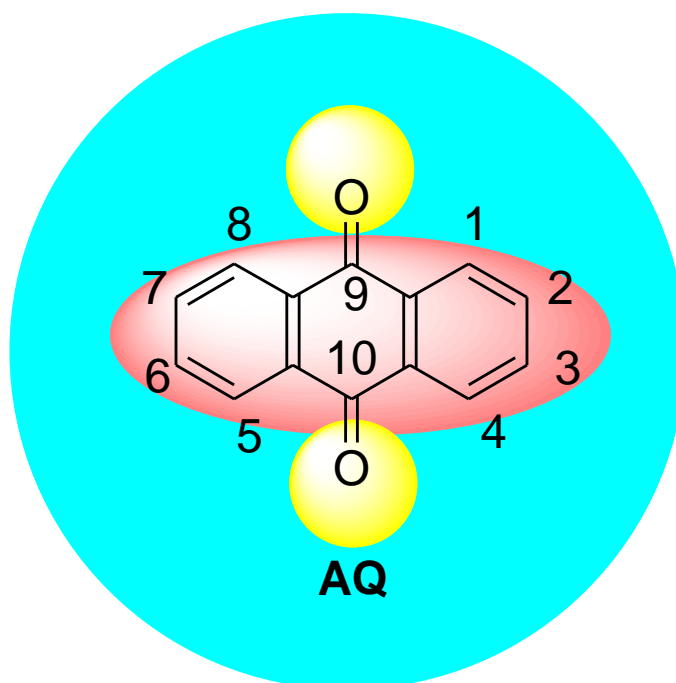

Fig. 2. Structure of anthraquinone.

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]

144   worked on anthraquinone, utilizing its exceptional redox ability in the rechargeable battery system.

145   Anthraquinone having two carbonyl functionality can undergo stepwise two reversible redox

146   reactions at around -1.3 and -1.6V that shows its characteristic of two electron transfer cycle per

147   anthraquinone molecule. This property of two electrons reversible cycle is of keen interest to the

148   scientist for the last 40-50 years. Recently, various anthraquinone derivative with simple to high

149   molecular weight structure was synthesized and investigated. The entire recently reported

150   anthraquinone derivative exhibits remarked life cycle and increase the durability of storage

151   batteries. The resultant of anthraquinone charge/discharge characteristic gives a capacity fade up

152   to 255 mAh/g [54] that signifies the two electron shift reaction of anthraquinone as shown in Fig.
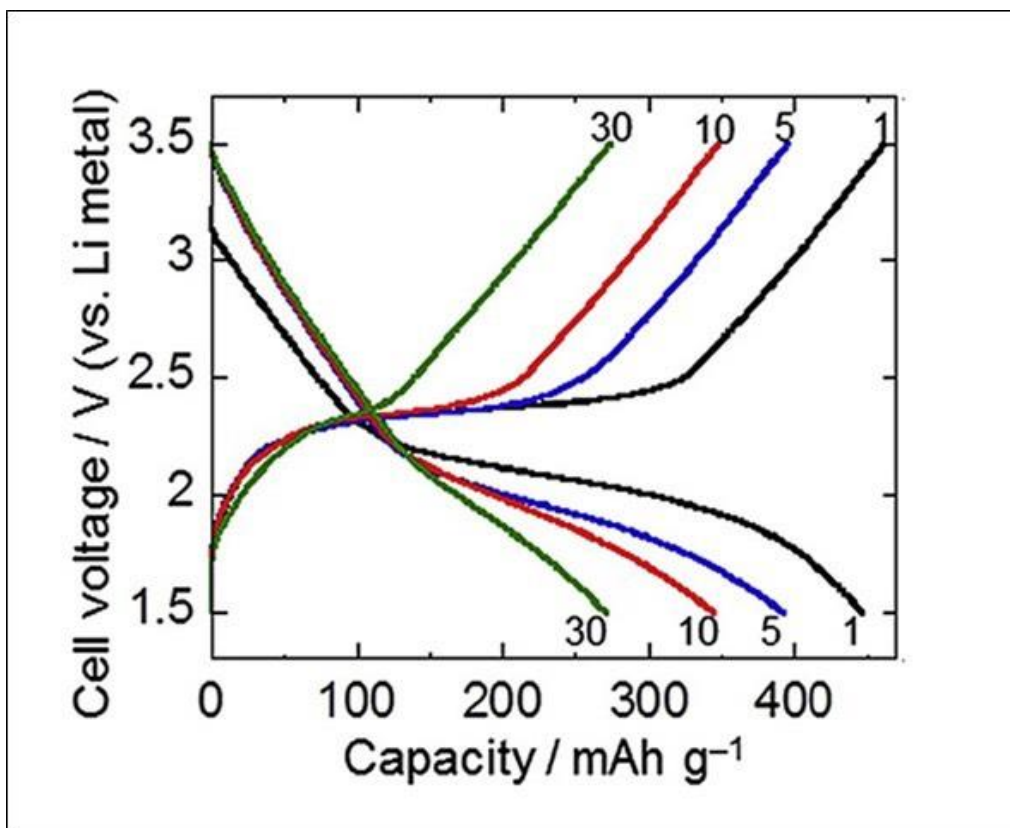
153   3 and Fig. 4.

154
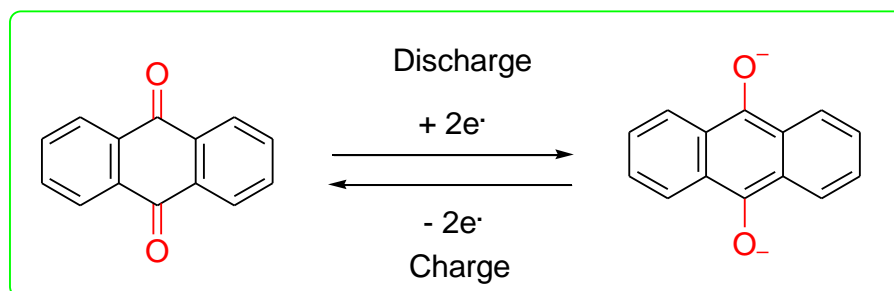
155
156   **Fig. 3.** Electron shift of anthraquinone.

157

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

9

171 remould anthraquinone to achieve better processibility and sustainability. A great concern about

172 the synthesis and characterization of EAPs has been observed. Herein, we describe an overview of

173 the work of some researchers on EAPs based on anthraquinone, its derivatives and a substituted

174 anthraquinone for rechargeable batteries.

175

176 Song et al. (2015) [55] polymerized the 1, 4-dichloroanthraquinone (1,4-DCAQ) to get (**2**) and

177 isomer P15AQ as shown in Fig. 5 This polymer based on simple structures shows unprecedented

178 implementation and better performance to achieve effective cycle stability. Due to the high

179 solubility of (**2**) in CHCl$_3$, it could be used effectively in flexible, high-performance and green

180 energy-storage devices. While Zhou *et al*. (2015) [56] analyzed the Ketjenblack carbon supported

181 polyanthraquinone (P26AQ) (**4**) synthesized according to the method shown in Fig. 5, in aprotic

182 electrolytes as a pseudo-supercapacitor electrode material. The quinone molecules on the

183 carbonated support mainly polymerized by this method could increase the conductivity, reduce the

184 possibility of proton donation and enhance the performance. The electrochemical studies divulge

185 that these composite materials have good cycling stability, large energy or power density and high

186 specific capacitance.

187

188 Poly-AQS (**6**) as an active material for rechargeable batteries instead of using simple

189 polyanthraquinoe (PAQ) made according to the Phillips method by polycondensation as shown in

190 Fig. 5. The analysis of cathode active material in ether and ester electrolyte shows better

191 cyclability and sustainability because of attached sulphide group in any solvent but in term of

192 energy density, it provides not a better alternative because of its lower discharge voltage [57].

193

194   By following the method of song et al. Xu *et al*. (2012) [58] synthesized isomer of PAQS that is

195   P15AQS and P18AQS. The analysis of the performance and electrochemical behaviour of these

196   anthraquinone derivatives was done. These organic cathode materials due to their different site

197   and less steric hindrance of substitution on anthraquinone give remarkable effect on the

198   performance of batteries system and higher capacity and rate capability. By replacing Li (smaller)

199   ions with Na (larger) ions, the redox reaction of anthraquinonoid group could easily be done. Deng

200   *et al*. (2013) [30] prepared Na-ion battery based on PAQS (by following the scheme of Song et

201   al.) [57] as an organic redox active anode and polytriphenylamine (PTPAn) cathode. The above

202   synthesized battery system proposed a high energy density storage system but have a drawback

203   that the excessive amount of electrolytic solvent is required for the fast conducting reaction.

204   Instead of using Na and Li, Bitenc and coworkers [59] use Mg powdered metal anode. They

205   produced PAQS (**6**) as redox active cathode by the same scheme used by song and coworkers. In

206   different electrolyte systems, the rate capability of PAQS assessed the best performance in terms

207   of capacity, but show no major development in long-term cycling with respect to the other two

208   electrolytes used.

