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Novel Polyaromatic Quinone Imines[1]

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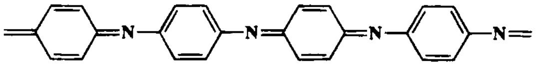
ABSTRACT: A novel synthetic route to poly(quinone imines) has been developed. Reaction of anthraquinone (AQ) with aromatic diamines in the presence of titanium tetrachloride and 1,4-diazabicyclo[2.2.2]octane (Dabco) as base in refluxing chloro- or *o*-dichlorobenzene led to high molecular weight polymers with the poly(quinone diimine) structure. Polymerization of AQ with methylene-4,4′-dianiline resulted in a mixture of high molecular weight polymer (M_w 15 000) and oligomeric macrocycles. The polymerization of AQ was also accomplished with 4,4′-oxy- and 4,4′-thiodianiline, as well as with *p*-phenylenediamine. The latter polymer is the dibenzo analog of the pernigraniline base form of polyaniline. *tert*-Butylanthraquinone was also successfully used as a comonomer with the various aromatic diamines. All these polymers are red in color, soluble in organic solvents, and film-forming. Polymerizations of the aromatic diamines with heterocyclic-substituted benzoquinones, such has benzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-dione, 2,2′-dialkylbenzo[1,2-*d*:5,4-*d*′]dioxazole-4,8-dione, and *N,N*′,2,2′-tetraalkylbenzo[1,2-*d*:5,4-*d*′]imidazole-4,8-dione, were also investigated.

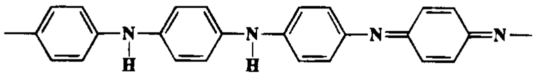
Introduction

Polyaniline, prepared by chemical or electrochemical oxidation of aniline, possesses in part a polyaromatic quinone imine structure. Its remarkable electrical, electrooptical, and tensile properties have drawn attention to the importance of this type of polymer structure.[2] There are three reported forms of polyaniline which differ in oxidation state. The pernigraniline base (PNB) is the fully oxidized form, the leucoemeraldine base (LB) is the fully reduced form, and the 1:1 copolymer of the previous two oxidation states is the emeraldine base (EB). The conducting form is the salt of the EB form of polyaniline.

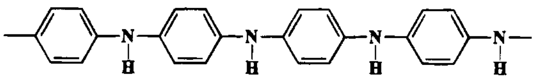
Significant advances have been made recently to improve the oxidative synthesis of polyanilines, but it is still limited as to monomer structures and functionalities.[3] One recent example of a small structural variation is the oxidative polymerization of 1-aminonaphthalene to form a derivative of the EB form of polyaniline, which might be considered a monobenzo analog of polyaniline.[4] However, substituted anilines generally polymerize less successfully than aniline itself. A different approach was taken by Jenekhe et al.,[5] who describe the synthesis and properties of poly(4,4′-diphenylamine methylenes) which are polyaniline derivatives in which one nitrogen atom out of two is substituted by a carbon atom.



pernigraniline base PNB



emeraldine base EB



leucoemeraldine base LB

A *polycondensation* route to polyanilines would be a desirable synthetic alternative in order to allow a wider variety of monomers to participate and also to give a cleaner, better-defined polymer than the nondiscriminating oxidative polymerization. An important step in this direction was described by Wudl and co-workers.[6] The condensation polymerization of 1,4-cyclohexanedione-2,5-dicarboxylic acid and an aromatic diamine was followed by a pyrolitic decarboxylation and partial dehydrogenation to yield the emeraldine form of polyaniline. The obtained polymer was identical to poly-

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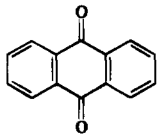
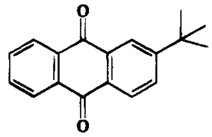
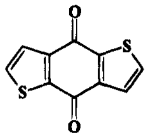
aniline made by the oxidative route, but this path was only used to synthesize the unsubstituted polyanilines.

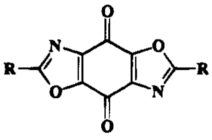
The most direct polycondensation route to polyaniline would be to prepare a polymer with the aromatic quinone imine backbone, as found in the PNB form, from a quinone and a diamine and eventually reduce this polymer to the conducting EB form. Initial investigations determined that the polymer could not be prepared from the direct condensation of benzoquinone and aromatic diamines. As expected Michael addition was preferred over the desired condensation reaction,[7] in contradiction to an earlier report.[8] Our attempts to proceed from 1,4-cyclohexanedione were thwarted by the facile aldol condensations of this carbonyl compound.

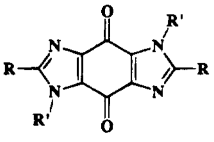
To prevent the undesirable Michael addition, substituted quinones that cannot undergo this side reaction were used. The chosen quinones have two fused aromatic rings attached to the benzoquinone moiety, such as anthraquinone (AQ), *tert*-butylanthraquinone (tBuAQ), benzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-dione (bisthiophenobenzoquinone, SQ), 2,2′-dialkylbenzo[1,2-*d*:5,4-*d*′]dioxazole-4,8-dione (bis(oxazolo)benzoquinone, BOBQ), and *N*,*N*′,2,2′-tetraalkylbenzo[1,2-*d*:5,4-*d*′]imidazole-4,8-dione (bis(imidazolo)benzoquinone, BIBQ).


