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Synthesis of anthraquinone based electroactive polymers: A critical review

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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

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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].

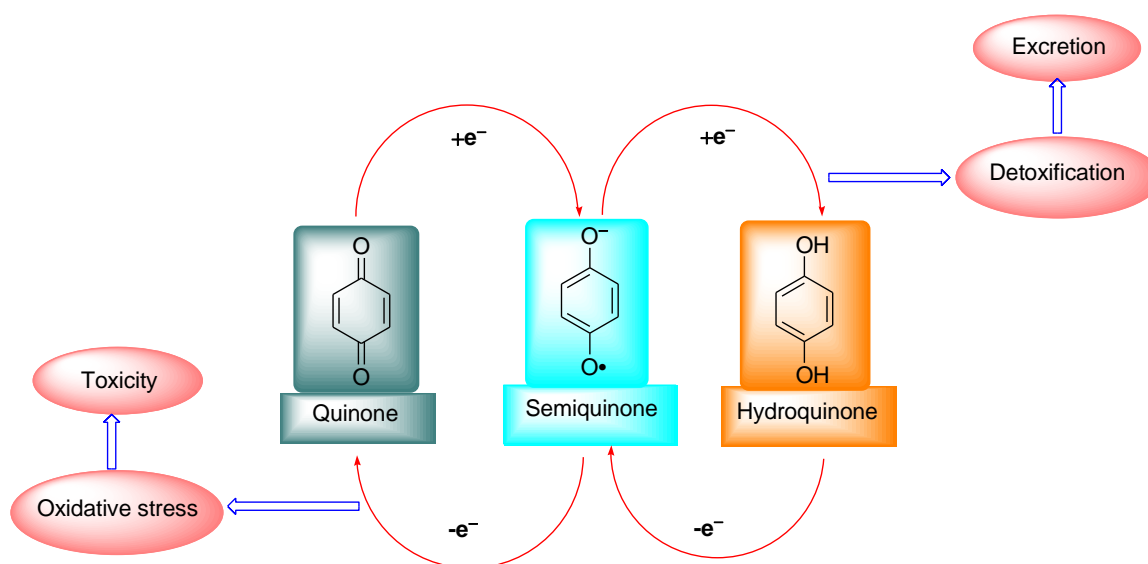
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75 In all evolving fields, organic based conducting polymer have been extensively studied due to their
76 potential application in electronics, sensors, artificial muscles, electrochromic devices, capacitors
77 and electromagnetic radiation shielding 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

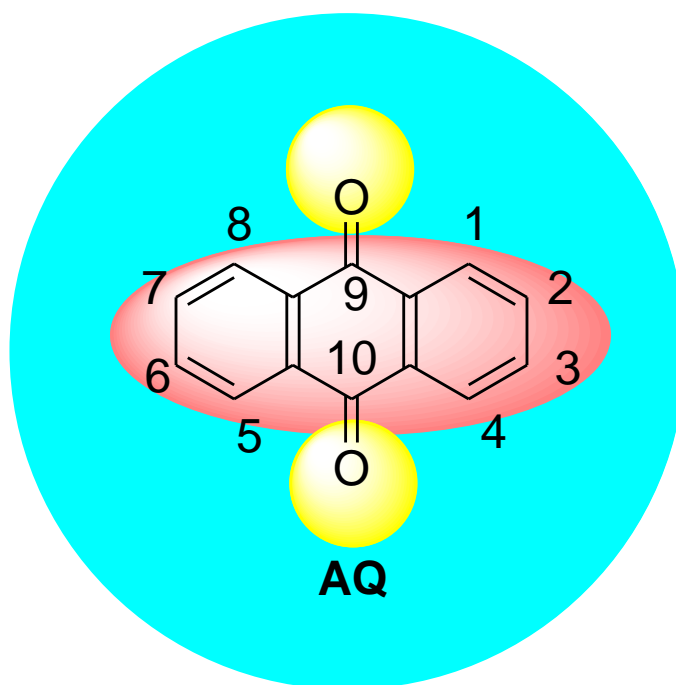
95 Predominantly, anthraquinones exhibit a faster reaction at heterogeneous rate constant for the
96 electrode reaction ($>10^{-2}$ cm/s) at moderately negative potential (-0.8V) [33]. Anthraquinone also
97 possesses the obvious chemical potential because of the absence of α -hydrogen which mostly
98 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.

129 2 Structure and electrochemistry of anthraquinone

130 The structure of anthraquinone (AQ) was first evaluated by Sen in 1948 and then was further
131 refined by Murty in 1960. The final refinement of the structure was carried out by Prakash in 1966
132 and nomenclature by Moss in 1998. Structure of anthraquinone consists of a planar, rigid structure
133 having three conjugated aromatic rings resembling anthracene ring system Fig. 2. The anthracene
134 ring functionalized with the keto function at the 9 and 10 positions [47-49]. This compound
135 anthraquinone was already synthesized with the nitric acid oxidation of anthracene by Laurent
136 [43].



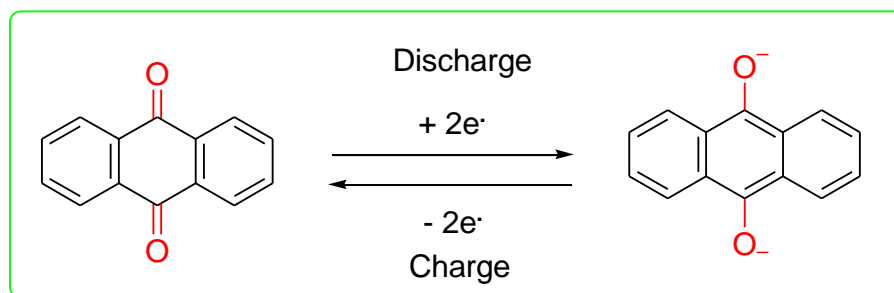
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139

Fig. 2. Structure of anthraquinone.

140 After the structure elucidation of anthraquinone (AQ), electrochemical investigations of the
141 compound were made by different scientist groups because of their incredible reversible redox
142 reaction ability. The anthraquinone moiety has been used commendably not only in energy storage
143 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

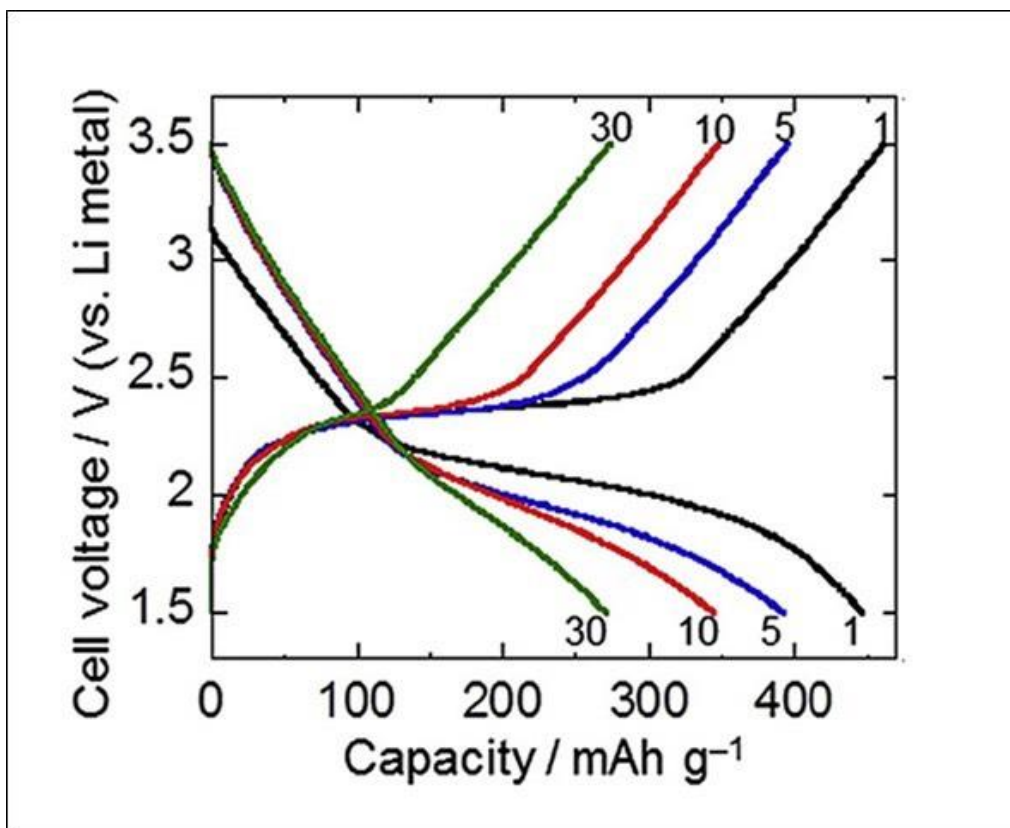


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156

Fig. 3. Electron shift of anthraquinone.

157



158
 159 **Fig. 4.** Graph exhibiting the charge/discharge behaviour of AQ at the scan rate of 0.2C. Charge/discharge
 160 curves of AQ for 1st, 5th, 10th and 30th cycles shows capacity fade up to 255 mAh/g [54].

161
 162 Be contrary to the anthraquinone, its high molecular weight analogues pentacenetetrone showed
 163 higher initial discharge and prominent cycle stability due to the extended π system and
 164 delocalization of electrons. Nevertheless, the cycle life, durability, stability and capacity of
 165 anthraquinone could effectively increase by extended delocalization or by different methods. To
 166 overcome the shortcomings of anthraquinone, different approaches were made by simple
 167 substitution, derivatization or by polymerization.