209

210   In 2016 Pan and co-workers [60] work on 14PAQ, 26PAQ and PAQS and evaluated their

211   electrochemical properties for rechargeable Mg-ion batteries. The comprehensive study on these

212   three compounds tells that Mg-ion battery of 14PAQ rather than 26PAQ and PAQS give a very

213   small capacity fading during cycle life and give best cycle stability. To attain the better cycle

214   stability the carbonyl group is replaced with thio-carbonyl group to synthesize the

215   monothioanthraquinone polymer as described in Fig. 5. The analyses with the positive active

216   electrode in a mixture of solvents shows the better cycle-life stability of monothioanthraquinone

217   (MTAQ) (**8**) than anthraquinone (AQ) but MTAQ (**8**) have a disadvantage as the specific capacity

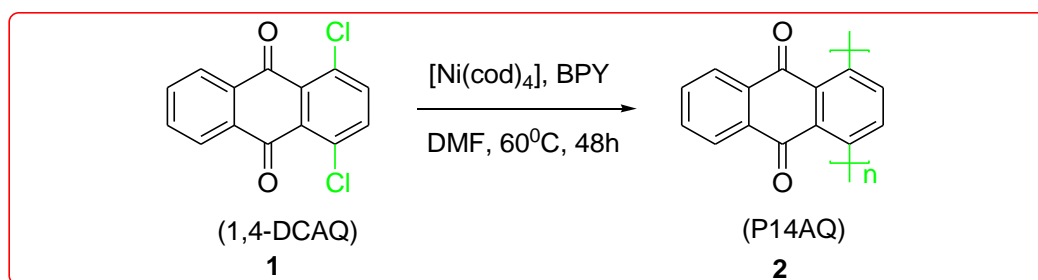218   decreases after 5 cycles due to the dissolution of active material [32].

219

220   A conducting polymer such as poly-diaminoanthraquinone (Poly-DAAQ) having amino

221   substituted anthraquinone was studied as a capacitor Fig. 5. The study shows two reversible redox

222   reactions for continuous cycles in non-aqueous media. The spectroscopy proposed that the two

223   sets of redox reaction observed is due to the quinone group and p-conjugated system. The study

224   reveals that Poly-DAAQ could be used as a capacitor and in rechargeable battery systems can

225   serve as polymer cathode [61]. The unique polymer poly (5-amino-1,4-dihydroxy anthraquinone)

226   (**12**) synthesized according to Fig. 5 by a facile oxidation process for lithium batteries as the

227   cathode material and characterized by different electrochemical methods. The study reveals that

228   PADAQ shows an amended cycle performance and a high rate capacity compared to its monomer

229   amino dihydroxyanthraquinone ADAQ but for discharge depth of (**12**) was sensitive and its cycle

230   performance is poor when discharged to 1.0 V [62].

231

232   Wang and their workmate [63] examined anthraquinone derivative (**13**) Fig. 5 by nucleophilic

233   aromatic substitution of triethylene glycol derivative into 1,5-dichloroanthraquinon. This modified

234   anthraquinone (AQ) molecule form a different redox current flow battery with the increased

235   solubility and stability for its imminent large-scale applications. While Choi and their colleague

236   [34] synthesize poly (2-vinylanthraquinone) (**18**) by substituting vinyl derivative to anthraquinone

237   to increase the formula weight Fig. 5. They analyzed it as anode active material in the aqueous

238   electrolyte. They concluded that PVAQ is not only insoluble in aqueous electrolyte but also have
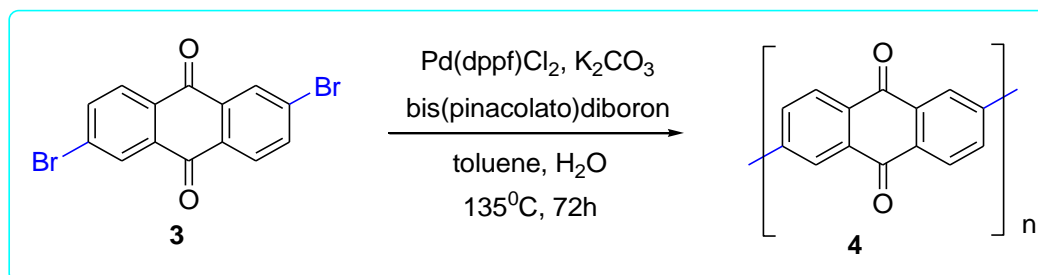
239   stable cell capacity even after 300 cycles compared to that of conjugated, non-conjugated and

240   polysulfide analogue.

241

242   The successful examination of novel bio-based battery material via pGD-AQ (**22**) (collecting from

243   the biodiesel processing unit as a bio-based polymer) and redox-active anthraquinone unit utilizing

244   as a positive electrode for Li-ion battery (synthesized according to Fig. 5) shows high capacity and

245   greater cycle-life stability due to the incorporation of anthraquinone in polyglycidol (**22**) [64].
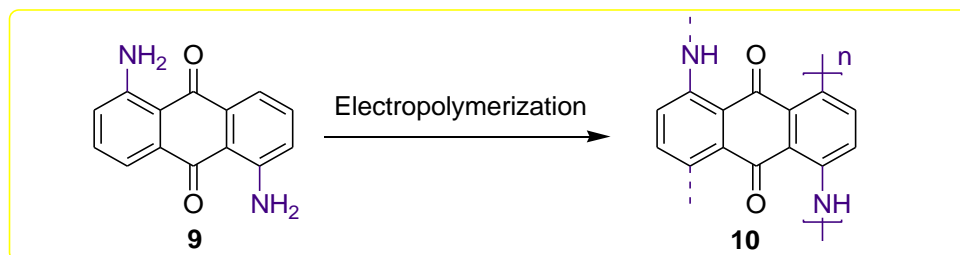
246

247

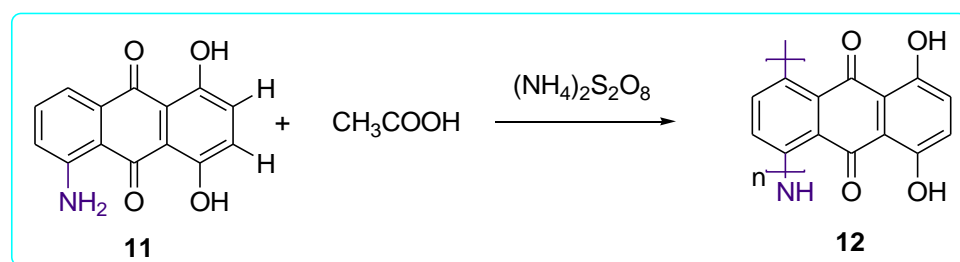
248

249

13

250

7 → **8**

S , di- methylformamide

$-N_2$, 130-150 ^{0} C

251

9 → **10**

Electropolymerization

252

11 + CH_3COOH → **12**

$(NH_4)_2S_2O_8$

253

5 + $CH_3(OCH_2CH_2)_3OH$ → **13**

KOH

$< 100^oC$

$CH_3(OCH_2CH_2)_3O$

$O(CH_2CH_2O)_3CH_3$

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.
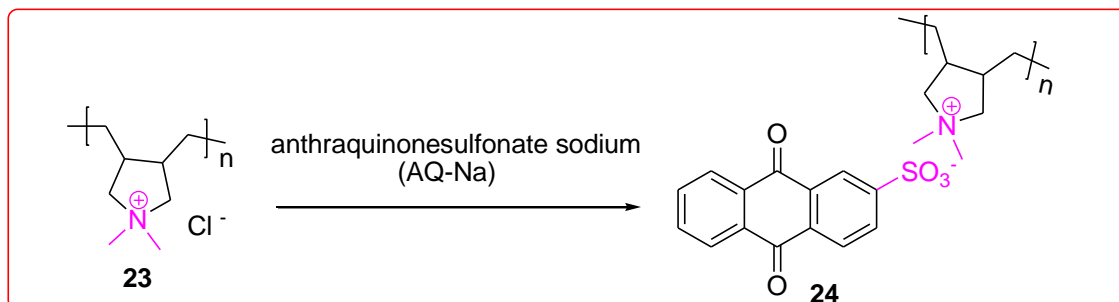
Fig. 6. Ionic anthraquinonoid polymer.

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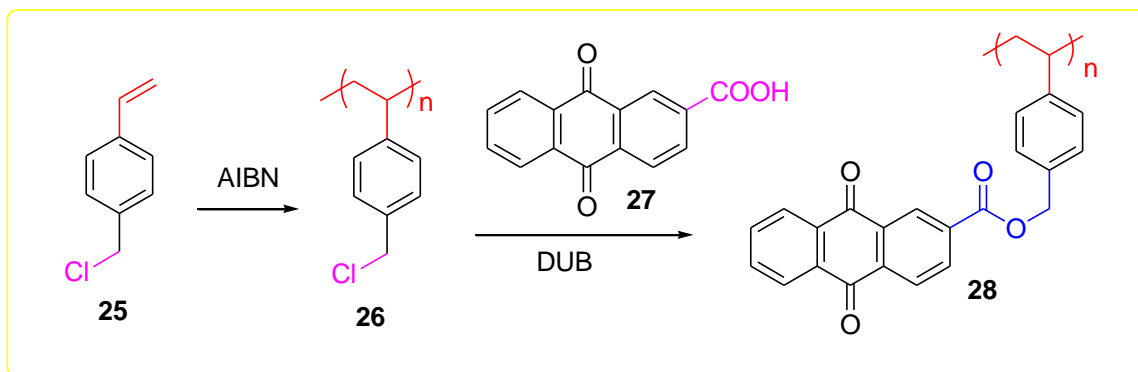
Fig. 7. Anthraquinone reaction with the polystyrene derivative **25-28**.