AQ


tBuAQ


SQ


BOBQ


BIBQ

Our earlier investigation into the formation of aromatic quinone imines had involved the reaction of AQ and aromatic diamines in poly(phosphoric acid) (PPA).[9] This led to black polymers which did possess the polyaromatic quinone imine structure according to IR spectroscopy and elemental analysis. However, these polymers were intractable and insoluble. Upon doping with either iodine or hydrochloric acid, they did not display significant electrical conductivities. We also attempted to use the chemistry developed by Froyen and co-workers which utilizes a *N*-Wittig reaction between *N*-phenyltriphenylarsinimine and benzoquinone.[10] The Froyen method, discussed in the following paper, failed to produce the model compounds in the quantitative yields and therefore could not be used for a successful condensation polymerization.[11]

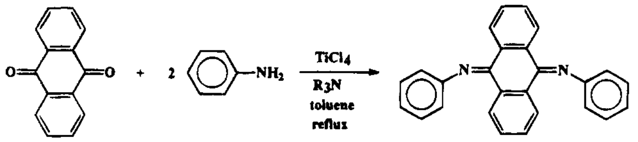
This paper presents a clean synthesis of soluble, tractable, moderately high molecular weight poly(arylquinone imines) via the condensation reaction between aromatic diamines and polyaromatic quinones in the presence of titanium tetrachloride and 1,4-diazabicyclo[2.2.2]octane (Dabco). The synthesis was optimized by systematically varying the factors in the preparation of the model compound, *N*,*N*′-diphenylanthraquinone diimine, from AQ and 2 equiv of aniline using $TiCl_4$ and various tertiary amines and solvents.

Results and Discussion

Optimization of Imine Formation. The synthesis of the model compound was used for the optimization and detailed study of the imine-forming reaction. The initial synthetic strategy for this synthesis was to react anthraquinone and 2 equiv of aniline in the presence of titanium tetrachloride and a tertiary amine, namely, triethylamine. Several parasubstituted anilines were reacted in these conditions with anthraquinone, but no quantitative yields were obtained. Therefore, we investigated several variations of this strategy to prepare the model compound in the quantitative yield necessary for the preparation of the corresponding polymer via a condensation polymerization.

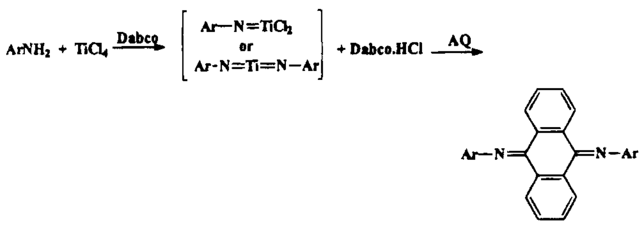
Table 1. Order of Addition Study for the Model Compound Reaction

reactant	order of addition					
aniline	1	1	1	2	3	4
triethylamine	2	4	4	3	4	1
titanium tetrachloride	3	3	2	4	1	2
anthraquinone	4	2	3	1	2	3
% yield	99	92	84	82	81	69



A first optimization process using AQ and unsubstituted aniline determined that the yield increased significantly if a 50% excess of $TiCl_4$ was used. A larger excess of $TiCl_4$ did not lead to any further increases in model compound yield. The yield was then further optimized with an order of addition study of the four reactants using the statistical approach of Carlson and co-workers.[12] As shown in Table 1, the optimum order of addition was determined to be aniline and triethylamine first, next $TiCl_4$, and AQ last.

The fact that optimum yields were obtained when titanium tetrachloride and aniline were mixed before the addition of the anthraquinone indicates that a titanium/aniline species is a reactive intermediate in this synthesis. The lowest yields were obtained when $TiCl_4$ and AQ were mixed before the addition of the amines. Therefore, $TiCl_4$ is not functioning as a classical Lewis acid catalyst which would coordinate with the carbonyl oxygen making the carbonyl more susceptible to nucleophilic attack by the amine. During the course of our study, Carlson and co-workers also applied their statistical order of addition method to an imine synthesis and proposed a similar intermediate.[13]

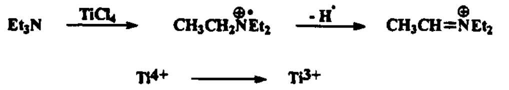


A black tarry byproduct formed in all of the above reactions. This side reaction was not observed when preparing imines from aldehydes and amines.[14] However, Antler and co-workers reported a similarly colored product when studying the reactions between trimethylamine and $TiCl_4$ at room temperature.[15] The black byproduct formed immediately when $TiCl_4$ and triethylamine were mixed which induced us to investigate

Table 2. Effect of Tertiary Amine on Model Compound Reaction

tertiary amine	% yield	tarry byproduct present
N,N-diethylaniline	80	✓
triethylamine	99	✓
ethyldiisopropylamine	89	✓
dimethylhexylamine	99	✓
N-methylpiperidine	99	✓
DBN	86	✓
Dabco	99	
quinuclidine	99	
none	32	

several tertiary amines. Of all the tertiary amines studied (Table 2), two did not form the black byproduct, and quantitative yields of the model compound were still obtained. These were quinuclidine and Dabco.[16] We propose that the reaction between the tertiary amine and titanium tetrachloride is a redox reaction. The amine is oxidized to a cation radical by Ti^{4+}, and an α-hydrogen is lost to stabilize the oxidized amine as the immonium ion. This leads to the decomposition products. The bicyclic bases, Dabco and quinuclidine, cannot lose an α-hydrogen because this would result in a bridgehead olefin in direct violation of Bredt's rule.[17] Of the two amines, Dabco was chosen because it is cheap and easy to purify.