168 **3 Synthesis of low molecular weight anthraquinone derivative**

169 Up till now from the discovery of first organic anthraquinone polymer, numerous developments
 170 have been taken place in this field. Most of the reports published in the last few years aim to

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 CHCl₃, 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 polyanthraquinone (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].

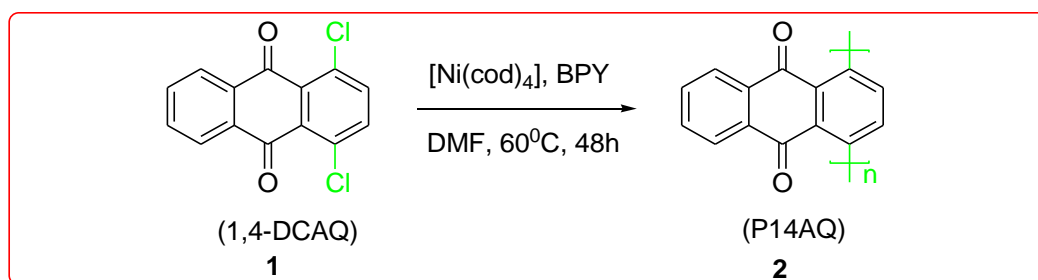
219
220 A conducting polymer such as poly-diaminoanthraquinone (Poly-DAAQ) having amino
221 substituted anthraquinone was studied as a capacitor Fig. 5. The study shows two reversible redox
222 reactions for continuous cycles in non-aqueous media. The spectroscopy proposed that the two
223 sets of redox 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

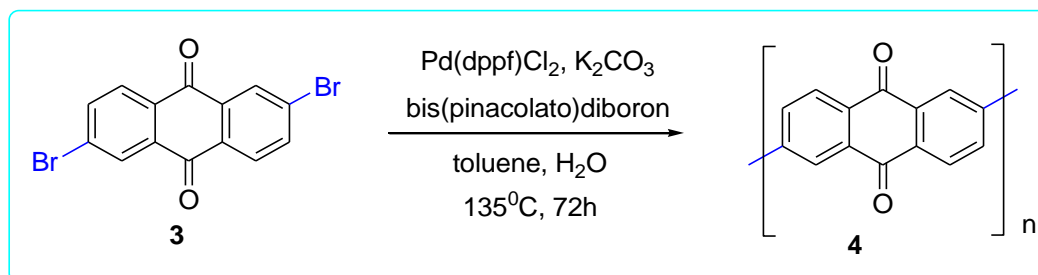
239 stable cell capacity even after 300 cycles compared to that of conjugated, non-conjugated and
240 polysulfide analogue.

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].

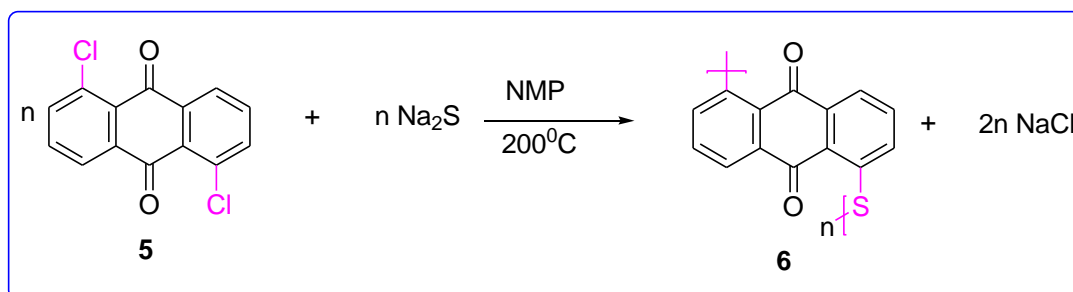
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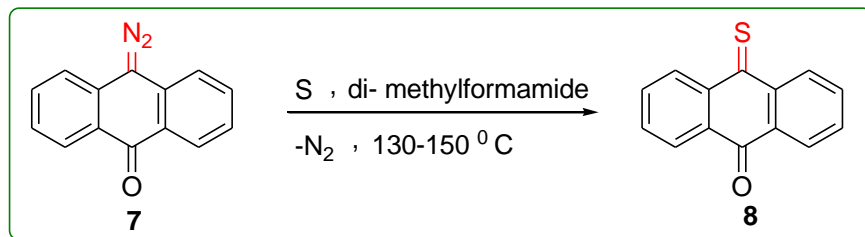
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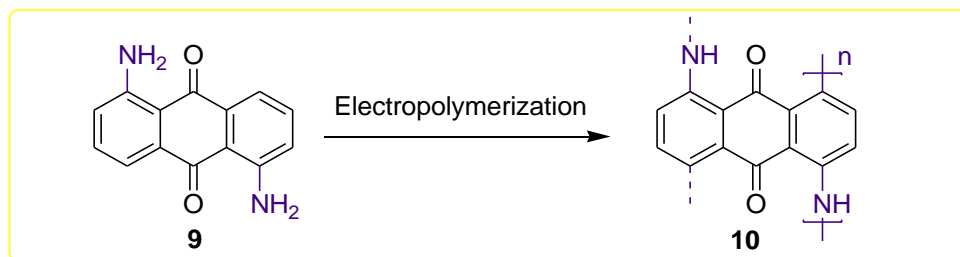
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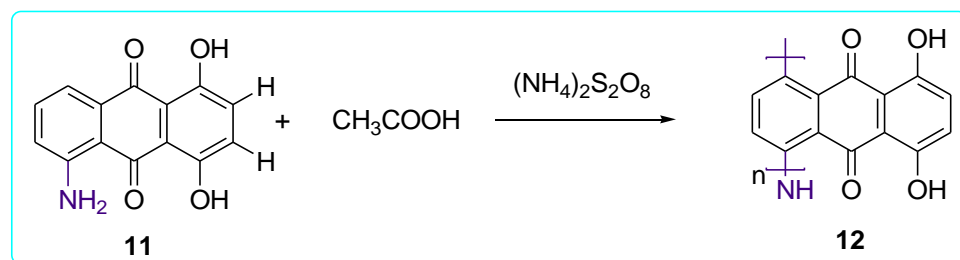
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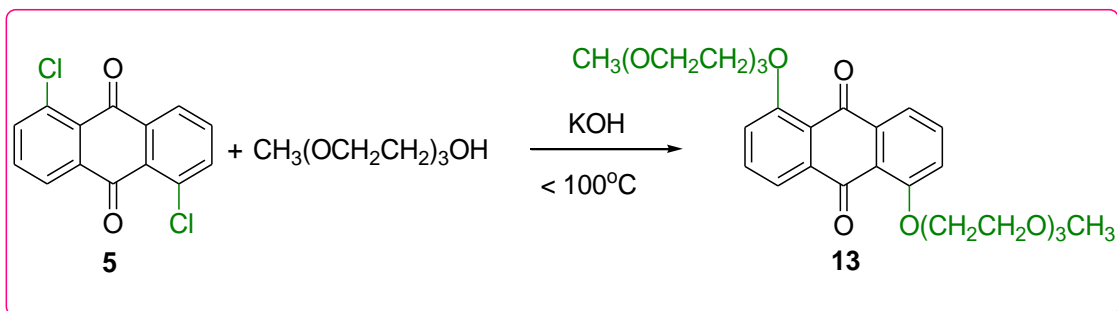
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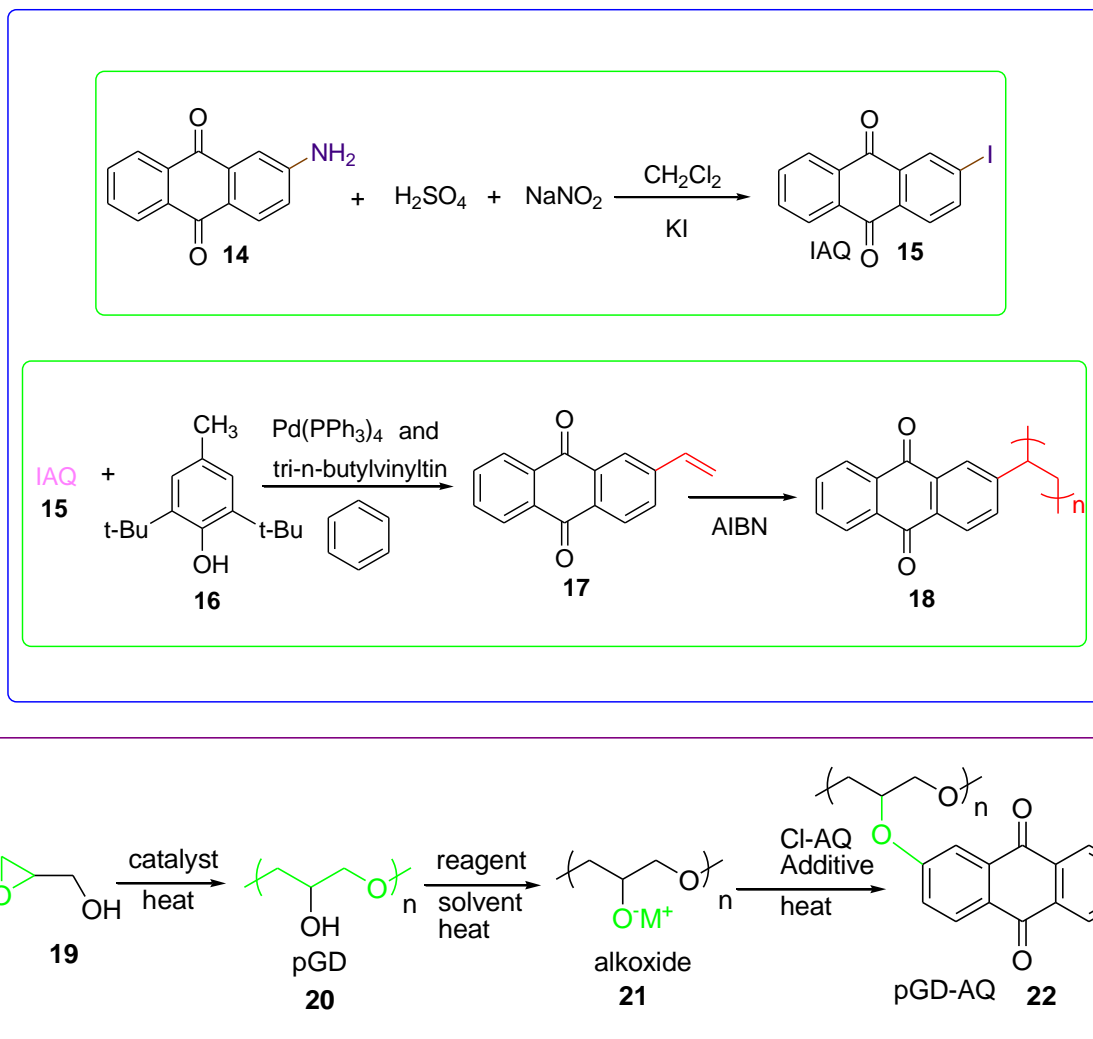