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 (**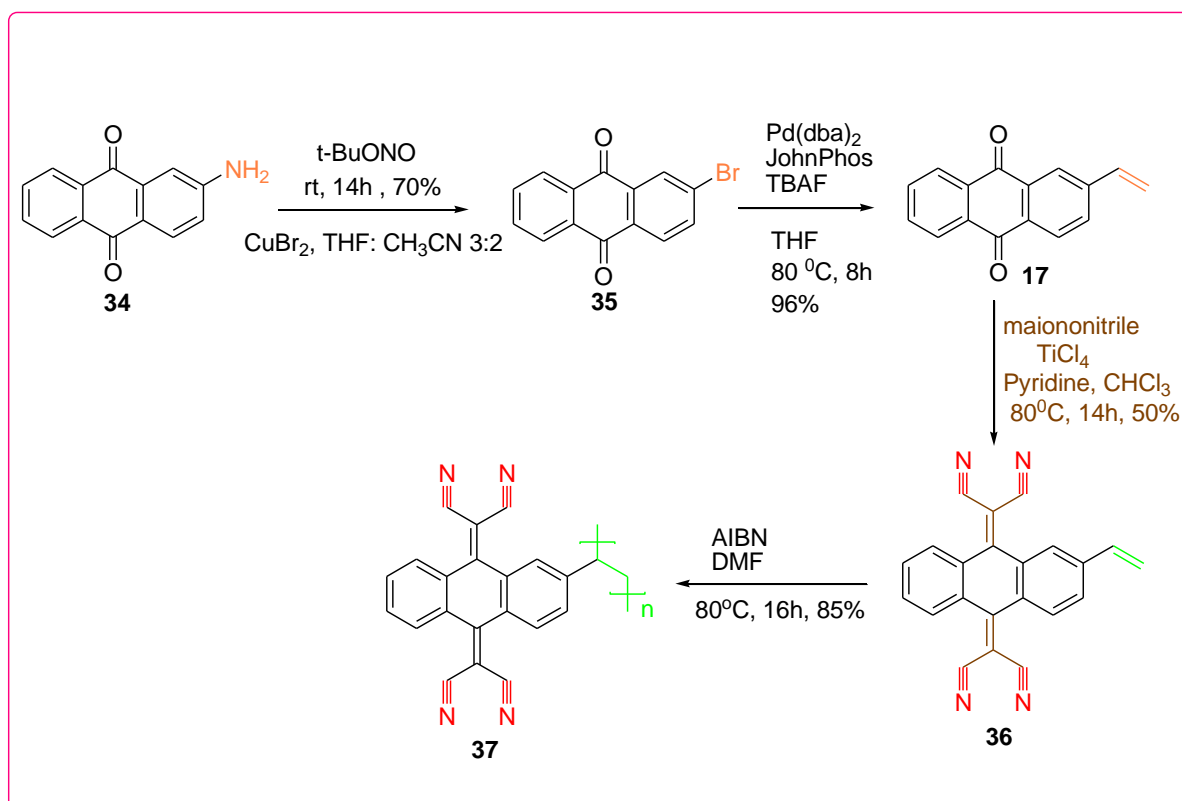37**) as mentioned in Fig. 8 synthesized in four simple steps. Poly-TCAQ exhibits a high material activity of 97%, the excellent columbic efficiency of 99% and high rechargeability with only 12% loss [66].
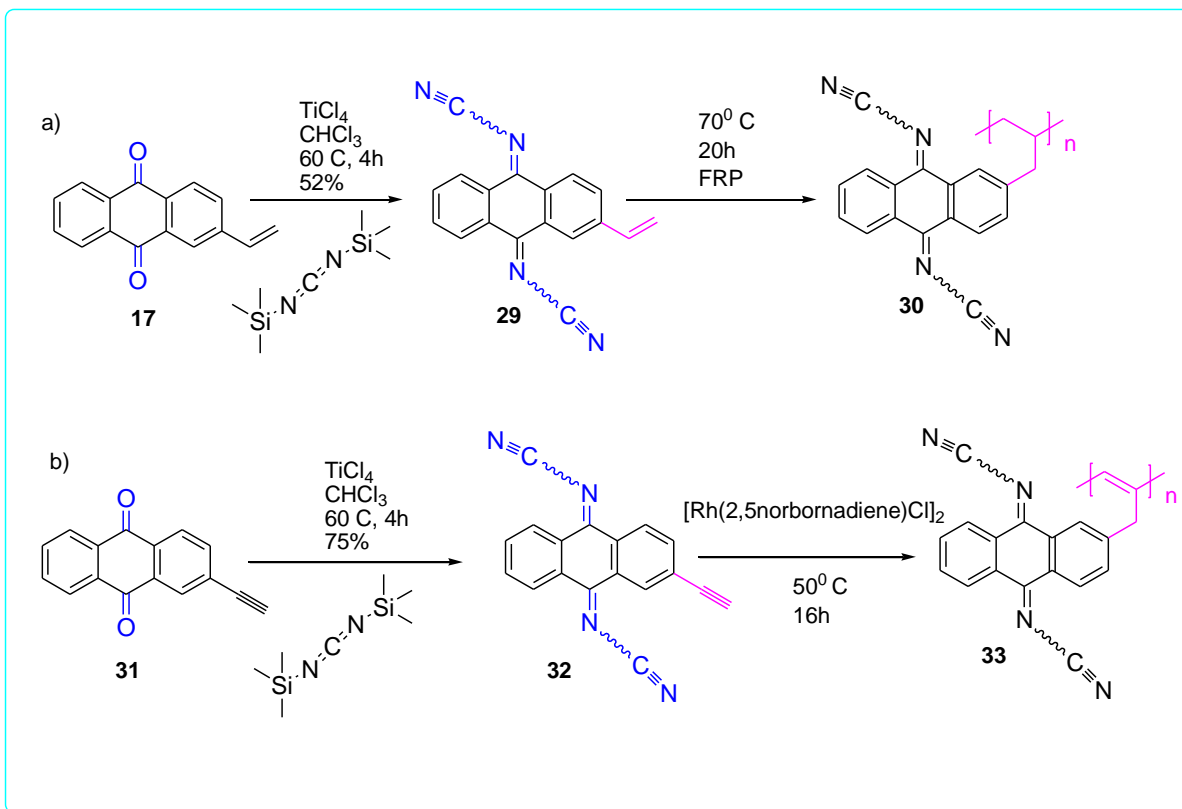
297

298

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

300   Foremost to bipolar compounds, the carbonyl functional group modified with three different

301   moieties that is are Thione (**42**), dicaynomethylene (**43**) and N-caynoimine (**44**). The scrutinization

302   of these redox active compound, which polymerizes with the vinyl group through free radical

303   polymerization method Fig. show limited reversibility. Due to the limited reversibility and side

304   reactions, these compounds could be used after further optimization in organic batteries [67].
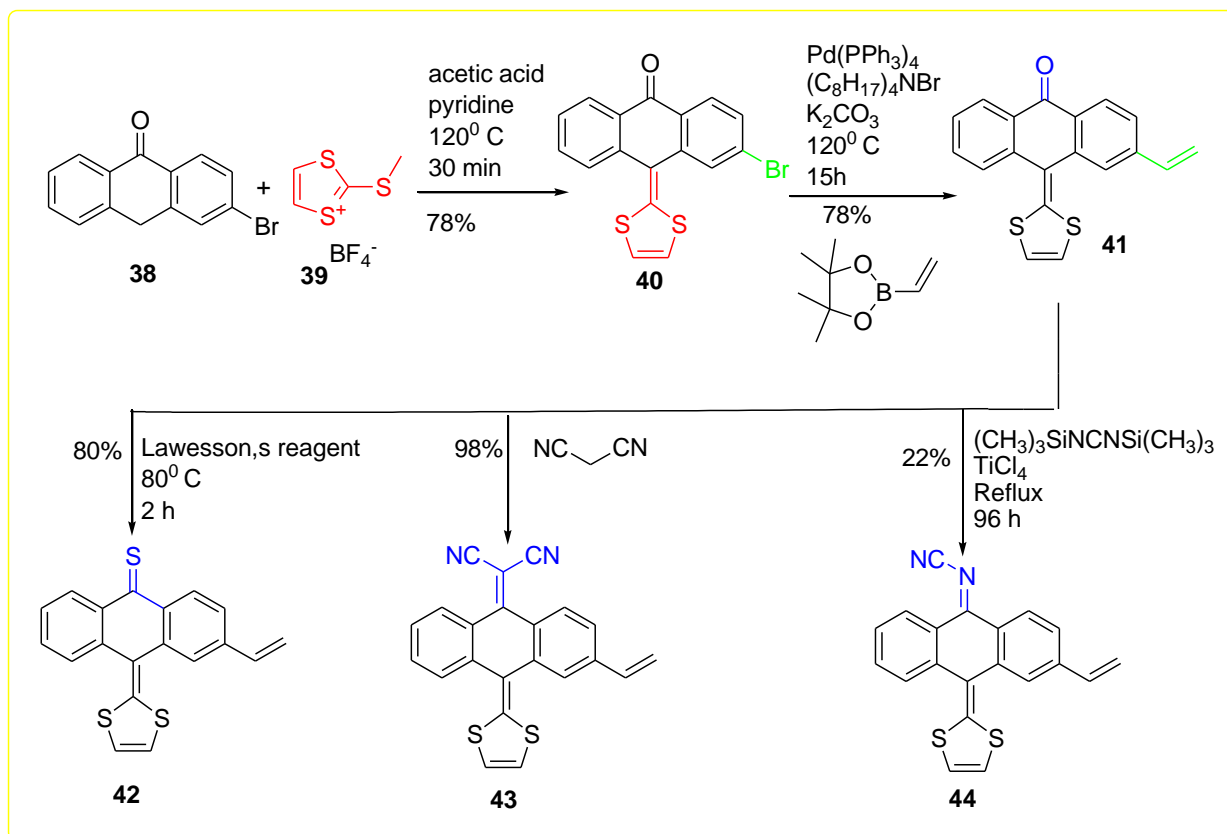
305
306   **Fig. 9.** Thione (**42**), dicyanomethylene (**43**) and N-cyanoimine (**44**) functionalized anthraquinone
307   derivative.