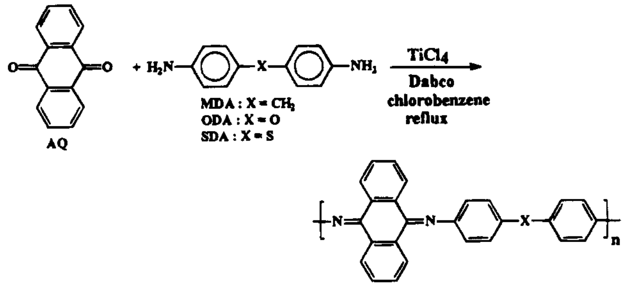


$$Et_3N \xrightarrow{TiCl_4} CH_3CH_2\overset{\oplus\bullet}{N}Et_2 \xrightarrow{-H^{\bullet}} CH_3CH{=}\overset{\oplus}{N}Et_2$$

$$Ti^{4+} \longrightarrow Ti^{3+}$$

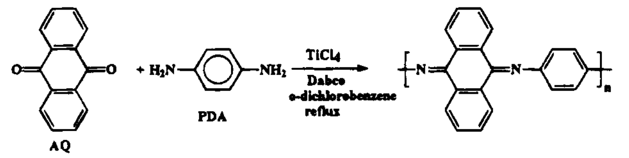
Polymers from Anthraquinone. Previous work from this laboratory indicated that fully conjugated polymers of anthraquinone might be insoluble and intractable materials.[8] Therefore, unconjugated aromatic diamines were first used to obtain more soluble polymers. The increased polymer solubility should allow for easier analysis of the polymers to confirm the predicted backbone structure. The diamines chosen were 4,4′-methylenedianiline (MDA), 4,4′-thiodianiline (SDA), and 4,4′-oxydianiline (ODA).

The attempted polymerization of AQ and MDA in toluene using the optimum technique developed in the model compound study led only to a 51% yield. The polymerization is heterogeneous, with titanium salts, titanium dioxide, Dabco salts, and polymer of significant molecular weight precipitating. By switching to chlorobenzene as solvent, the polymer was prepared in quantitative yield. We postulate that the improved yield is not a function of solvent selectivity but instead is due to the increased reaction temperature, as chlorobenzene has a reflux temperature 21 °C higher than toluene. The higher reaction temperature results in increased solubility and increased reactivity of the monomers and the growing polymer chain ends. The same methodology was used successfully to synthesize polymer with AQ and either SDA or ODA.



The polymers were isolated as red powders, which were soluble in common organic solvents such as chlorobenzene, tetrahydrofuran, and chloroform. The polymers were purified by dissolving the polymer in chloroform and precipitating in hexanes. The precipitated polymers formed transparent red films upon slow evaporation of solvent.

To prepare a formally conjugated polymer, *p*-phenylenediamine (PDA) and AQ were reacted using the same polycondensation procedure in chlorobenzene as solvent. A red powder was isolated in high yield, but only a small fraction of this material possessed high molecular weight. The remainder consisted of low molecular weight oligomers. The polymerization can be improved by changing the solvent to *o*-dichlorobenzene (bp 179 °C). Keeping the reaction at reflux temperature for 1 day allows for the formation of a higher molecular weight polymer from AQ/PDA in which >75% of the polymer is high molecular weight material.



Structure Determination of AQ Polymers. IR, ^1H and ^{13}C NMR, UV–vis, and elemental analysis were used in the structural confirmation of the poly(quinone imines). The imine peak was detected in the IR spectrum at 1619 cm^{-1} just as in the model compound. The end groups of the poly(arylquinone imine), amino and carbonyl, would have characteristic peaks in the IR spectrum at 3300 and 1688 cm^{-1}, respectively. No end-group peaks were detected, indicating that a polymer of significant molecular weight was prepared.

The ^1H and ^{13}C NMR confirmed that the polymer backbone was similar to the model compound since the chemical shifts of the polymer peaks were identical to those of the model compound. However, detailed stereochemical information could not be obtained from the spectra of the polymers due to the complexity of the spectra. The buckled structure of the AQ moiety[8] leads to asymmetry of the whole polymer and gives rise to a number of peaks in the ^{13}C NMR spectrum which could not be individually assigned.

The UV–vis spectra of the anthraquinone polymers exhibit absorption maxima at 410–470 nm, which are shifted higher than the corresponding *N,N*′-diphenylanthraquinone diimine model compound (398 nm). The polymers containing 4,4′-thiodianiline and 4,4′-oxydianiline absorbed at a higher wavelength than the polymer containing 4,4′-methylenedianiline. The extinction coefficients of the model compound and the polymers are of the same order of magnitude, namely, 8.0×10^4 M^{-1} cm^{-1}. These data indicate that the incorporation of the oxo, and especially the thio linkage, in the aromatic diamines results in somewhat increased conjugation. The highest values for λ_{max} were obtained for the formally fully conjugated phenylenediamine polymers (470 nm). The UV spectra were virtually the same if they were measured in solution or in film form. The difference in color between the model compound and the polymers, yellow and red, respectively, is due to the increased conjugation length in the polymer. It could also be due to increased intermolecular association in

Table 3. Molecular Weights of Poly(quinone imines)

		SEC data	
quinone monomer	diamine monomer	% high MW of reaction mixture	M_w of high MW fraction
AQ	MDA	93	14 600
AQ	SDA	69	15 400
AQ	ODA	85	15 400
AQ	PDA	75	24 400
tBuAQ	MDA	39[a]	22 400
tBuAQ	SDA	89[a]	9 700
tBuAQ	ODA	75[a]	16 000
tBuAQ	PDA	62	18 600
SQ	MDA	10	3 000
BIBQ	MDA	65	4 350
BIBQ	PDA	51	2 800

[a] % high molecular weight from the precipitated fraction.

the polymer (see discussion in the following paper[9]), even though the UV spectra recorded on films contradict this supposition.

The λ_{max} for the fully conjugated phenylenediamine polymer is 470 nm, in contrast to the λ_{max} for the poly(pernigraniline base) (540–560 nm).[4] We can only speculate that the added steric hindrance by the anthraquinone units causes the poly(quinone imine) polymer to be less conjugated than the parent polyaniline.