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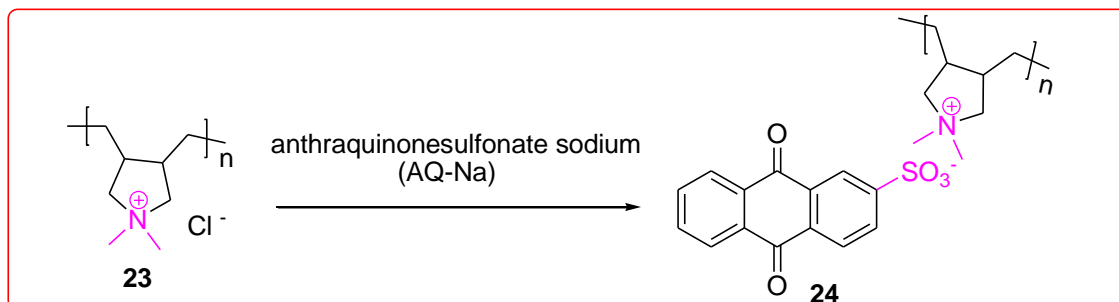
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256 **Fig. 5.** Synthetic routes to anthraquinonoid derivatives poly-1,4-anthraquinone (P14AQ), poly-2,6-
 257 anthraquinone (P26AQ), polyanthraquinone sulphide (PAQS), monothioanthraquinone (MTAQ), poly-
 258 diaminoanthraquinone (Poly-DAAQ), poly-5-amino-1,4-dihydroxy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

260

261 Currently, Hernandez and coworkers [65] give a new approach toward a green future and examined
 262 the new polymeric redox-active poly (ionic liquids) (24). They incorporated the redox active
 263 counterions, anthraquinone and nitroxide into the poly (ionic liquids) which enhances the
 264 application of these materials in energy storage systems. Polyionic liquids synthesized by simple
 265 ions exchange reactions. Among the reported compounds, the schematic procedure mentioned here

266 in Fig. 6 show remarkable properties. The electrochemical study shows that these materials have
267 specific property to be used in energy storage systems. The homopolymer having 100% of
268 anthraquinone units exhibits a very good capacity and stable life cycle when used as the electrode
269 in lithium batteries.
270

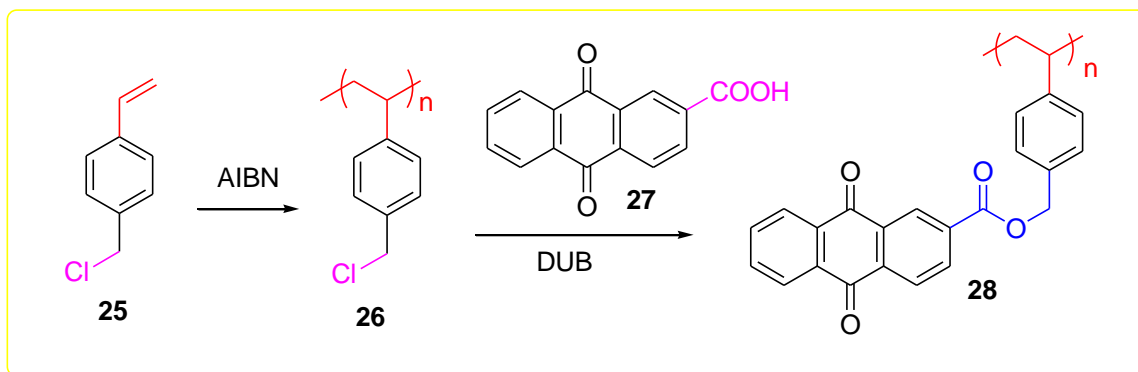


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Fig. 6. Ionic anthraquinonoid polymer.

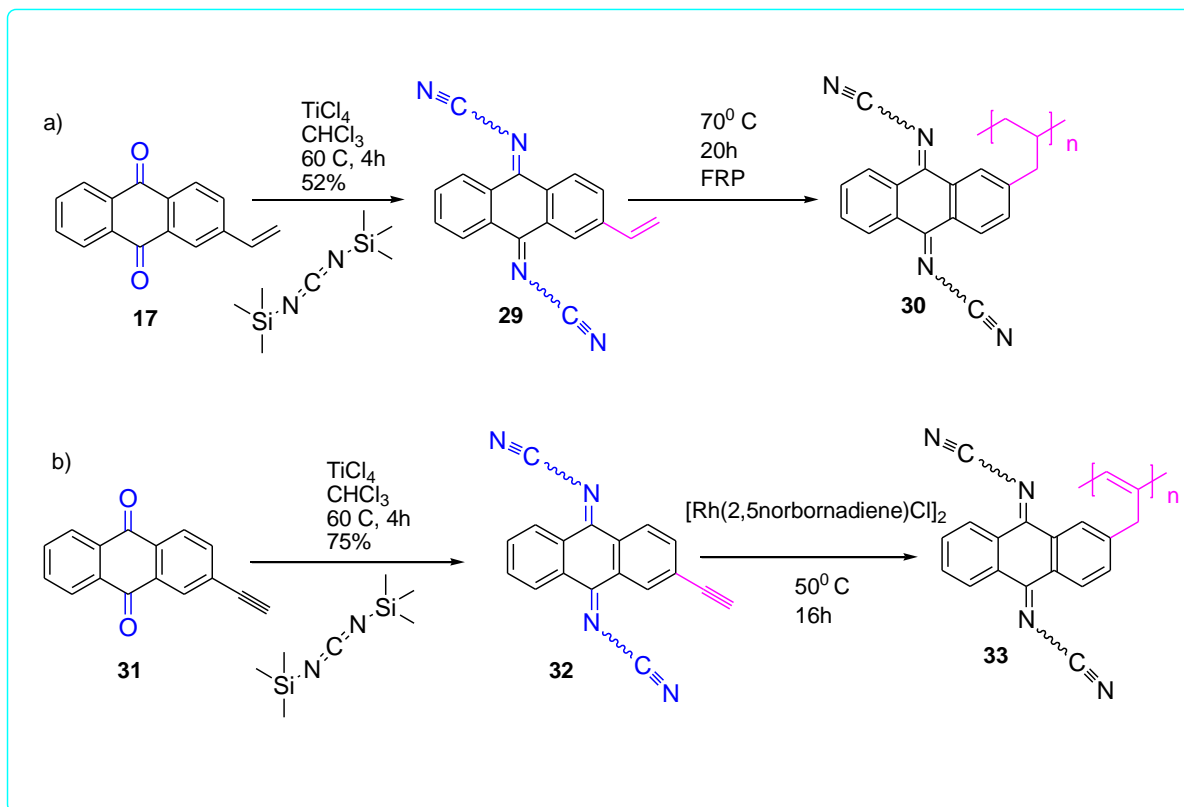
274 **4 Synthesis of high molecular weight anthraquinone derivative**