308

309   Seidel and their workmates synthesized, designed and characterized the fourteen novel products

310   of 9,10-anthraquinone and 9,10-dimethoxy anthracene from which the synthesis of two are

311   mentioned in Fig. 10. The corresponding compounds due to the π conjugated thiophene ended side

312   groups linked with the anthracene core at 1 and 5 position give somewhat stable compounds [68].
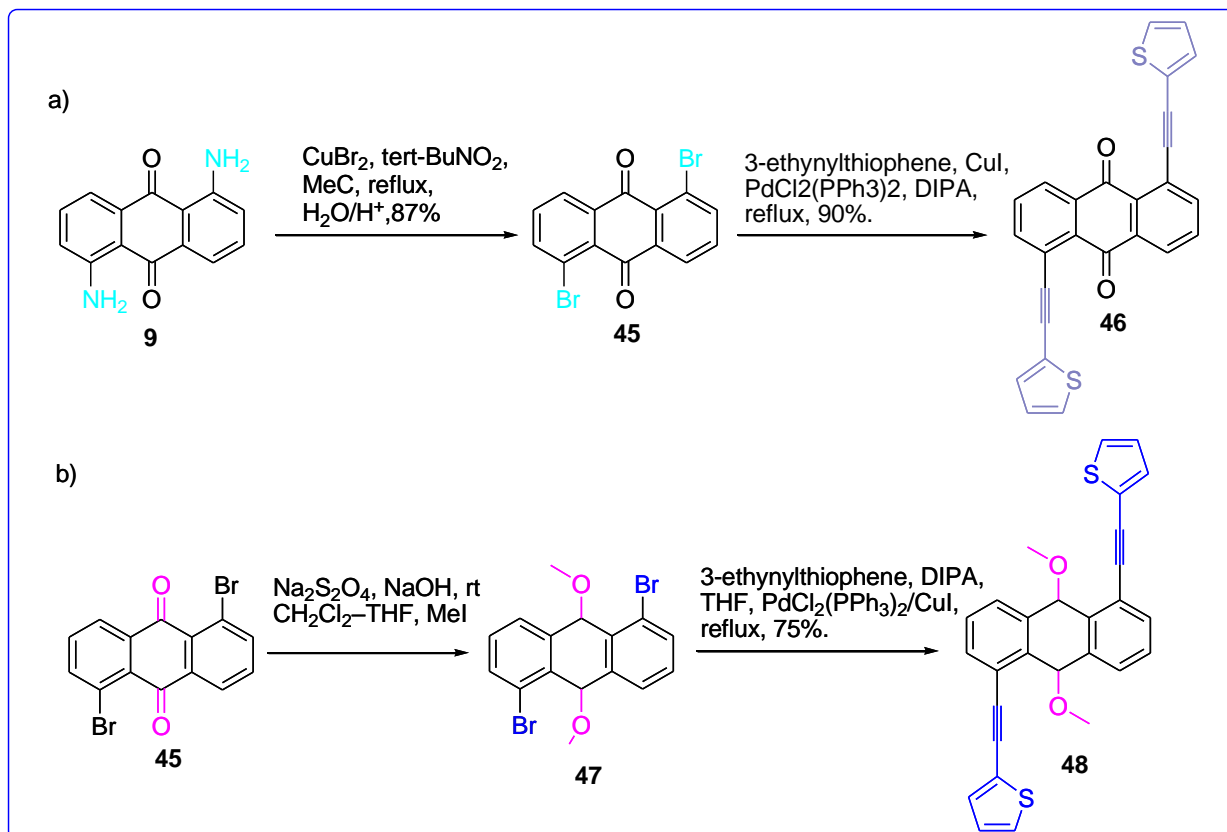
Fig. 10. Anthraquinone having thiophene terminated groups **45-48**.

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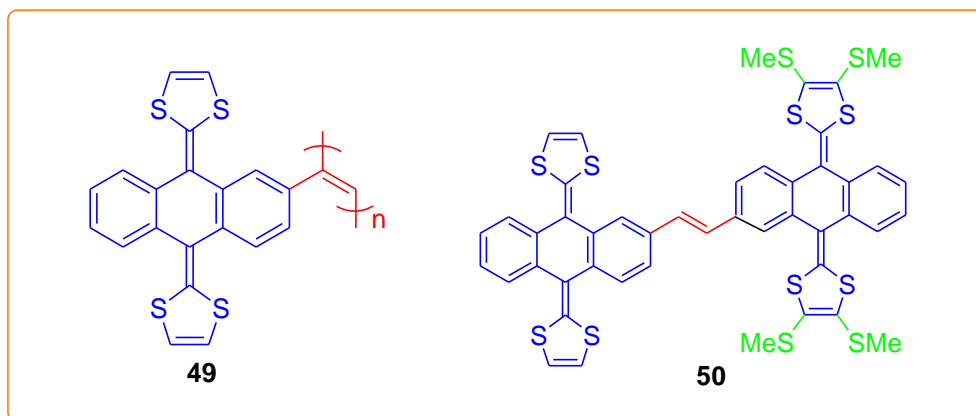
Fig. 11. Structures of anthraquinone containing exTTF moieties [69, 70].

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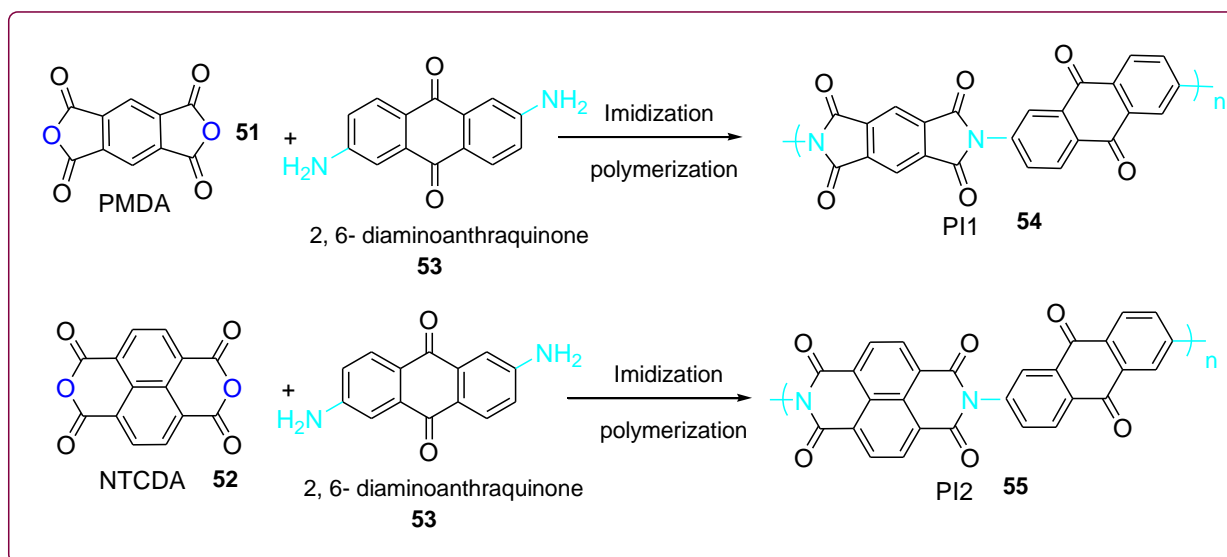
Fig. 12. Synthesis of anthraquinone derivative having polyimide side groups **51** and **52**.

335   Wang *et al*. (2010) [35] came out with a hybrid material having five membered cyclic rings with

336   central pyrrole ring from where the anthraquinone attached and produce SNS-1AQ and SNS-2AQ

337   (**56-57**). After the synthesis and electro polymerization of these moieties, they got polymer films.

338   As shown in Fig. 13 the conjugation of anthraquinone extends to a high degree through these five

339   membered conjugated rings due to which the products could effectively provide stable