Relative molecular weights were determined by SEC in THF, and the inherent viscosities of the polymers were measured in chloroform. At first the size-exclusion chromatographic analyses of the AQ/MDA polymer were run using chloroform as eluent. However, this gave completely unreasonable results. Very long elution times were observed, up to twice the times recorded for the 600 molecular weight polystyrene standard, while the viscosity data on these same polymers indicated molecular weights over 10 000. The poly(quinone imines) have a special affinity for chloroform. If the polymer has been dissolved in chloroform at any point during the workup, solvent molecules remain entrapped in the polymer as shown by elemental analysis and by X-ray fluorescence (XRF). The use of chloroform as eluent causes the polymer to be retained for very long times on the cross-linked polystyrene columns. The origin of this interaction is unknown but could be due to the presence of traces of HCl in chloroform. This anomalous behavior disappeared completely using THF as eluent.

The results of the molecular weight determinations are listed in Table 3. The SEC analysis of the polymers prepared from AQ and MDA revelaed that the sample was mostly high polymer with MW ~ 15 000. The remainder was a series of distinct low molecular weight components. The high and low molecular weight materials could be separated chromatographically or by precipitating the polymer into hexanes, the oligomers remaining soluble in hexanes. No end groups were detected in the high molecular weight fraction, consistent with the low concentration of end groups. However, the lack of end groups in the low molecular weight fraction was unexpected. It was impossible to fractionate these low MW products into individual oligomers. Oligomeric macrocyclic structures would explain the lack of end groups. Fast atom bombardment mass spectrometry (FAB-MS) analysis of the oligomers indeed confirmed that the low molecular weight fraction was a mixture of macrocycles where $n = 1-4$ as shown in Figure 1. The relative amount of each macrocycle could be determined by SEC analysis using a UV detector: dimer 59%, trimer 27%, tetramer 12%, and pentamer 2%.

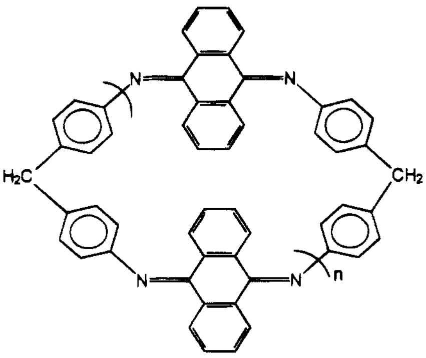


Figure 1. Structure of the macrocycles ($n = 1-4$).

Similar results were obtained for the copolymers of AQ and SDA or ODA. The oligomers were also detected in the SEC chromatogram, but no attempts were made to analyze these compounds. The conjugated poly(quinone diimine) prepared from AQ and PDA in refluxing *o*-dichlorobenzene had high molecular weights, up to 25 000, with no oligomeric species detected. The polymers of tBuAQ were also analyzed and high molecular weights were recorded. The presence of oligomers was not investigated for these polymerizations.

In our earlier work we used poly(phosphoric acid) (PPA) as the dehydrating agent in the polycondensation reaction.[8] All those polymers were black, in sharp contrast to the polymers synthesized in this study, which are bright red. Is the different appearance due to the synthesis method or to different polymer structure? The red AQ/MDA polymers were exposed to poly(phosphoric acid) at 250 °C for 1 h, which is similar to the conditions used in the PPA synthesis. Black intractable materials were isolated. Only a few minor shifts were detected when comparing the IR spectra of the original red polymer and the polymer exposed to poly(phosphoric acid). However, no new peaks were detected nor were there any peaks missing. This leads us to believe that only minor decomposition occurs in PPA.

Carbonyl Reactivity. A quinone carbonyl group is less reactive toward nucleophilic attack than an aliphatic carbonyl group, because it is part of a conjugated system. The second carbonyl, the one remaining in the monoimine derivative, could be more or less reactive than the first carbonyl group.

Since the macrocycles in the AQ/MDA system could not be readily separated, an attempt was made to prepare the macrocycles in a stepwise fashion. MDA was reacted with a 10-fold excess of AQ to synthesize a 2:1 AQ/MDA adduct. However, SEC analysis of the reaction mixture revealed that only 55% of the product was the desired 2:1 adduct, while the remaining product had a molecular weight of 3000–4500. The optimum synthetic strategy stipulates that the quinone be added to the system last. Anthraquinone is rather insoluble and probably does not immediately dissolve in hot chlorobenzene. Therefore, it is possible that there is initially excess diamine present in solution, allowing for molecular weight buildup until all of AQ is dissolved.

To verify this theory, AQ was replaced with 2-*tert*-butylanthraquinone. tBuAQ was predissolved in chlorobenzene and rapidly added to the MDA, Dabco, and titanium tetrachloride solution in chlorobenzene at 90 °C. This should eliminate the possibility of excess diamine being present in the system. However, product analysis still revealed the formation of 60% low molecular weight oligomers along with a low yield of the desired 2:1 adduct.

In contrast, the 1:2 AQ/MDA adduct could be prepared in quantitative yield from AQ and excess MDA. SEC analysis revealed that only the desired adduct and the excess MDA remained in the product mixture.

Reaction of 1,5-dichloroanthraquinone with 2 equiv of aniline in standard conditions, $TiCl_4$ and Dabco in chlorobenzene at reflux, led to the diimine in 39% isolated yield. Only diimine and starting material were detected by HPLC analysis. The diimine was purified by preparative column chromatography on silica. However, it partially hydrolyzed on the column, yielding the monoimine. This allowed us to verify the fact that it would have been possible to detect the monooimine by HPLC if it had been present in the original reaction mixture.

All of these data suggest that the second carbonyl is more reactive than the first. A proposed explanation is that when the first imine is formed, and anthraquinone system buckles and moves the second carbonyl out of conjugation. This buckling has been demonstrated in the X-ray structure of the diimine derivative.[8] An "aliphatic" isolated carbonyl is more susceptible to nucleophilic attack by the aromatic amine.