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

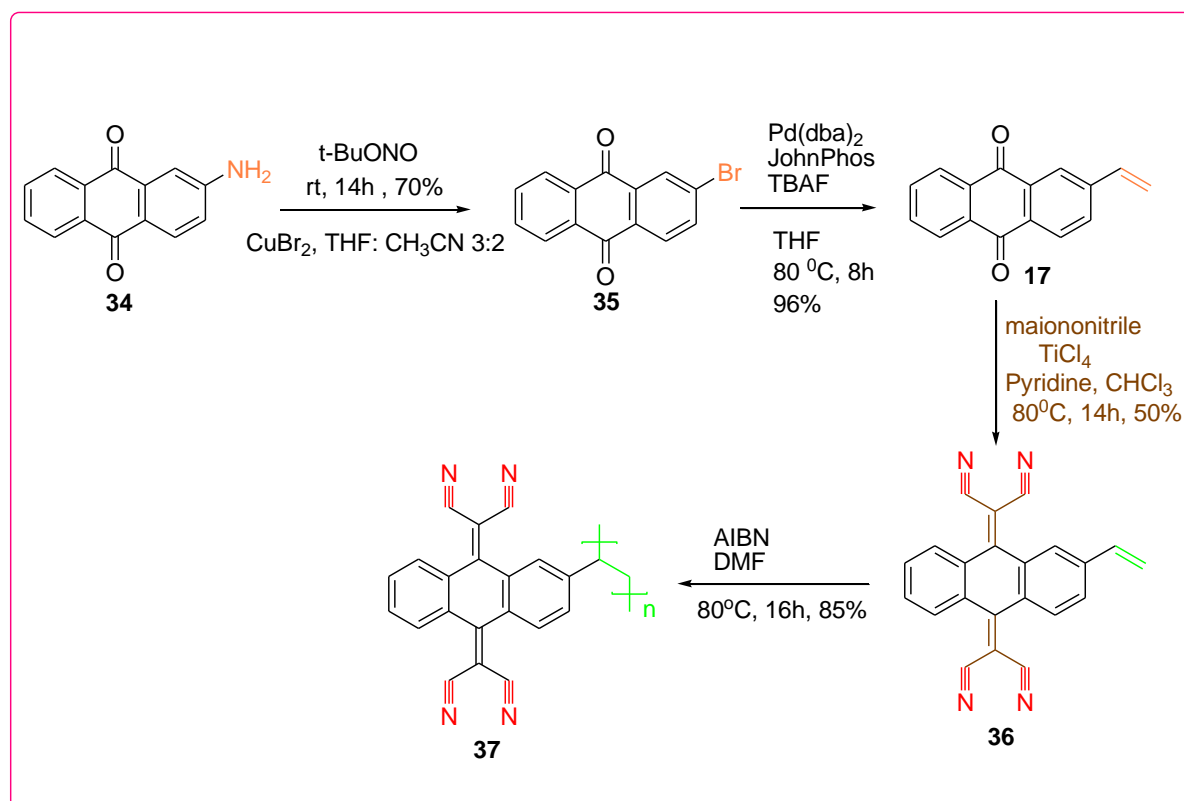


284
285 **Fig. 7.** Anthraquinone reaction with the polystyrene derivative 25-28.
286

287 The carbonyl group of AQ by substituting N-cyanoimine group gives N, N'-dicyanoanthraquinone
288 diamine (DCAQI) (**29**, **32**) (synthesized according to Fig. 8). The analyses of poly- DCAQI (**30**,
289 **33**) in dimethylformamide (DMF) electrolyte shows the stronger electron accepting properties of N-
290 cyanoimine group leads to higher reduction potentials compare to that of AQ. But the difficulty in
291 this compound utilization is the partial hydrolysis of cyanoimine group which ultimately give
292 higher reduction signal value of -1.26V [28]. Instead of using dicyano, a new tetracyano group
293 replace the carbonyl functionality and give tetracyano anthraquinone derivative (**36**). Poly-TCAQ
294 (**37**) as mentioned in Fig. 8 synthesized in four simple steps. Poly-TCAQ exhibits a high material
295 activity of 97%, the excellent columbic efficiency of 99% and high rechargeability with only 12%
296 loss [66].



297

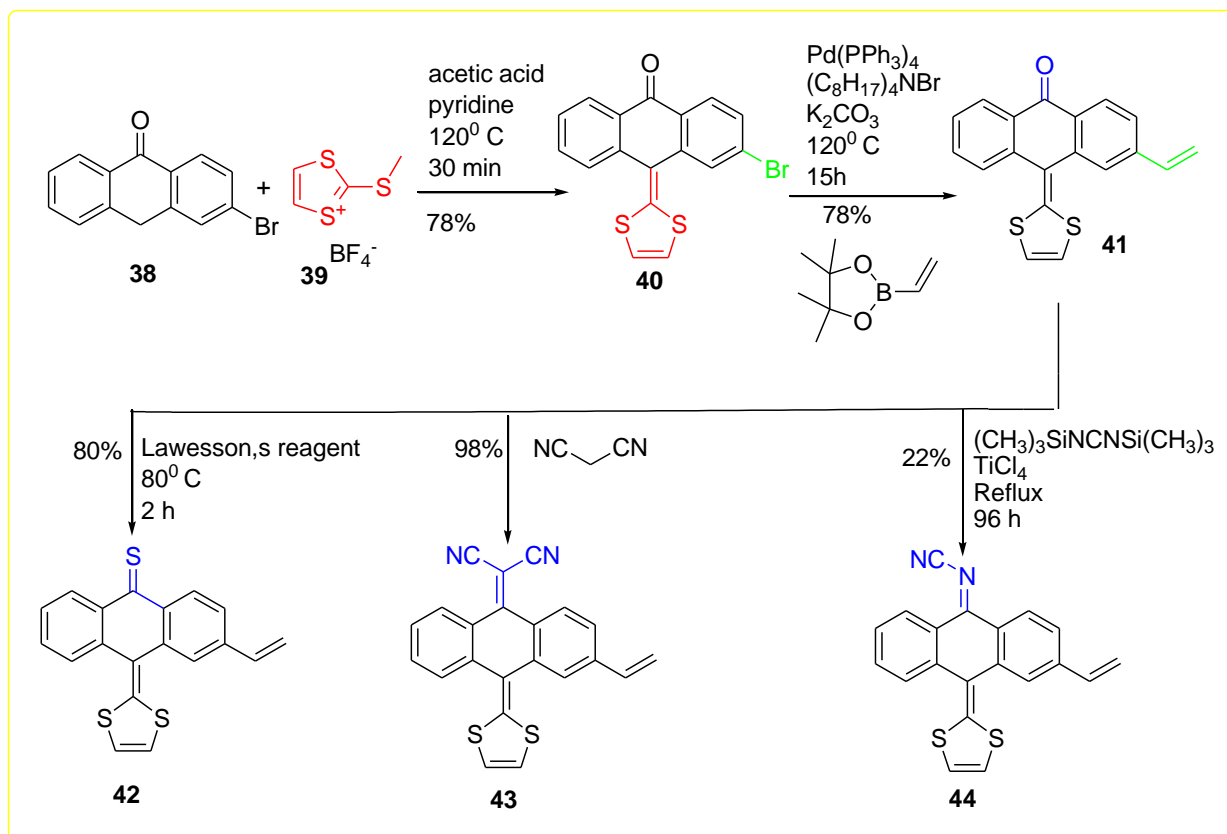


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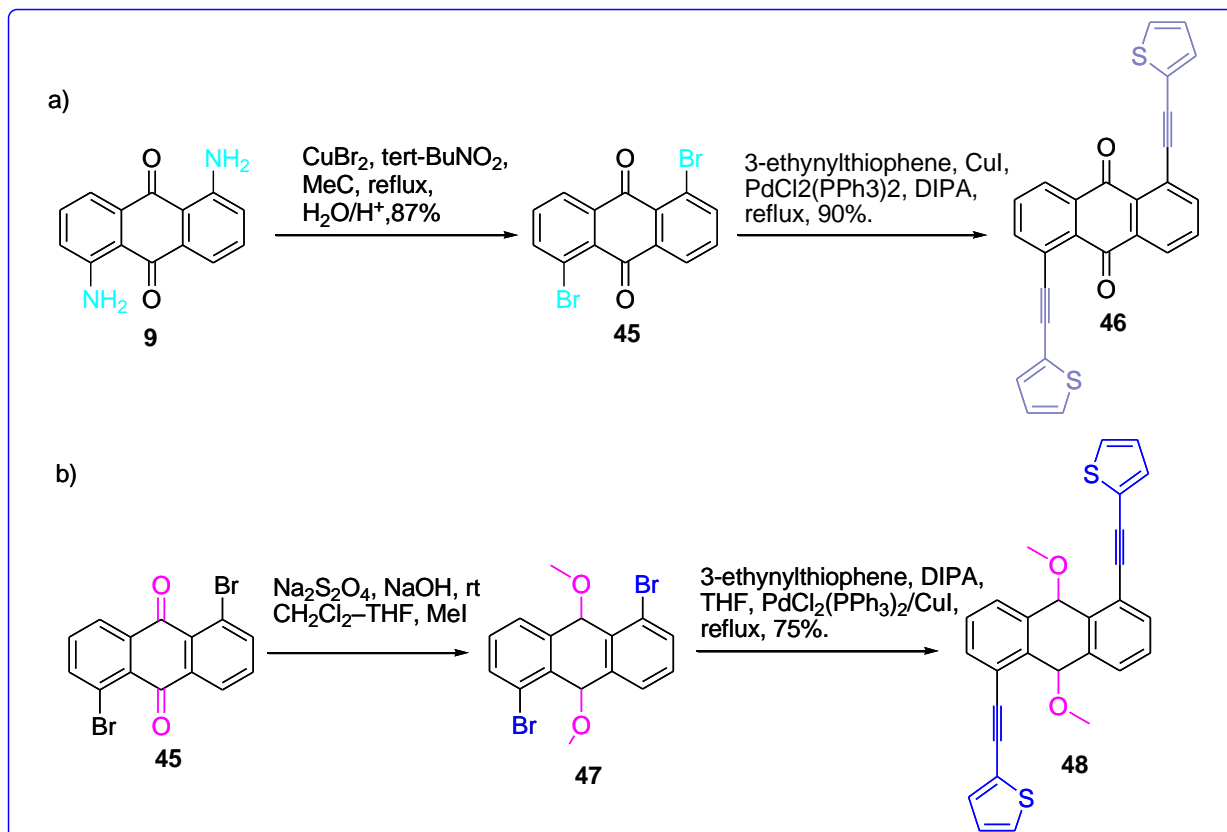
Fig. 8. Synthetic route to Poly-DCAQI (17, 29-33) and Poly-TCAQI (34-37).

300 Foremost to bipolar compounds, the carbonyl functional group modified with three different
 301 moieties that is are Thione (**42**), dicyanomethylene (**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].