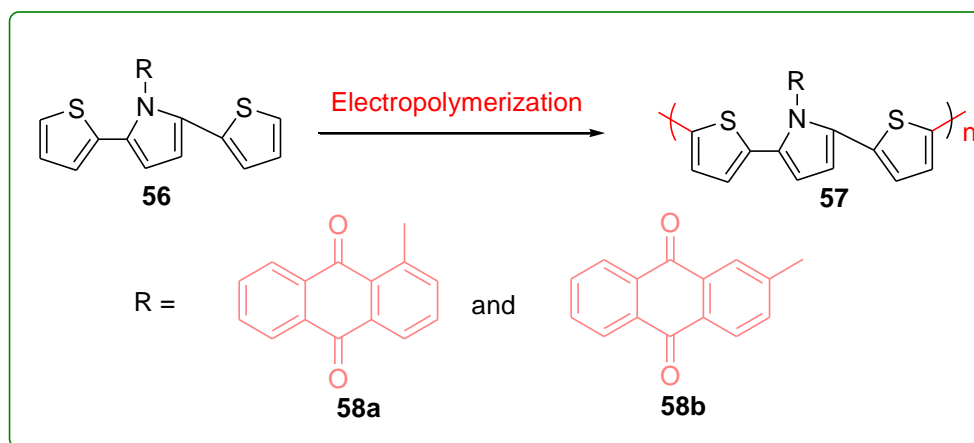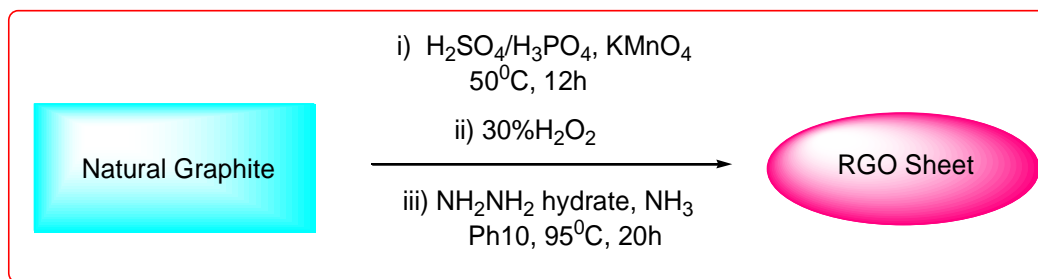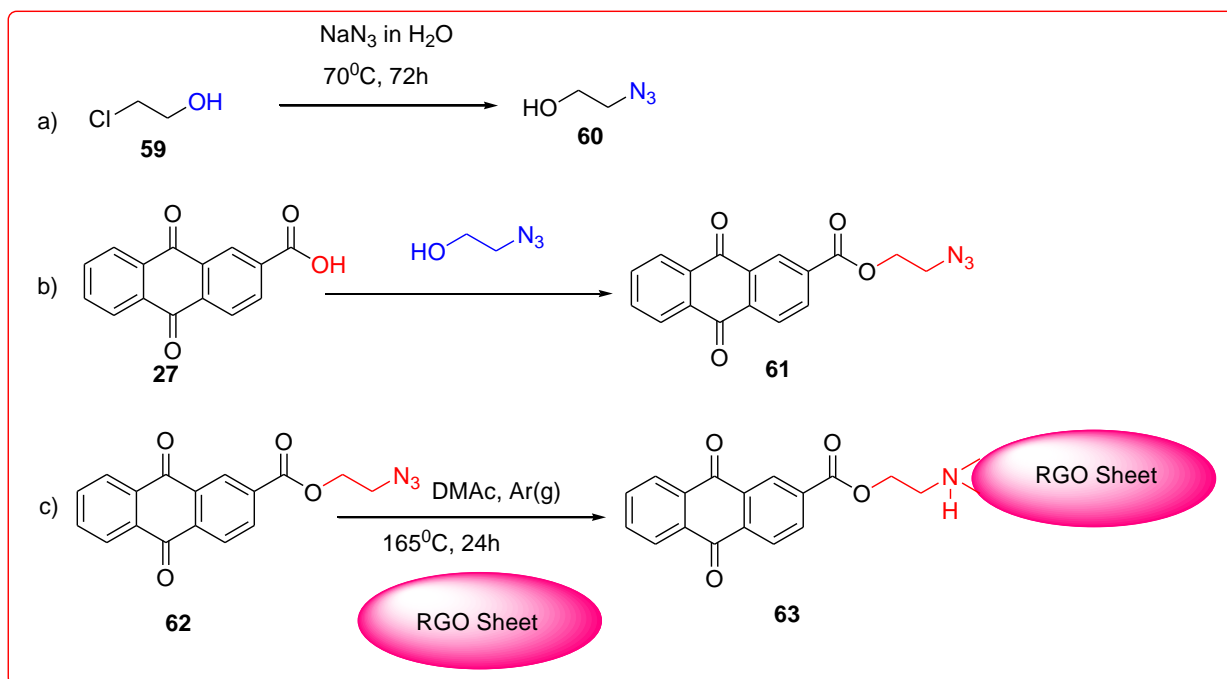340   electrochromic and redox couple behaviour.

341

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

343

344   Recently in 2017, the azide functionalized anthraquinone derivative is synthesized in one-step by

345   using nitrene and natural graphite; reduced graphene oxide RGO is formed which on reaction with

346   azide substituted anthraquinone derivative give amended reduced graphene oxide anthraquinone

347   (RGO-AQ).This product is basically considered as cathode active material. The results

348   demonstrated the prominent differences in capacity and performance of these newly synthesized

349   RGO-AQ (**63**) [71, 72].

350

i) H_2SO_4/H_3PO_4, $KMnO_4$
50^0C, 12h

ii) 30%H_2O_2

iii) NH_2NH_2 hydrate, NH_3
Ph10, 95^0C, 20h

Natural Graphite → RGO Sheet

351

a)

NaN$_3$ in H_2O

70^0C, 72h

59 → 60

b)

27 → 61

c)

62 + RGO Sheet

DMAc, Ar(g)

165^0C, 24h

→ 63 RGO Sheet

352
353

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

354

355 Recently a redox active polymer having anthraquinone moieties and cyclic structures in the

356 backbone is synthesized by the lead (Pd) catalysed cyclopolymerization of dienes as shown in Fig.

357 15. Cyclic voltammetry of monomer and polymer (**67**) supported by carbon paper were performed

358 which allow high electrochemical stability and reversible electrochemical property [73].

23
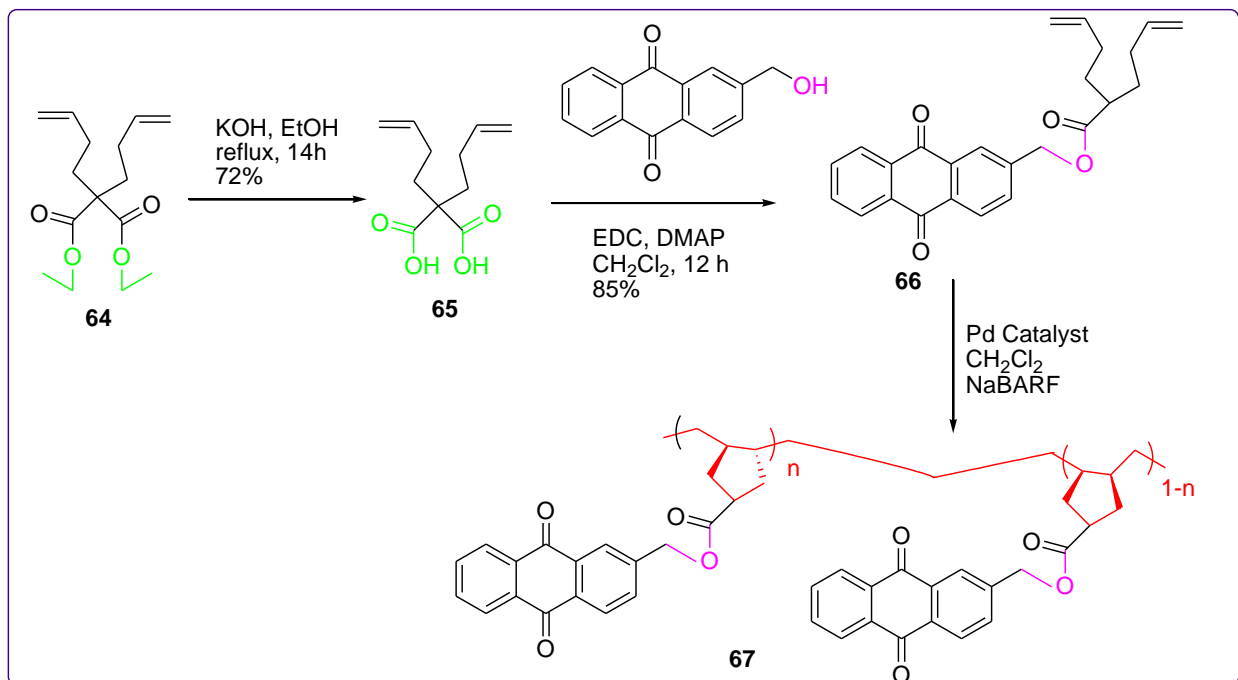
Fig. 15. Schematic representation of the polymer having a cyclic structure in the backbone (**64-67**).

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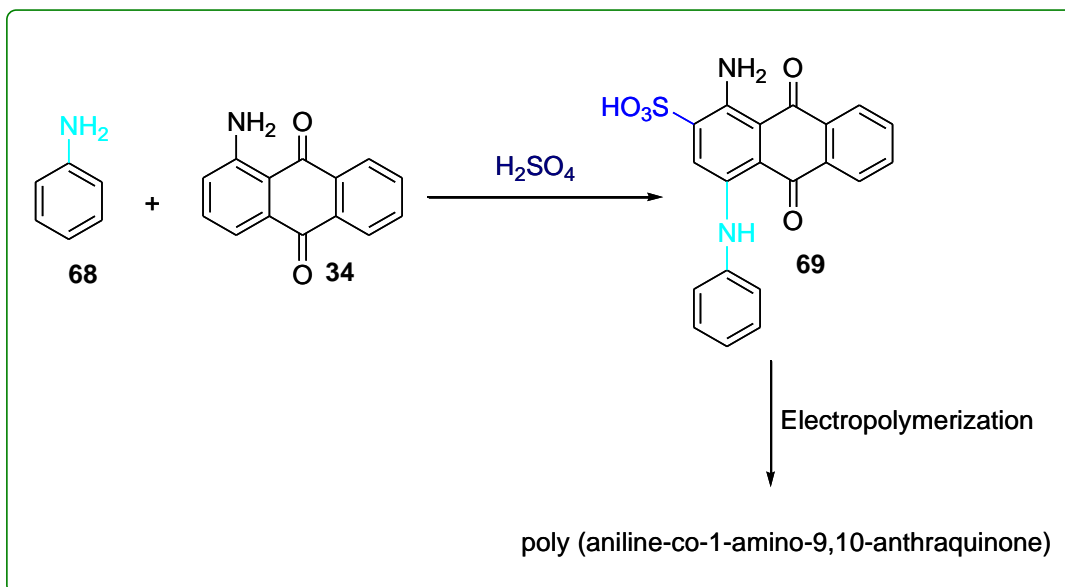
Fig. 16. The reaction of aniline with amino anthraquinone (**68**, **34** and **69**).