Polymers from Heterocyclic Benzoquinone. One of the goals of this research was to prepare fully conjugated polymers. As illustrated in our earlier work, the anthraquinone ring system does not remain planar upon formation of the diimine.[8] The buckling of the anthraquinone diimine structure is due to excessive steric hindrance between the *peri*-hydrogens of anthraquinone and the *N*-phenyl rings. As shown in the following paper[9] by X-ray crystal structure analysis of model compounds, replacing the phenyl rings on anthraquinone with heterocyclic five-membered rings reduces this steric hindrance, allowing the central ring structure to remain flat. However, the *N*-phenyl substituent is always rotated out of the plane of the central ring system to preserve the conjugation of the phenyl group with the lone pair on nitrogen. In this work the following heterocyclic quinones were used: bisthiophenobenzoquinone (SQ), bis(oxazolo)benzoquinone (BOBQ), and *N*-alkylated bis(imidazolo)benzoquinone (BIBQ).

A polymer was prepared from SQ and MDA utilizing the optimized polymer synthesis in chlorobenzene. The polymer precipitated out during the polymerization solution and could not be separated from TiO_2 due to its insolubility in organic solvents. A 19% yield of low molecular weight oligomer was isolated. These oligomers were an orange powder which exhibited the characteristic imine peak at 1597 cm^{-1} and the carbonyl and amino end-group peaks at 1643 and 3300 cm^{-1}, respectively. The same results were obtained using *o*-dichlorobenzene as the solvent for this polymerization. The low molecular weights are probably due to the low solubility of this polymer. This low solubility can be ascribed to several factors: the increased planarity of the central quinone moiety, producing a polymer backbone that is more planar than the AQ polymers, and the preference of the *N*-arylimine derivatives of SQ to orient in an anti-conformation as demonstrated by the X-ray structure of the model compound.[9] This would lead to a polymer with a more rigid-rod-like character than the corresponding AQ polymer.

We investigated the possible use of other five-membered heterocyclic-substituted quinones. The model reaction of bis(2-methyloxazolo)benzoquinone with aniline using $TiCl_4$ and Dabco led to the diimine in 95% yield. However, attempted polymerization with PDA led to an insoluble deep-blue material. Only a small fraction of the material could be separated from the TiO_2 by Soxhlet extraction with chloroform over 48 h. IR spectroscopy indicated a strong carbonyl absorption at 1689 cm^{-1} with a comparatively small imine peak at 1609 cm^{-1}.

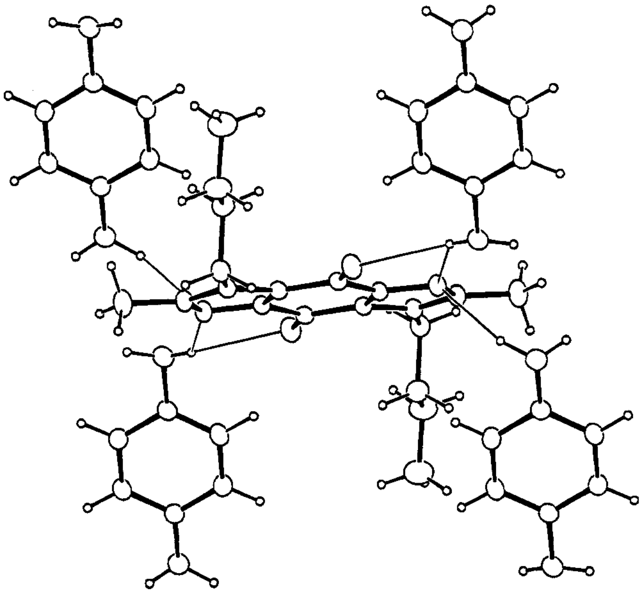


Figure 2. X-ray structure of the BIBQ/PDA complex.

To obtain a more soluble product, bis(2-hexyloxazolo)benzoquinone was synthesized. This monomer is used as a mixture with its methyl-substituted analog. The exact side-chain composition was determined by NMR prior to polymerization (57% hexyl derivative). Reaction of mixed bis(oxazolo)benzoquinone with any of the aromatic diamines again resulted in blue material which was identified as dimers and trimers by SEC. However, the color and the IR indicate a non-imine type product. ^1H NMR cannot be run due to low solubility. The exact nature of these reactions was not further investigated.

Another possible heterocyclic system is the imidazole ring. We chose the N-substituted bis(imidazolo)benzoquinone to avoid side reactions of $TiCl_4$ catalyst with the NH group. Model reactions of bis(*N*-butyl-2-methylimidazolo)benzoquinone (BIBQ) with aniline using $TiCl_4$ and Dabco only met with limited success due to purification problems, but the diimine could be synthesized using excess aniline as base. Polycondenation of BIBQ with the unconjugated aromatic diamines SDA and MDA led to low molecular weight polymers (MW 2500–5000) in high yield (>80%). This relatively low MW could be due to interaction between the imidazole ring and the Ti catalyst or to the insolubility of the formed polymer.

Reaction of BIBQ with PDA in standard conditions led to a dark purple product along with a trace of soluble oligomer. Single-crystal X-ray analysis identified this product as a 1:1 BIBQ/PDA complex (Figure 2). The hydrogen bonds between the aromatic NH_2, and the unsubstituted imidazole nitrogen and the carbonyl groups, form a network. The packing is A–B–A type layers: the A layer is formed by the PDA molecules, while the B layer consists of alternating diagonal BIBQ molecules. Polymerization of this complex was attempted in both refluxing chlorobenzene and in bulk. Neither method was successful in preparing the poly(quinone imine) from this complex due to its high stability. The X-ray structure determination is submitted as supplementary material.

Summary and Conclusions

A practical and reliable synthesis route to poly(quinone diimines) has been developed starting from tricyclic quinones and aromatic diamines. The use of $TiCl_4$ and Dabco has been shown to be crucial for the success of these polymerizations, as has the order of addition. The reaction temperature can be adjusted by the judicious use of high-boiling solvents, with higher reaction temperatures leading to higher molecular weight due to increased solubility of the polymer chain.