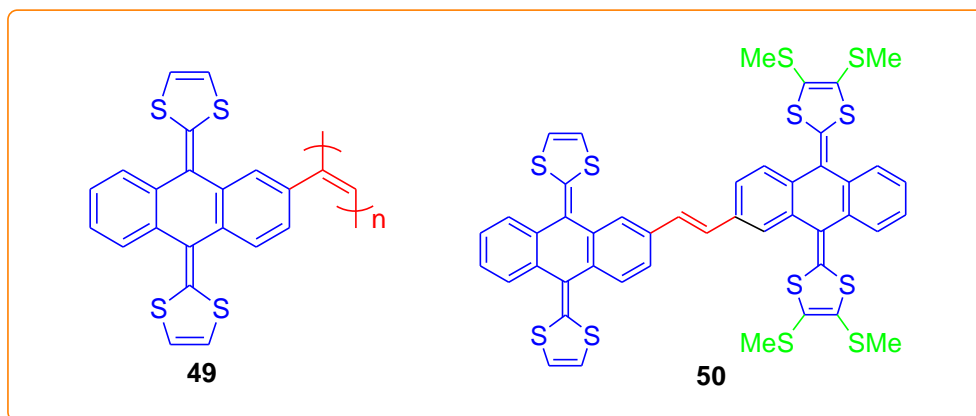
305
 306 **Fig. 9.** Thione (**42**), dicyanomethylene (**43**) and N-cyanoimine (**44**) functionalized anthraquinone
 307 derivative.

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].



313
314 **Fig. 10.** Anthraquinone having thiophene terminated groups 45-48.
315

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



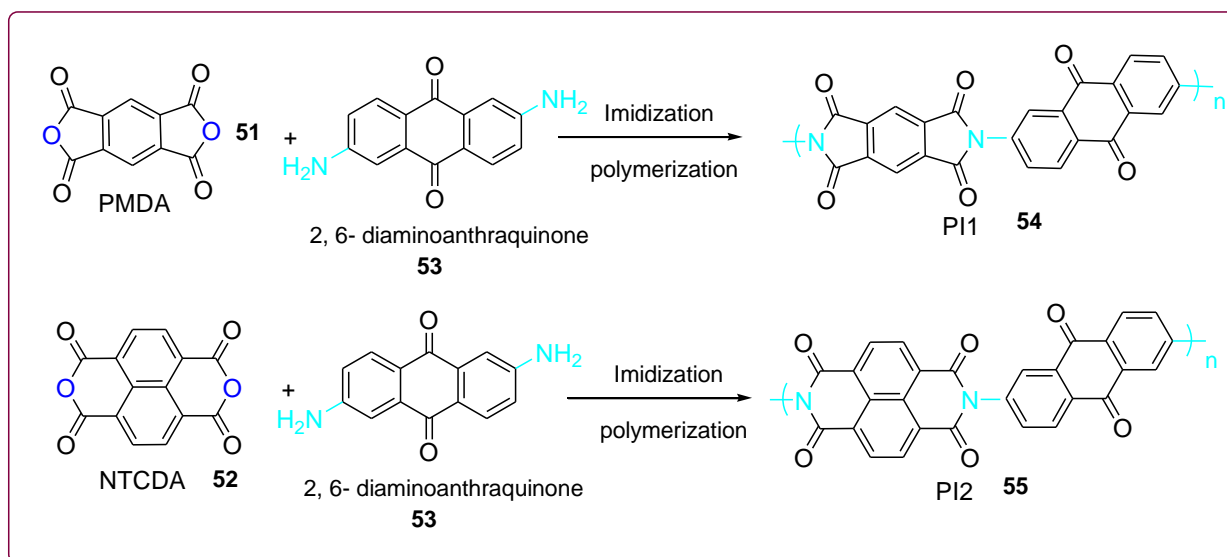
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325

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

326

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



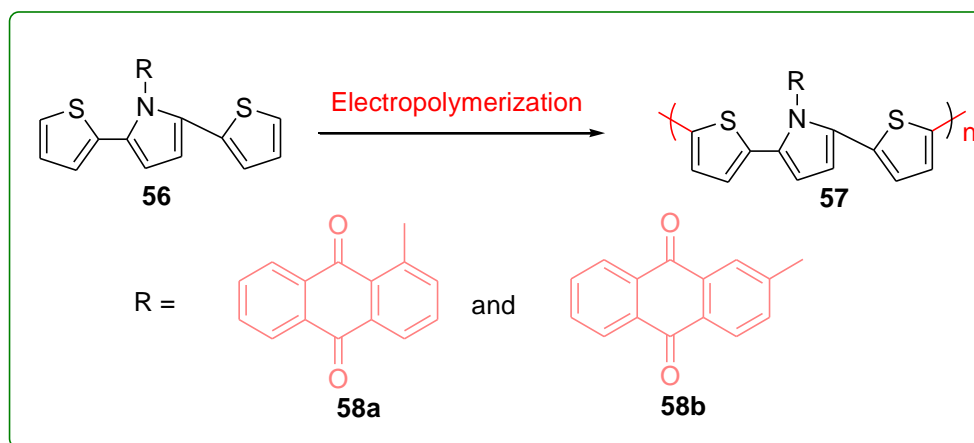
332

333

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

334

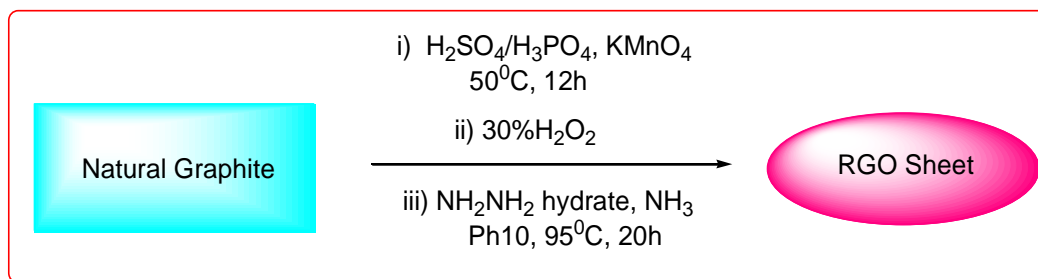
335 Wang *et al.* (2010) [35] came out with a hybrid material having five membered cyclic rings with
336 central pyrrole ring from where the anthraquinone attached and produce SNS-1AQ and SNS-2AQ
337 (**56-57**). After the synthesis and electro polymerization of these moieties, they got polymer films.
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.



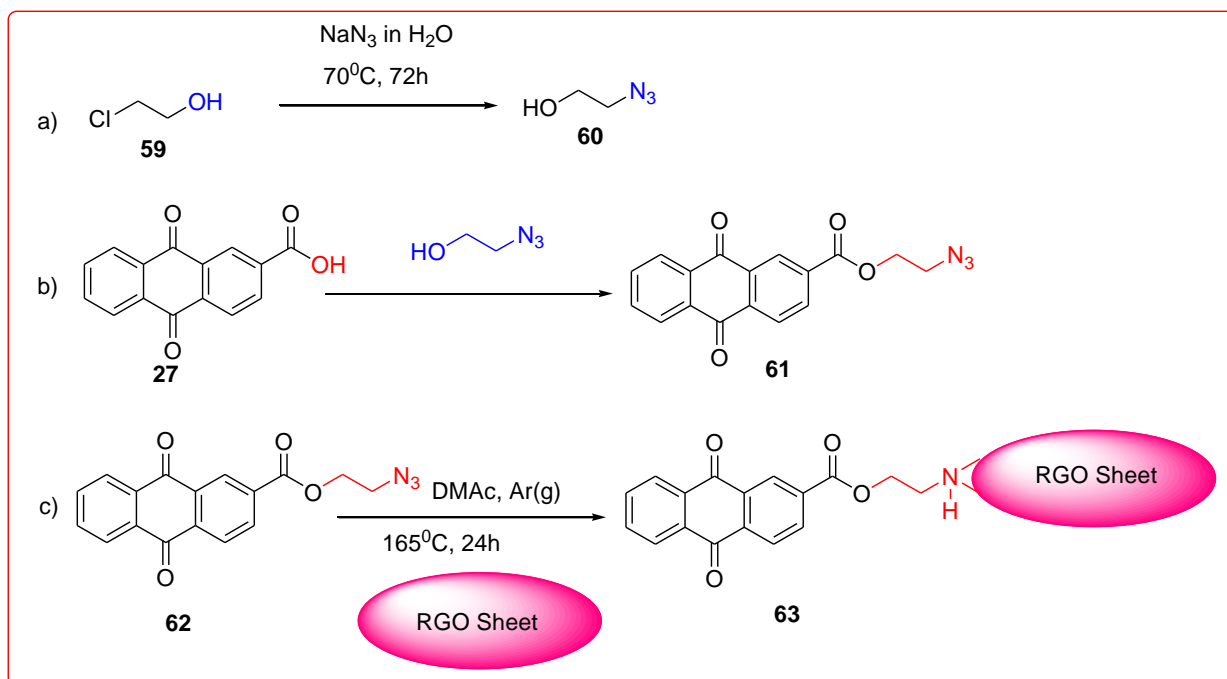
341
342 **Fig. 13.** Composite of polymer films with SNS-1AQ (**57-58a**) and SNS-2AQ (**57-58b**) moieties.