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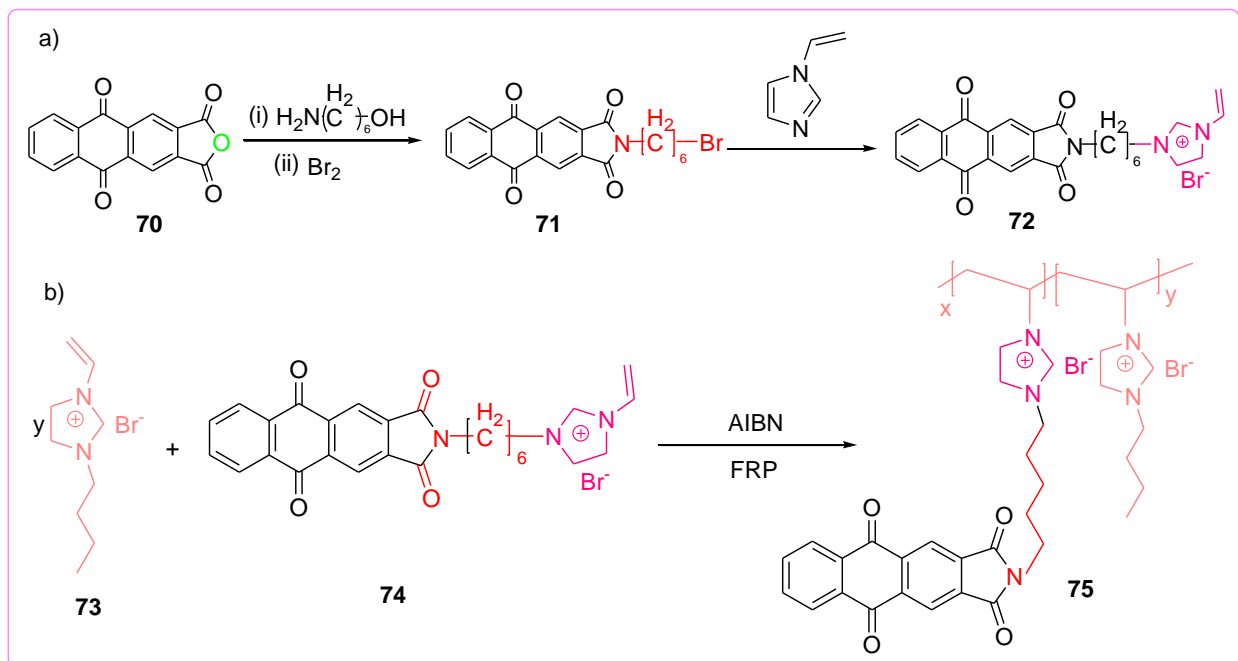
Fig. 17. Homo and copolymerized derivative of anthraquinone (**70-75**).

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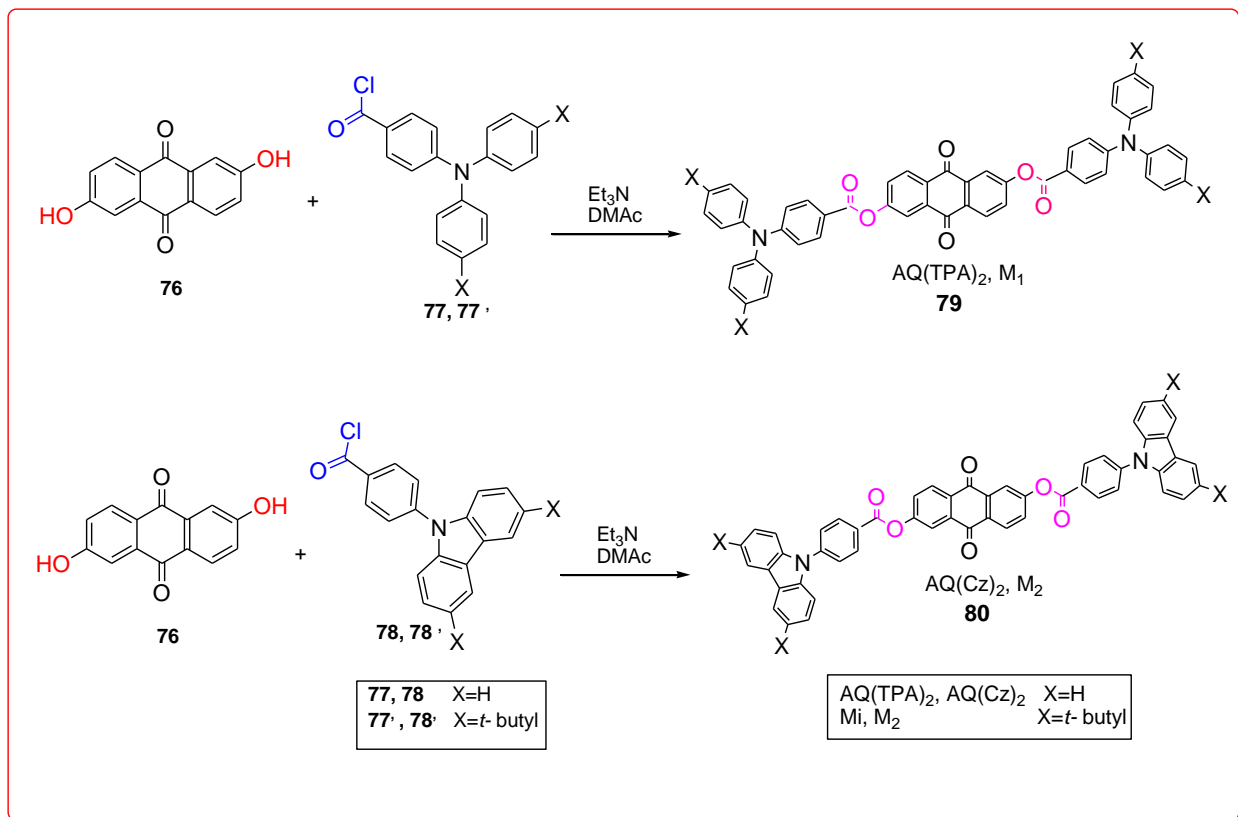
Fig. 18. General reaction of 2, 6-hydroxyanthraqunone (**76**) with carbazole (**78**) or triphenylamine (**77**) groups.