The polycondensation of anthraquinone with aromatic diamines yielded high molecular weight poly(quinone diimines). Particularly interesting is the dibenzo analog of fully oxidized polyaniline obtained by reaction of anthraquinone and *p*-phenylenediamine, which is formally conjugated. The polymers have well-defined structures and are red, soluble in common organic solvents, and processable into films. We anticipate all these polymers will have interesting electronic and optoelectronic properties,[5] and these properties will be further investigated.

The presence of cyclic oligomers in the anthraquinone/4,4′-methylenedianiline polymer was proven by mass spectrometry. These macrocycles also form with ODA and SDA but have not been investigated yet. The reaction conditions which favor the formation of these cyclic oligomers will be determined, and the potential complexing properties of these cycles will be studied.

The use of heterocyclic quinones in these polycondensation reactions has not led to any high molecular weight polymers yet. We postulate that the molecular weight buildup is hampered by the insolubility of the obtained polymers, due to the increased planarity of the polymer backbone. The solubility of the polymers can hopefully be increased by using alkyl-substituted aromatic diamines. This work is in progress.

Experimental Section

General Methods. UV−visible spectra were recorded in chloroform, in solution, or in film form on quartz plates using a Hewlett Packard 8452A diode array spectrophotometer. The NMR spectra were recorded at ambient temperature on a Bruker WM-250 NMR. The IR spectra (KBr pellets) were taken on a Perkin-Elmer 983 infrared spectrophotometer. Molecular weights were determined by size-exclusion chromatography using a Beckman 160 UV detector and Phenomenex Phenogel columns (10^3, 500, and 100 Å) in THF at ambient temperature. Chloroform should be avoided as the eluting solvent for these polymers. Molecular weight calculations were based on polystyrene standards. Inherent viscosities were measured at 30 °C, and the sample concentration was 0.10 g/10 mL in chloroform. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Fast atom bombardment mass spectrometry data were recorded on a MAT 311A mass spectrometer in the College of Pharmacy, University of Arizona, Tuscon, AZ. HPLC data were obtained using an Alltech Econosphere Silica 5 μm column and hexane/ethanol 95/5 as eluent and a UV detector at 254 nm.

Chemical Purification. The solvents, toluene, chlorobenzene, and *o*-dichlorobenzene, were dried over calcium hydride and distilled prior to use. Anthraquinone (AQ), 2-*tert*-butylanthraquinone (tBuAQ), and *p*-phenylenediamine (PDA), all from Aldrich, were sublimed prior to use. 4,4′-Methylenedianiline (MDA) and 4,4′-thiodianiline (SDA) were vacuum distilled in a Kugelrohr apparatus at 197 °C/0.8 mmHg and 200 °C/0.35 mmHg, respectively. 4,4′-Oxydianiline (ODA) was recrystallized from water. Aniline was dried over potassium hydroxide and vacuum distilled (68 °C/10 mmHg). Dabco was dried by azeotropical distillation of water with benzene, followed by recrystallization from ether. Titanium tetrachloride and 1,5-dichloroanthraquinone were used as received from Aldrich.

Quinones. Bisthiophenobenzoquinone (SQ),[9,18] bis(2-methyloxazolo)benzoquinone,[19] and bis(*N*-butyl-2-methylimidazolo)benzoquinone (BIBQ)[20] were all prepared according to literature procedures.

Bis(2-hexyloxazolo)benzoquinone was synthesized as a mixture with the 2-methyl derivative. 2,5-Diacetyl-3,6-dihydroxybenzoquinone[18] (3.22 g, 12.5 mmol) was reacted with heptanoic anhydride (25 mL, 0.1 mol) for 1 day at 150 °C. The yellow precipitate was filtered off and washed with ether. Yield: 79%. The obtained product is a mixture of 2-methyl- and 2-hexyl-substituted bis(oxazolo)benzoquinone. NMR ($CDCl_3$): δ 2.92 (t, α-CH_2 in hexyl), 2.66 (s, Me), 1.90 (p, β-CH_2 in hexyl), 1.35 (m, CH_2 in hexyl), 0.85 (t, terminal Me in hexyl). This sample contains 57% hexyl and 43% methyl groups.

Model Compounds. *N,N′*-Diphenylanthraquinone Diimine (DAO). Aniline (0.45 g, 4.8 mmol) and 1.62 g (14.4 mmol) of Dabco were dissolved in 15 mL of toluene while heating to 90 °C. Titanium tetrachloride (0.39 mL, 3.6 mmol) in 5 mL of toluene was added dropwise over 15 min, followed by the addition of 0.50 g (2.4 mmol) of anthraquinone and rinsing the powder addition funnel with 10 mL of toluene. The reaction mixture was heated to reflux overnight. The product was isolated by filtering off the precipitate and removing the solvent in vacuum and was recrystallized from acetone. Yield: 99%. Mp: 195−197 °C. ^1H NMR (DMSOd_6): δ 6.90 (d, 4H), 6.98 (q, 2H), 7.12 (t, 3H), 7.23 (t, 1H), 7.35 (t, 4H), 7.51 (t, 1H), 7.69 (dd, 1H), 8.35 (dd, 2H). ^{13}C NMR ($CDCl_3$): δ 119.2, 119.7 (d, C 2′), 123.7 (d, C 4′), 125.4, 126.9, 127.1, 128.6 (d, C1−8), 128.7 (d, C3′), 129.0 (s, C11−14 asym), 129.3 (s, bridgehead C's sym), 131.9 (s, C11−14 asym), 134.0 (d, C1−8), 136.1, 138.7 (s, bridgehead C's asym), 151.1 (s, C1′), 156.6 (s, C9, C10). The prime numbers refer to the *N*-phenyl substituent. IR: 1619 cm^{-1} (C=N). UV−vis: λ_{max} 398 nm, ϵ 4970 M^{-1} cm^{-1}. These data are in agreement with the data described in a previous paper.[8]

***N,N′*-Bis(*p*-fluorophenyl)anthraquinone Diimine.** The same procedure as for DAQ was used, except triethylamine was used as a base. Yield: 76% (yellow crystals). Mp: 174.5−175 °C. ^1H NMR ($CDCl_3$): δ 8.28 (d, 2H), 7.60 (t, 1H), 7.46 (t, 2H), 7.05 (m, 6H), 6.90 (m, 5H). IR (KBr): 1619 cm^{-1} (C=N). UV−vis: λ_{max} 398 nm. Elem. Anal. Calcd for $C_{26}H_{16}F_2N_2$: C, 79.18; H, 4.09; N, 7.10. Found: C, 79.04; H, 4.03; N, 7.10.