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



351

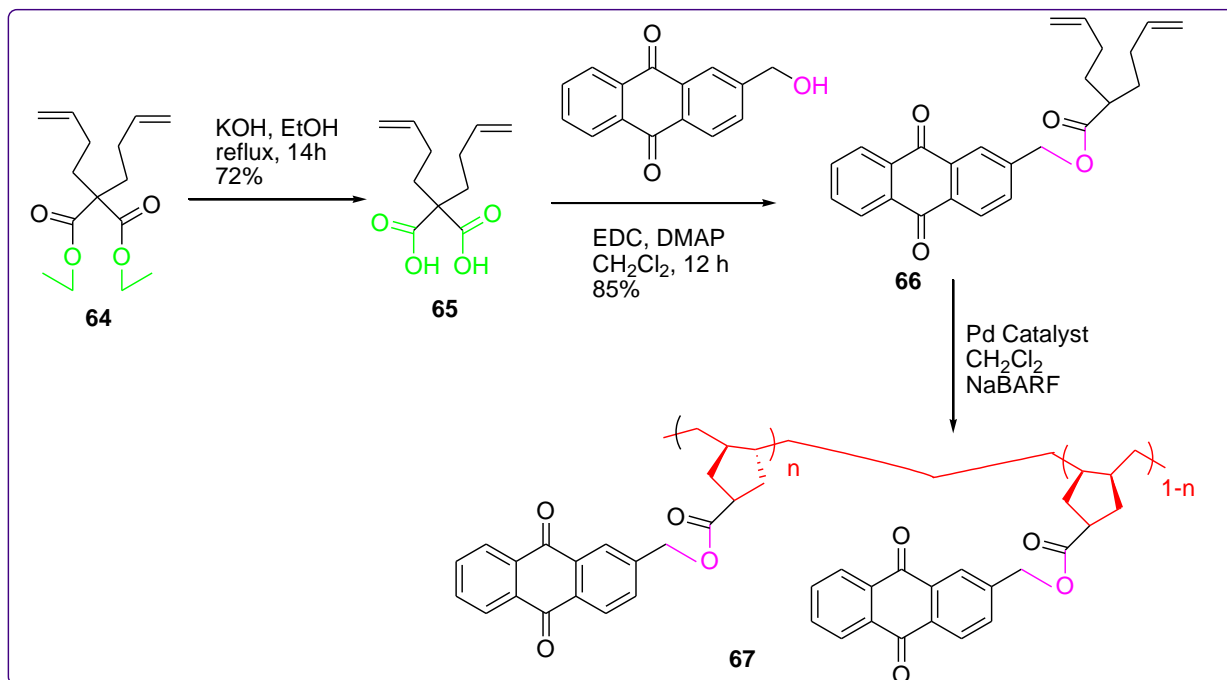


352
353

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].



359

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

361

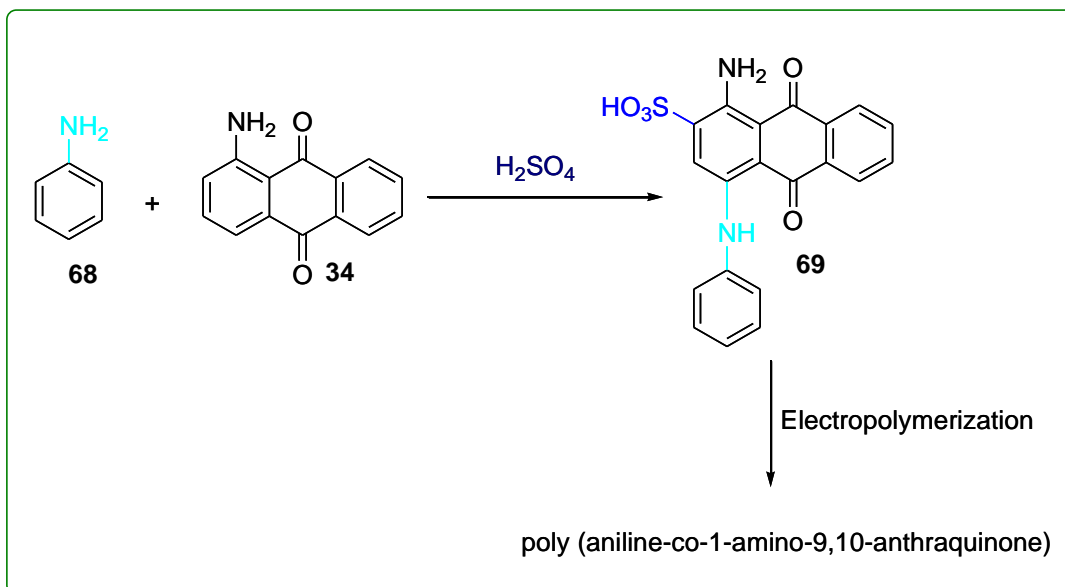
362 Palaniappan and Manisankar [74] examined the effect of using copolymers rather than simple

363 carbonyl polymers on sensing and electrocatalytic applications. They worked with aniline (**68**) and

364 amino anthraquinone (**34**) in single step reaction and electropolymerized the product (Fig. 16). The

365 result of this analysis permits the preparation of the copolymer having a maximum conductivity

366 and stability up to pH 7 useful for fuel cell application.



367
368 **Fig. 16.** The reaction of aniline with amino anthraquinone (68, 34 and 69).
369

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

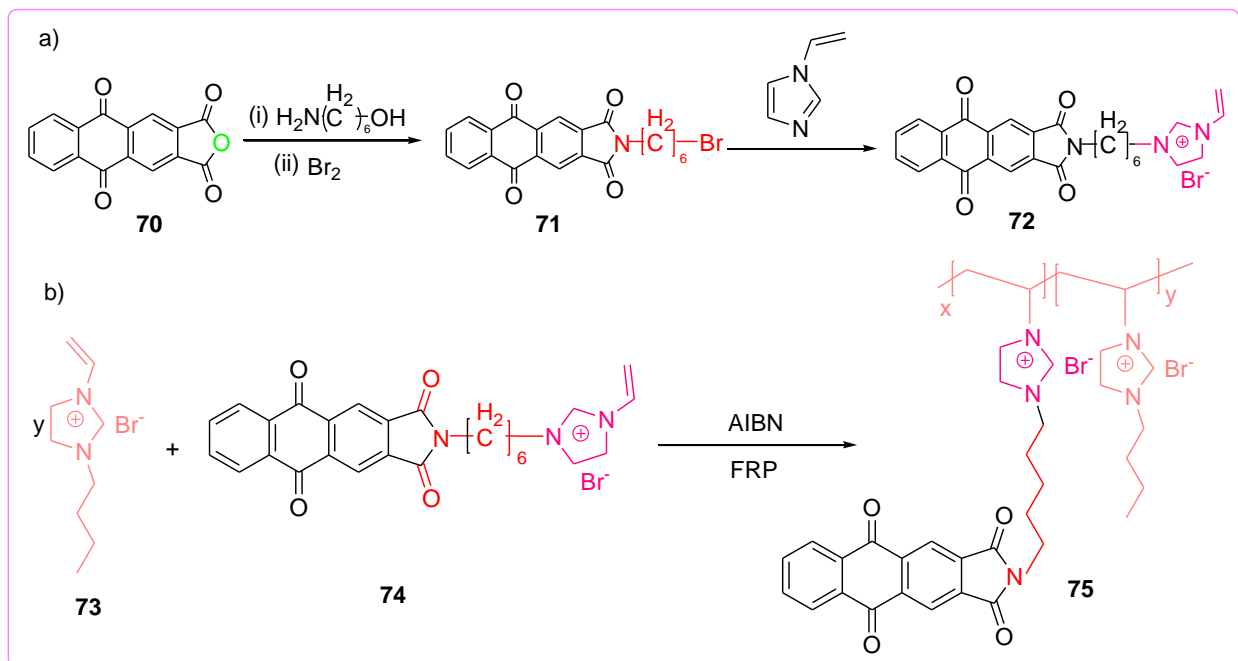


Fig. 17. Homo and copolymerized derivative of anthraquinone (70-75).

375

376

377

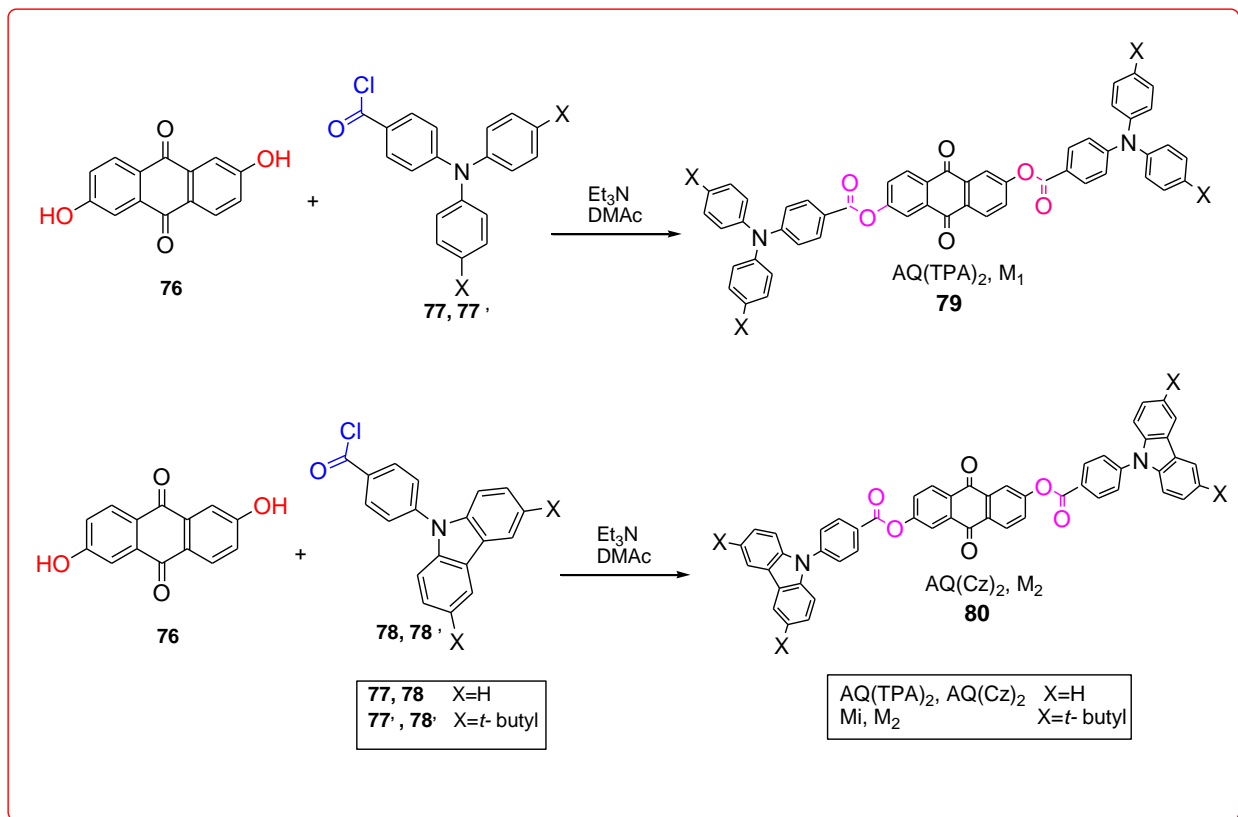
378 The anthraquinone as a central core with carbazole or triphenylamine side groups having two ester

379 linkage was synthesized Fig. 18. The electrochemically generated polymer films of the

380 triphenylamine (TPA), biscarbazole unit and anthraquinone shows two reversible oxidation redox

381 couples and two quasi-reversible one-electron reductions respectively and exhibits strong colour

382 changes upon electro-reduction / oxidation [76].