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].
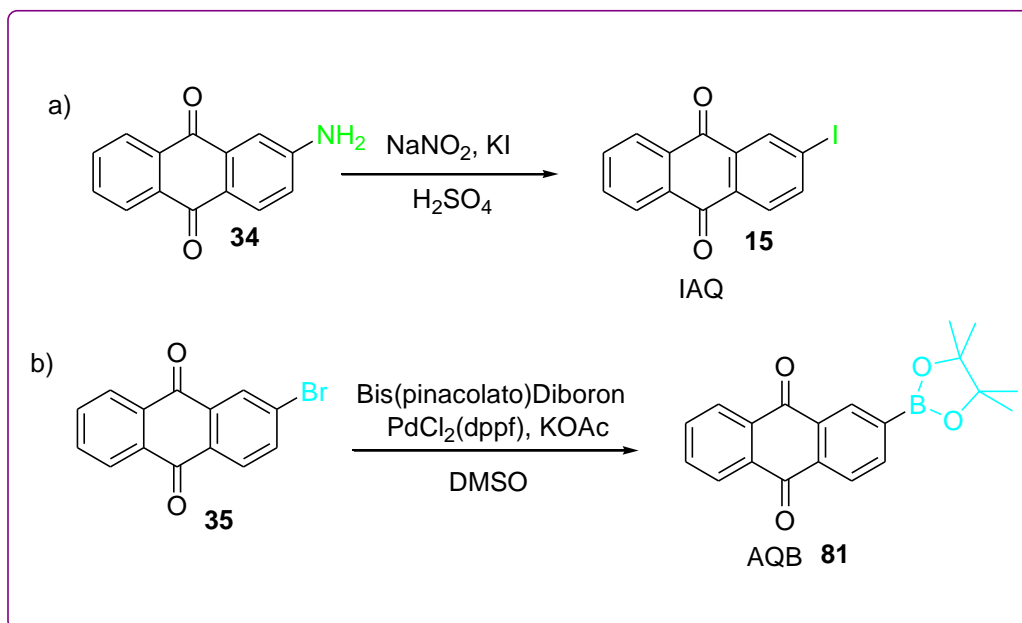
Fig. 19. Synthesis of high molecular weight norbornene substituted anthraquinone (**34**, **15**, **35** and **81-83**).
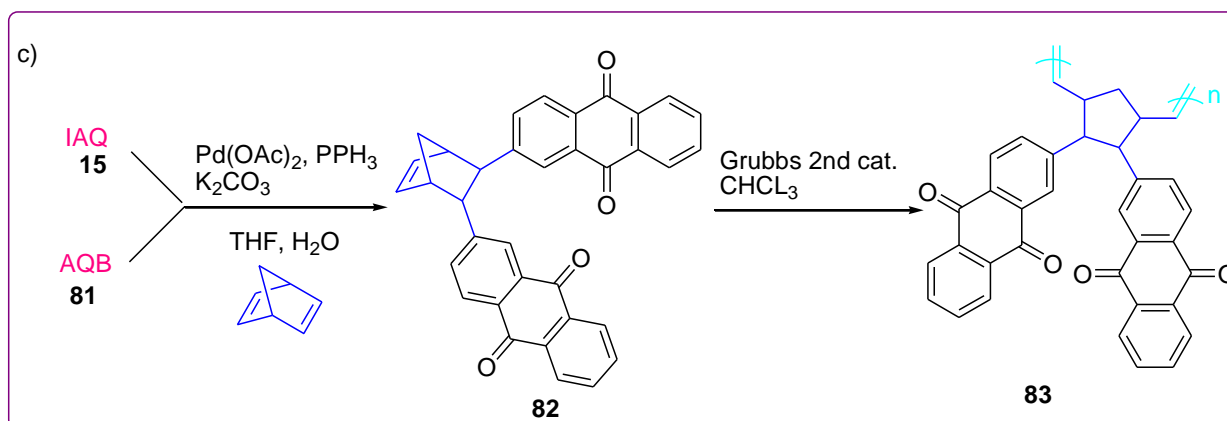
Hsiao and Lin [78] worked on the synthesis of polyetherimides (**90**) with CF_3 substituted diethylamine which is formed according to the synthetic route described in Fig. 20. Due to the enhanced covered volume due to the bulky group CF_3, all fluorinated polyether imide exhibited optical transparency, improved solubility and film-forming capability.
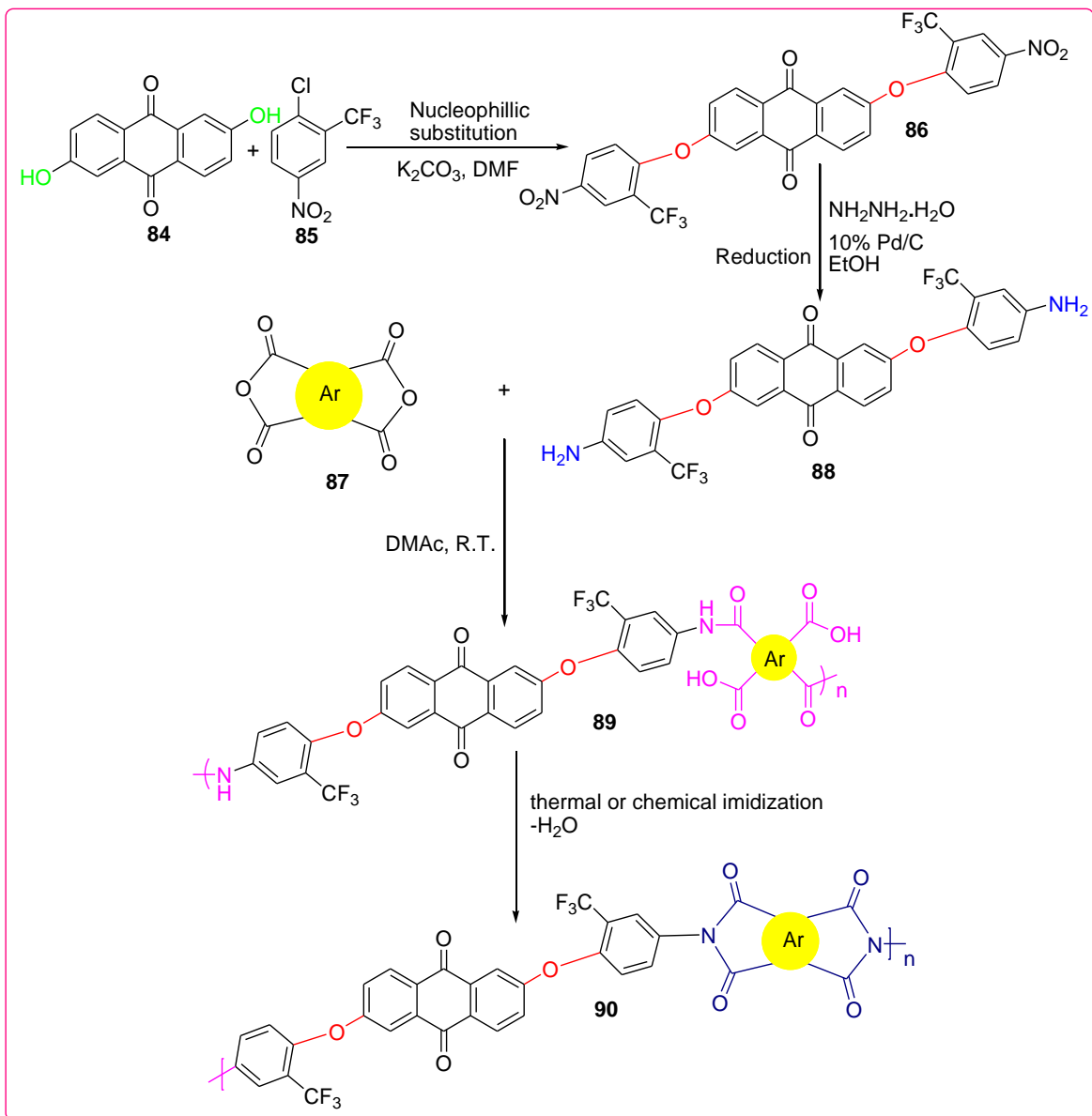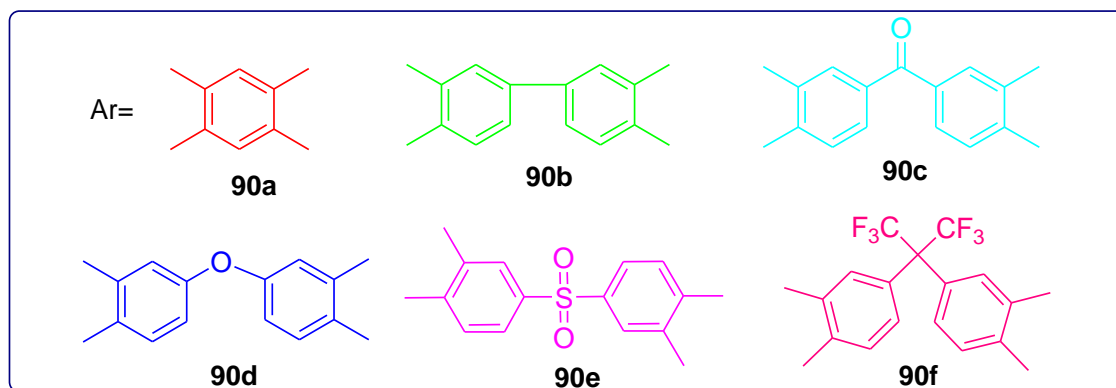
Fig. 20. Diagrammatic representation to the formation of CF_3 substituted anthraquinone incorporated polyetherimide (**84-90**).

406

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].

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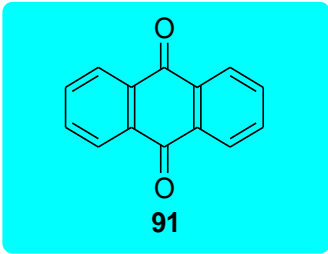
5 Electrochemical applications

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.

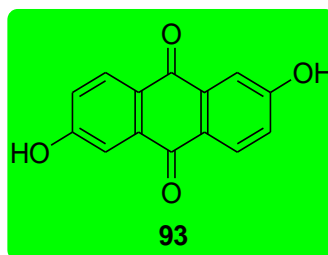| Entry	Category	Structural formula	Capacity (mAhg^{-1})	Life-time (Cycle)	Current (C)
1	Monomer	**91**	212	50	0.1C
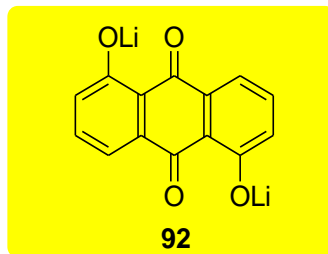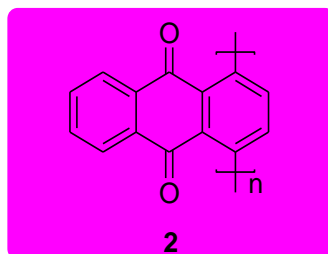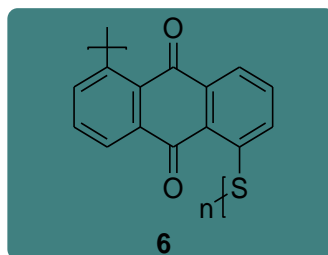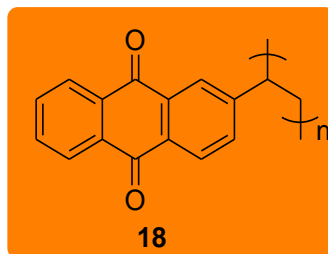
2		**92**	120	50	0.1C
3		**93**	100	100	0.1C
4	Polymer	**2**	260	100	0.2C
5		**6**	30	100	0.5C
6		**18**	>200	300	15C
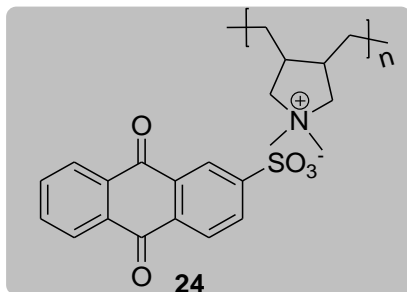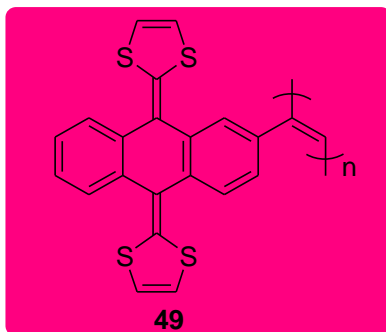
7		130	100	1C
8		105	1000	120C
9		192	150	3.2C
10		212	500	1.2C
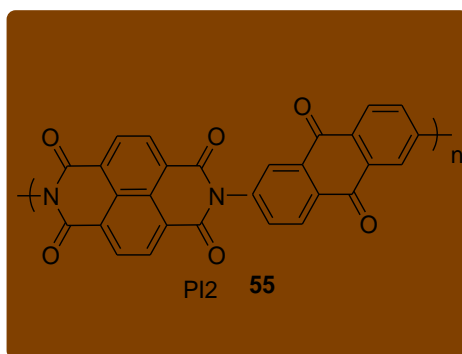
6 Future prospective

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 mat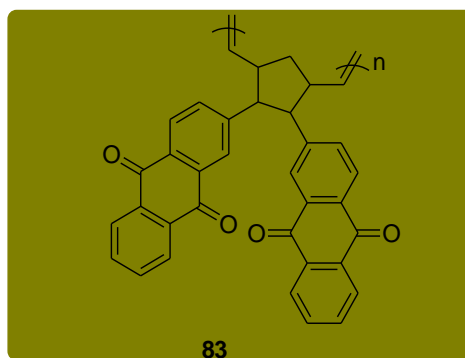erials. In future, these limitations can be overawed by modifying the moieties and functionalities of anthraquinone and by replacing traditional components with greener, nontoxic and organic material. Still, there is a need to think about the right combination of compounds to exercise these materials 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

461   anthraquinone polymers, polyionic liquids emerged as a potential compound as it is synthesized

462   by simple one step ion exchange reaction and exhibits good capacity, less fading and stable cell

463   cycle. Though, among high molecular weight anthraquinone polymer, catalytically polymerize

464   norbornene substituted dianthraquinone, due to incorporation of two molecules of anthraquinone,

465   give high cycle stability up to 500 cycles which gives a long battery life cycle. However, the

466   synthetic pathway is time consuming and needs attention to figure out more facile pathway to

467   synthesize this compound, while, polyimide synthesis provides the one pot synthetic pathway that

468   gives reversible comparable capacity and excellent cyclability with four electron transfer system.