***N,N′*-Bis(*p*-methoxyphenyl)anthraquinone Diimine.** The same procedure as for DAQ was used, except triethylamine was used as a base. Yield: 86% (brick-red crystals). Mp: 179.5−180 °C. ^1H NMR ($CDCl_3$): δ 8.29 (d, 2H), 7.56 (m, 1H), 7.45 (m, 1H), 7.15 (m, 3H), 7.01 (m, 1H), 6.90 (d, 8H), 3.82 (s, 6H). IR (KBr): 1616 cm^{-1} (C=N). UV−vis: λ_{max} 422 nm. Elem. Anal. Calcd for $C_{28}H_{22}N_2O_2$: C, 80.34; H, 5.30; N, 6.69. Found: C, 80.45; H, 5.28; N, 6.71.

***N,N′*-Bis(*p*-nitrophenyl)anthraquinone Diimine.** The same procedure as for DAQ was used, except triethylamine was used as a base. Yield: 46% (brick-red crystals). Mp: 286−287 °C. ^1H NMR ($CDCl_3$): δ 8.28 (d, 5H), 7.41 (s, 4H), 7.21 (s, 1H), 7.15 (d, 1H), 7.01 (d, 5H). IR (KBr): 1639 cm^{-1} (C=N). UV−vis: λ_{max} 390 nm. Elem. Anal. Calcd for $C_{24}H_{16}N_4O_4$: C, 69.64; H, 3.60; N, 12.49. Found: C, 70.41; H, 3.64; N, 12.41.

***N,N′*-Diphenylbisthiophenobenzoquinone Diimine.** The same procedure as for the preparation of DAQ was used, but substituting bisthiophenobenzoquinone for the anthraquinone. Yield: 95%. Mp: 296−298 °C. ^1H NMR (CD_2Cl_2): δ 6.90 (d, 2H), 7.44 (m, 10H), 7.73 (d, 2H). IR: 1597 cm^{-1} (C=N). UV−vis: λ_{max} 424 nm, ϵ 3280 M^{-1} cm^{-1}. Elem. Anal. Calcd for $C_{22}H_{14}N_2S_2$: C, 71.32; H, 3.81; N, 7.56; S, 17.31. Found: C, 71.21; H, 3.77; N, 7.81.

***N,N′*-Diphenylbis(2-methyloxazolo)benzoquinone Diimine.** The same procedure as for the preparation of *N,N′*-diphenylanthraquinone diimine was used, but substituting bis(2-methyloxazolo)benzoquinone for AQ. Yield: 95%. Mp: 253–255 °C. ^{1}H NMR (CDCl$_3$): δ 7.38 (m, 4H), 7.23 (m, 2H), 7.06 (m, 4H), 2.40 (s, main isomer), 2.72, 2.49, 2.13 (s, minor isomers, 6H). ^{13}C NMR (CDCl$_3$) (only the signals for the main isomer, which is symmetrical, are given): δ 14.1, 14.4 (q, CH$_3$), 119.5 (d, C2′), 128.2 (d, C3′) 140.6 (s, C7a, C3a), 141.1 (s, C4a, C6a), 143.0 (s, C2, C5), 150.2, (s, C1′) 164.7 (s, C7, C8). IR (KBr): 1606 cm^{-1}. UV–vis: λ_{max} 456 nm, ε 1950 M^{-1} cm^{-1}. Elem. Anal. Calcd for $C_{22}H_{16}N_4O_2$: C, 71.72; H, 4.37; N, 15.21. Found: C, 71.25; H, 4.32; N, 15.23.

***N,N*′-Diphenylbis(N-butyl-2-methylimidazolo)benzoquinone Diimine.** The standard procedure did not yield pure material due to difficulties in the separation from Dabco/hydrochloride. Better results were obtained by using an 8-fold excess aniline. The filtered reaction mixture was evaporated, and the solid residue was dissolved in methanol. Upon dilution with water the imine precipitates. Yield: 91%. Mp: 230–231 °C. ^{1}H NMR (CDCl$_3$): δ 7.34 (m, 4H), 7.10 (m, 2H), 6.94 (m, 4H), 4.40 (t, 4H), 2.25 (s, 6H), 1.71 (m, 4H), 1.35 (m, 4H), 0.89 (t, 6H). ^{13}C NMR (CDCl$_3$) (only trans isomer detected): δ 13.7, 13.8 (q, 2CH$_3$), 19.9, 32.3, 45.4 (t, 3CH$_2$), 119.5 (d, C2′), 123.0 (d, C3′), 128.2 (d, C4′), 130.8 (s, C2, C5), 134.7 (s, C7a, C4a), 144.9 (s, C3a, C6a), 148.3 (s, C1′), 151.6 (s, C7, C8). IR (KBr): 1599 cm^{-1}. UV–vis: λ_{max} 436 nm, ε 3570 M^{-1} cm^{-1}. Elem. Anal. Calcd for $C_{30}H_{34}N_6$: C, 75.27; H, 7.16; N, 17.56. Found: C, 74.46; H, 6.93; N, 16.87 (2% inorganic residue was not removable on repeated reprecipitations).