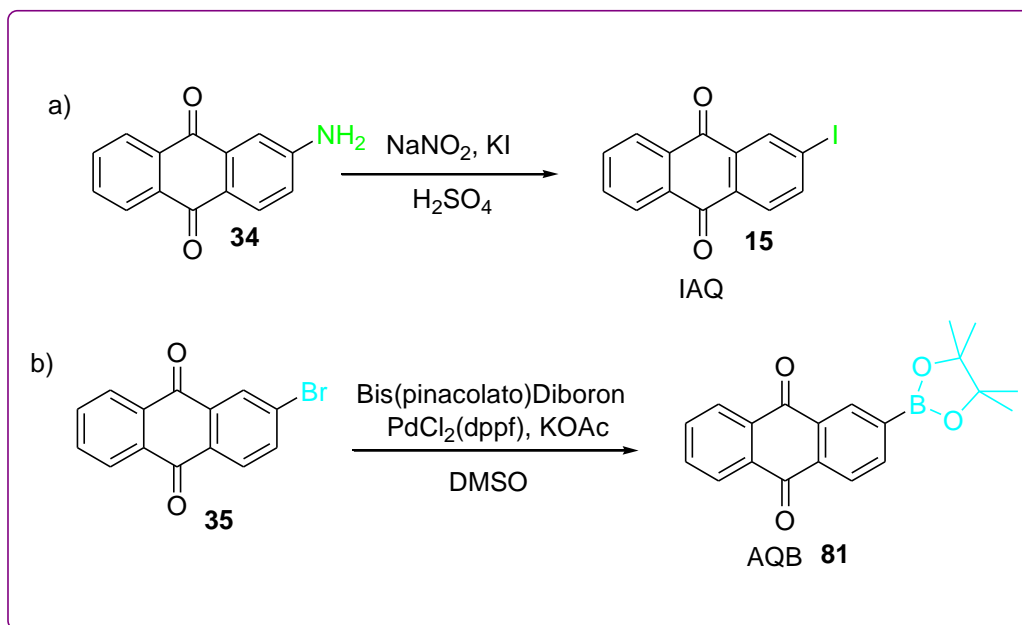
383
 384 **Fig. 18.** General reaction of 2, 6-hydroxyanthraquinone (**76**) with carbazole (**78**) or triphenylamine (**77**)
 385 groups.

386

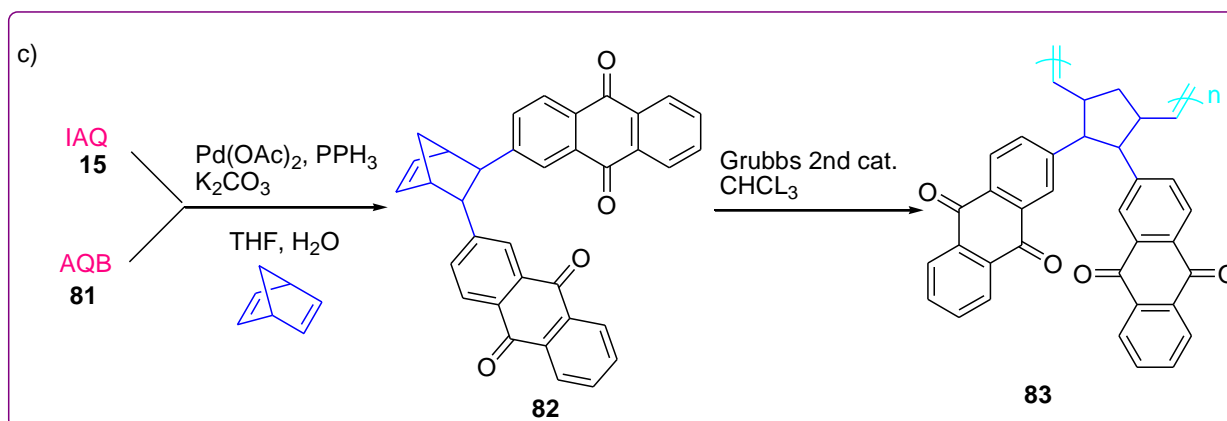
387 However, some researcher reconnoitred the high molecular weight redox active poly
 388 (dianthraquinone -substituted norbornene **83**), synthesized according to Fig. 19, working as an
 389 anode for high-power organic batteries. Due to the incorporation of nor-bornene the two sites of
 390 AQ indicate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

392

393



394

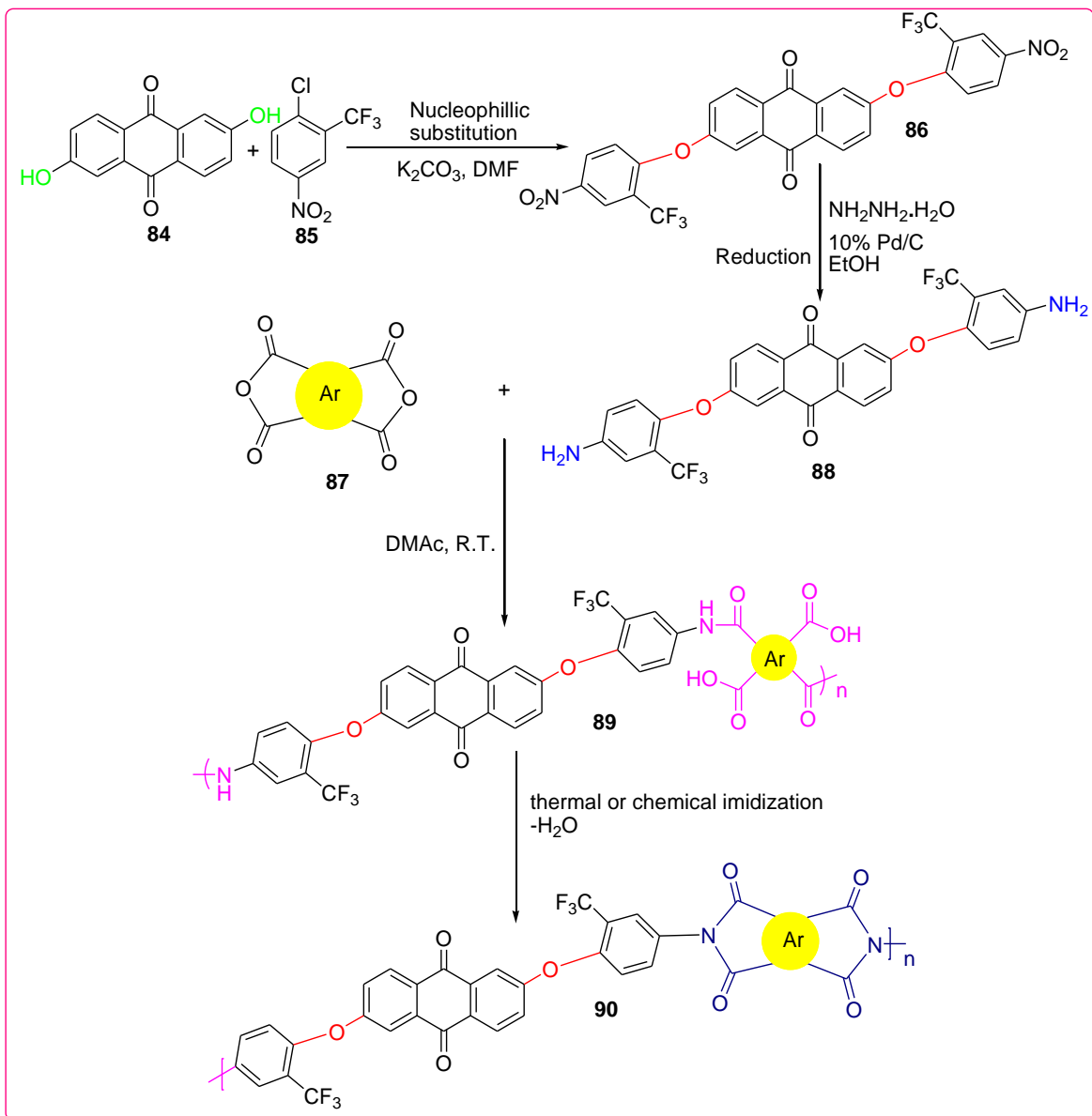


395

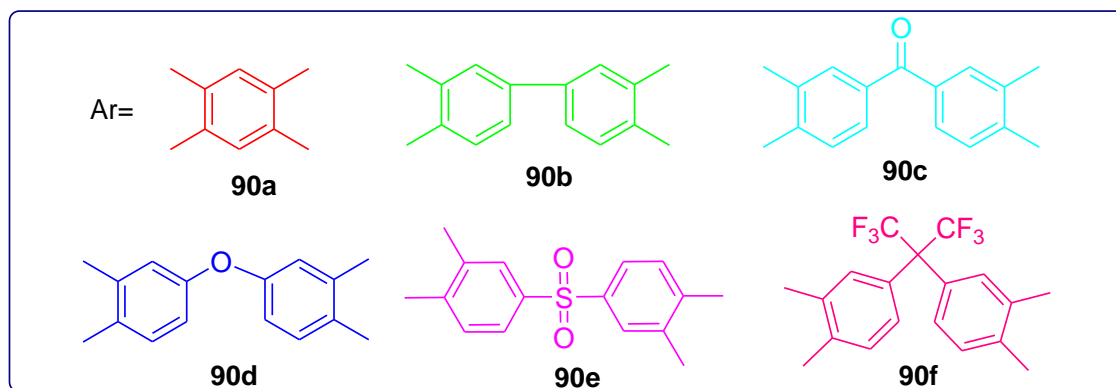
396 **Fig. 19.** Synthesis of high molecular weight norbornene substituted anthraquinone (**34**, **15**, **35** and **81-83**).