469   Based on these critical analyses we conclude that in comparison to simple and substituted

470   anthraquinone, synthetic polymers of anthraquinone are most important as it gives high cycle

471   stability, facile synthetic approach, less dissolution and comparable storage cell capacity. Hence,

472   commercially anthraquinone derivatives would be very important in the energy storage system,

473   automotive, biomedical, aircraft, pharmaceutical, electrochromic, paints, dyes industries and could

474   be very helpful in flourishing these industries in near future.

475

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.

516   18.   Inzelt, G., Conducting polymers: a new era in electrochemistry. 2012: Springer Science &
517   Business Media.
518   19.   Son, E.J., et al., Quinone and its derivatives for energy harvesting and storage materials.
519   Journal of Materials Chemistry A, 2016. 4(29): p. 11179-11202.
520   20.   Esteves, C.H.A., et al., Identification of Tobacco Types and Cigarette Brands Using an
521   Electronic Nose Based on Conductive Polymer/Porphyrin Composite Sensors. ACS
522   omega, 2018. 3(6): p. 6476-6482.
523   21.   Ha, D., Z. Fang, and N.B. Zhitenev, Paper in electronic and optoelectronic devices.
524   Advanced Electronic Materials, 2018. 4(5): p. 1700593.
525   22.   Fannir, A., et al., Linear Artificial Muscle Based on Ionic Electroactive Polymer: A
526   Rational Design for Open-Air and Vacuum Actuation. Advanced Materials Technologies,
527   2019. 4(2): p. 1800519.
528   23.   Takalloo, S.E., H. Seifi, and J.D. Madden. Design of ultra-thin high frequency trilayer
529   conducting polymer micro-actuators for tactile feedback interfaces. in Electroactive
530   Polymer Actuators and Devices (EAPAD) 2017. 2017. International Society for Optics and
531   Photonics.
532   24.   Gazotti Jr, W.A., et al., A Solid-State Electrochromic Device Based on Two Optically
533   Complementary Conducting Polymers. Advanced Materials, 1998. 10(1): p. 60-64.
534   25.   Sharma, P., et al., Perylene-polyimide-Based organic electrode materials for rechargeable
535   lithium batteries. The Journal of Physical Chemistry Letters, 2013. 4(19): p. 3192-3197.
536   26.   Karlsson, C., Conducting Redox Polymers for Electrical Energy Storage: Backbone-
537   Substituent Interactions in Quinone Polypyrrole Model Systems. 2014, Acta Universitatis
538   Upsaliensis.
539   27.   Waterlot, C., D. Couturier, and B. Hasiak, Synthesis of new electron transfer polymers for
540   the reduction of dissolved oxygen in water. Journal of applied polymer science, 2001.
541   80(2): p. 223-229.
542   28.   Schmidt, D., et al., Poly (DCAQI): Synthesis and characterization of a new redox-active
543   polymer. Journal of Polymer Science Part A: Polymer Chemistry, 2016. 54(13): p. 1998-
544   2003.
545   29.   Brunmark, A. and E. Cadenas, Redox and addition chemistry of quinoid compounds and
546   its biological implications. Free Radical Biology and Medicine, 1989. 7(4): p. 435-477.
547   30.   Deng, W., et al., A low cost, all-organic Na-ion battery based on polymeric cathode and
548   anode. Scientific reports, 2013. 3: p. 2671.
549   31.   Milczarek, G. and O. Inganäs, Renewable cathode materials from biopolymer/conjugated
550   polymer interpenetrating networks. Science, 2012. 335(6075): p. 1468-1471.
551   32.   Iordache, A., et al., Monothioanthraquinone as an organic active material for greener
552   lithium batteries. Journal of Power Sources, 2014. 267: p. 553-559.
553   33.   Oyaizu, K., W. Choi, and H. Nishide, Functionalization of poly (4-chloromethylstyrene)
554   with anthraquinone pendants for organic anode-active materials. Polymers for Advanced
555   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.

596   51.   Cui, Z., et al., New Type of Eco-Friendly Polymeric Dye by Covalently Bonding
597   Anthraquinone into Polyphenylsulfone. Macromolecular Materials and Engineering, 2019:
598   p. 1800692.
599   52.   Jing, Y., et al., Two novel anthraquinones with cytotoxicity from Hedyotis caudatifolia.
600   Phytochemistry Letters, 2019. 29: p. 134-137.
601   53.   Feijen, E.A., et al., Derivation of anthracycline and anthraquinone equivalence ratios to
602   doxorubicin for late-onset cardiotoxicity. JAMA oncology, 2019.
603   54.   Takeda, T., et al., Electron-deficient anthraquinone derivatives as cathodic material for
604   lithium ion batteries. Journal of Power Sources, 2016. 328: p. 228-234.
605   55.   Song, Z., et al., Polyanthraquinone as a reliable organic electrode for stable and fast lithium
606   storage. Angewandte Chemie, 2015. 127(47): p. 14153-14157.
607   56.   Zhou, Y., et al., Polyanthraquinone-based nanostructured electrode material capable of
608   high-performance pseudocapacitive energy storage in aprotic electrolyte. Nano Energy,
609   2015. 15: p. 654-661.
610   57.   Song, Z., H. Zhan, and Y. Zhou, Anthraquinone based polymer as high performance
611   cathode material for rechargeable lithium batteries. Chemical communications, 2009(4): p.
612   448-450.
613   58.   Xu, W., et al., Factors affecting the battery performance of anthraquinone-based organic
614   cathode materials. Journal of Materials Chemistry, 2012. 22(9): p. 4032-4039.
615   59.   Bitenc, J., et al., Anthraquinone-Based Polymer as Cathode in Rechargeable Magnesium
616   Batteries. ChemSusChem, 2015. 8(24): p. 4128-4132.
617   60.   Pan, B., et al., Polyanthraquinone-Based Organic Cathode for High-Performance
618   Rechargeable Magnesium-Ion Batteries. Advanced Energy Materials, 2016. 6(14): p.
619   1600140.
620   61.   Naoi, K., S. Suematsu, and A. Manago, Electrochemistry of poly (1, 5-
621   diaminoanthraquinone) and its application in electrochemical capacitor materials. Journal
622   of The Electrochemical Society, 2000. 147(2): p. 420-426.
623   62.   Zhao, L., et al., A novel polyquinone cathode material for rechargeable lithium batteries.
624   Journal of Power Sources, 2013. 233: p. 23-27.
625   63.   Wang, W., et al., Anthraquinone with tailored structure for a nonaqueous metal–organic
626   redox flow battery. Chemical communications, 2012. 48(53): p. 6669-6671.
627   64.   Tsuzaki, A., et al., A New Bio-based Battery Material: Effect of Rate of Anthraquinone
628   Skeleton Incorporation into Polyglycidol on Battery Performance. Energy Procedia, 2016.
629   89: p. 207-212.
630   65.   Hernández, G., et al., Redox-active poly (ionic liquid) s as active materials for energy
631   storage applications. Journal of Materials Chemistry A, 2017. 5(31): p. 16231-16240.
632   66.   Häupler, B., et al., PolyTCAQ in organic batteries: enhanced capacity at constant cell
633   potential using two-electron-redox-reactions. Journal of Materials Chemistry A, 2014.
634   2(24): p. 8999-9001.

635 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.

638 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.

640 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.

642 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.

644 71. Xu, F., J. Xia, and W. Shi, Anthraquinone-based polyimide cathodes for sodium secondary batteries. Electrochemistry Communications, 2015. 60: p. 117-120.

646 72. Sertkol, S.B., et al., An anthraquinone-functionalized reduced graphene oxide as electrode material for rechargeable batteries. Carbon, 2017. 116: p. 154-166.

648 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.

651 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.

654 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.

657 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.

660 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.

663 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.

666 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.

669 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.

672 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.

674 82. Lin, K., et al., Alkaline quinone flow battery. Science, 2015. 349(6255): p. 1529-1532.

675   83.   Cao, J., et al., A new redox-active conjugated polymer containing anthraquinone pendants
676   as anode material for aqueous all-organic hybrid-flow battery. Journal of Power Sources,
677   2019. 423: p. 316-322.
678   84.   Juvenal, F., et al., Ultrafast Photo-Induced Electron Transfers in Platinum (II)-
679   Anthraquinone Diimine Polymers/PCBM Films. The Journal of Physical Chemistry C,
680   2019.
681   85.   Tang, W., et al., Highly Stable and High Rate-performance Na-ion Batteries by Using
682   Polyanionic Anthraquinone as the Organic Cathode. ChemSusChem, 2019.
683