397

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



402



403

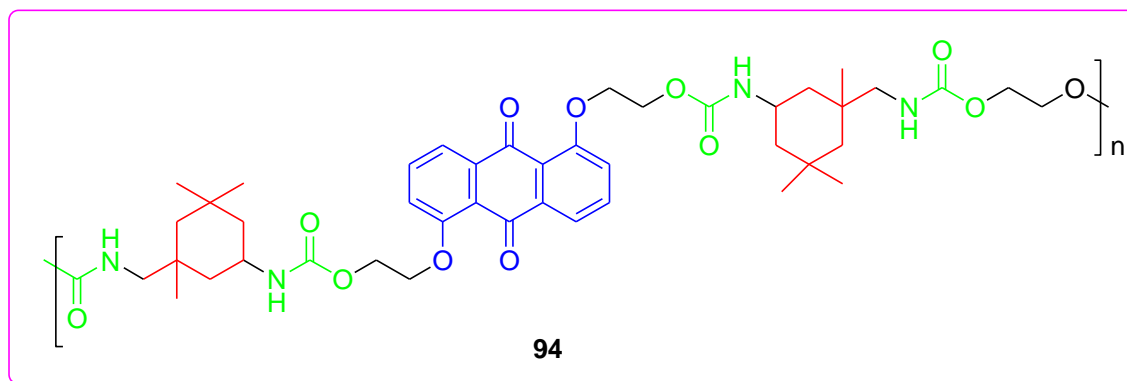
404

405

Fig. 20. Diagrammatic representation to the formation of CF₃ substituted anthraquinone incorporated polyetherimide (84-90).

406

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



411

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

413

414 **5 Electrochemical applications**


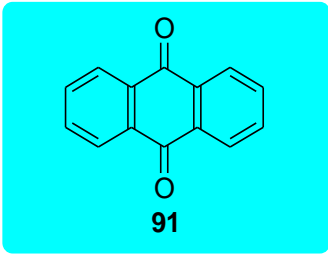
415 Due to the dissolution of an electrode made up of monomeric anthraquinone **91-93** [80-82] in the
416 electrolyte, chemists polymerize anthraquinone derivative to solve this problem. Polymerization
417 of varying degree in active material not only solve the solubility issues but also increases cell life,
418 stability and capacity [83-85]. In literature, we found many examples of monomers and polymers
419 containing anthraquinone, some of them are given in Table 1. Poly-1,4 anthraquinone **2** [55] shows
420 a significantly enhanced capacity of 260 mAhg^{-1} and long lifetime up to 100 cycles. While in
421 comparison to **2**, polyanthraquinone sulphide **6** [57] cannot be able to provide a better cyclability
422 in Mg ion batteries and face the capacity fading issues. Although, by the incorporation of the
423 polymerizable vinyl group with anthraquinone **18** [34] resolves the issue of capacity fading and

424 have a long lasting life time up to 300 cycles. While the substitution of exTTF moiety instead of
425 the carbonyl group in AQ **49** [69] gives a stable system even up to 1000 cycles and reasonable
426 capacity of 105 mAhg⁻¹.

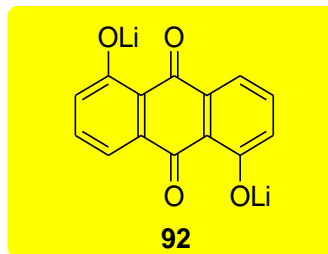
427
428 Recently a new system generated by the incorporated redox active counter ions i.e. anthraquinone
429 and nitroxide into the poly (ionic liquids) **24**, enhances the utilization of these materials as redox
430 active material in various energy storage technologies. This system **24** [65] gives a stable lifecycle
431 and good capacity. Although, cyclic voltammetry of **55** [71] revealed that this polyimide (PI2) as
432 a cathode active material for sodium secondary batteries endure a reversible four-electron transfer
433 because of cycle stability and good capacity. While the data of poly-dianthraquinone substituted
434 norbornene **83** [77] illustrates the swift electron self-exchange reaction, a high redox capacity and
435 stable cyclability up to 500 cycles which is due to the incorporation of nor-bronene and the two
436 redox active sites (i.e. AQ) per repeating unit.

437

438 **Table 1.** Comparison between the electrochemical properties of anthraquinone derivative.

Entry	Category	Structural formula	Capacity (mAhg ⁻¹)	Life- time (Cycle)	Current (C)
1			212	50	0.1C

2

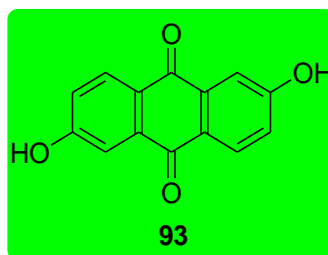


120

50

0.1C

3

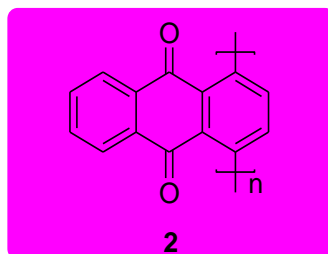


100

100

0.1C

4

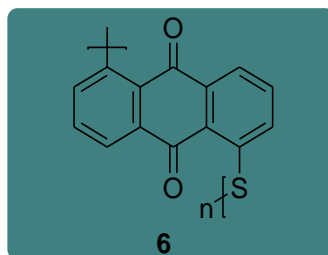


260

100

0.2C

5

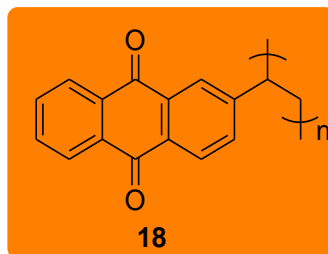


30

100

0.5C

6

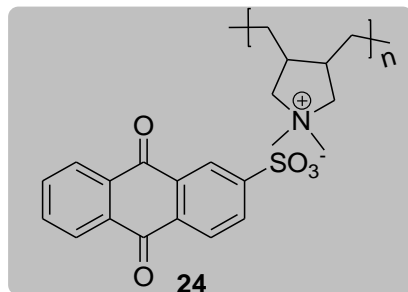


>200

300

15C

7

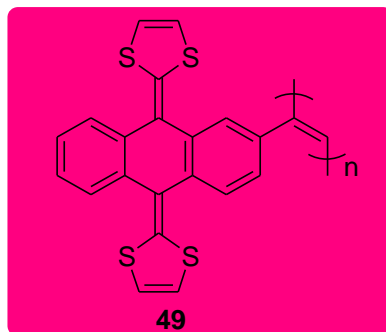


130

100

1C

8

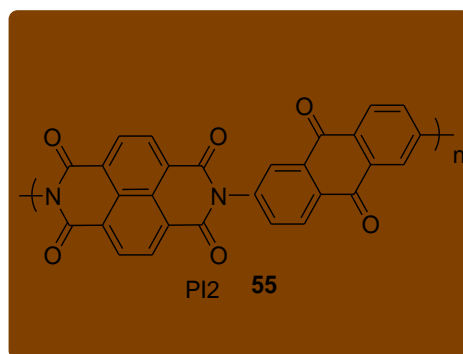


105

1000

120C

9

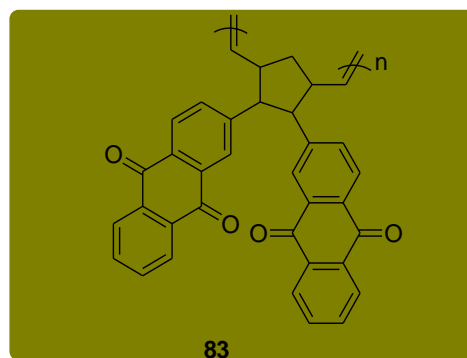


192

150

3.2C

10



212

500

1.2C

439

440 **6 Future prospective**

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

453 **7 Conclusions**

454 Among quinone, anthraquinone is the most promising compound due to its eco-friendly nature,
455 process ability, sustainability, high electrochemical application and flexibility in term of its use as
456 an anode as well as a cathode. Owing to its important features, great concern on its synthesis and
457 potent applications brought it in front of scientific research. The structural and electrochemical
458 behaviour of AQ shows reversible two-electron redox system. Having high cycle reversibility and
459 unotoxicity, several synthetic approaches are developed either by converting anthraquinone to
460 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

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