2:1 Adduct of Anthraquinone/4,4′-Methylenedianiline. 4,4′-Methylenedianiline (1.21 g, 6.08 mmol) and 4.09 g (36.5 mmol) of Dabco were dissolved in 20 mL of chlorobenzene while heating to 90 °C. Titanium tetrachloride (1.00 mL, 9.12 mmol) dissolved in 5 mL of chlorobenzene was added dropwise over 15 min, and the funnel was rinsed with 5 mL of chlorobenzene. Anthraquinone (5.06 g, 24.3 mmol) was added and the addition funnel rinsed with 30 mL of chlorobenzene. The reaction mixture was heated at reflux overnight. The insoluble materials were filtered off, and the filter cake was washed with hot chlorobenzene. The filtrate was concentrated in vacuo. Yield: 55% by chromatography. ^{1}H NMR (CDCl$_3$): δ 4.03 (s), 6.79 (d), 7.21 (d), 7.32 (m), 7.52 (m), 7.70 (m), 8.30 (m), 8.47 (m). IR (KBr): 1619 (C=N), 1688 (C=O) cm^{-1}.

1:2 Adduct of Anthraquinone/4,4′-Methylenedianiline. 4,4′-Methylenedianiline (0.99 g, 5.0 mmol) and 0.34 g (3.0 mmol) of AQ are dissolved in 10 mL of chlorobenzene while heating to 90 °C. Titanium tetrachloride (0.08 mL, 0.75 mmol) in 5 mL of chlorobenzene was added dropwise over 15 min. The addition funnel was rinsed with 5 mL of chlorobenzene. Anthraquinone (0.10 g, 0.5 mmol) was added and the funnel washed with 5 mL of chlorobenzene. After 4 h at reflux the insoluble material was filtered off and rinsed with hot chlorobenzene. The solvent was removed from the filtrate in vacuo. Yield: 100% by chromatography. ^{1}H NMR (CDCl$_3$): δ 4.03 (s), 7.70 (m), 8.30 (m), 8.47 (m). IR (KBr): 1619 (C=N), 3300 (NH$_2$) cm^{-1}.

***N,N*′-Diphenyl-1,5-dichloroanthraquinone Diimine and *N*-Phenyl-1,5-dichloroanthraquinone Monoimine.** Aniline (0.22 g, 2.4 mmol) is mixed with Dabco (0.81 g, 7.2 mmol) in chlorobenzene, and TiCl$_4$ is added to the reaction mixture. 1,5-Dichloroanthraquinone (0.33 g, 1.2 mmol) is added, and the mixture is heated to reflux for 18 h. The crude reaction mixture is analyzed by HPLC, and only diimine and the starting material are detected. Column chromatography on silica using chloroform as eluent results in three fractions: diimine, monoimine, and starting material 1,5-dichloroanthraquinone, as confirmed by GC–MS analysis.

Diimine. Isolated yield: 38.8%. Mp: 185–188 °C. ^{1}H NMR (CDCl$_3$): δ 8.06 (t, 1H), 7.56 (d, 1H), 7.46 (t, 2H), 7.34 (m, 1H), 7.21 (m, 2H), 7.02 (m, 4H), 6.91 (m, 5H). IR (KBr): 1619 (C=N) cm^{-1}. UV–vis: λ_{max} 372 nm, ε 2350 M^{-1} cm^{-1}. MS: *m/e* 426 (M$^+$, 100%), 391 (M − Cl), 355 (M − Cl, HCl), 207, 178. Elem. Anal. Calcd for $C_{26}H_{16}Cl_2N_2$: C, 73.08; H, 3.77; N, 6.56; Cl, 16.59. Found: C, 70.17; H, 3.87; N, 6.01; Cl, 15.68.

Monoimine. ^{1}H NMR (CDCl$_3$): δ 8.05 (m, 2H), 7.52 (t, 3H), 7.15 (m, 4H), 6.75 (d, 2H). UV–vis: λ_{max} 396 nm, ε 8720 M^{-1} cm^{-1}. MS: *m/e* 351 (M$^+$), 316 (100%, M − Cl), 251, 126, 77.

Polymers. General Polymerization Procedure. Aromatic diamine (2.40 mmol) and 14.40 mmol of Dabco were dissolved in 10 mL of chlorobenzene while heating to 90 °C. Titanium tetrachloride (3.60 mmol) in 5 mL of chlorobenzene was added dropwise over 15 min. The addition funnel was washed with 5 mL of chlorobenzene. The quinone (2.40 mmol) was added to the system via a powder addition funnel, and the funnel was washed with 10 mL of chlorobenzene. After maintaining the reaction at reflux for 24 h, the precipitate was filtered off. Depending on the solubility of the polymer structure, most of the formed polymer will be in solution or in the filter cake. The filter cake was washed repeatedly with hot chlorobenzene until the characteristic red color of the polymers is removed. Chlorobenzene was removed from the filtrate in vacuum, and the product was purified by dissolving it in chloroform and precipitating it in hexanes. Macrocyclic oligomers were isolated from the hexanes fraction. The polymerizations incorporating either *p*-phenylenediamine or bisthiophenobenzoquinone were conducted in refluxing *o*-dichlorobenzene.

Polymerization of 4,4′-Methylenedianiline and Anthraquinone. Yield: 99%. ^{1}H NMR (CDCl$_3$): δ 8.28 (m), 7.55 (m), 7.35 (m), 7.19 (m), 6.87 (m), 2.94 (s). IR: 1619 cm^{-1} (C=N). UV–vis: λ_{max} 410 nm, ε 7300 M^{-1} cm^{-1}. η_{inh} = 0.19 dL/g. Elem. Anal. Calcd for $C_{27}H_{18}N_2$: C, 87.54; H, 4.90; N, 7.56. Found: C, 86.97; H, 5.01; N, 7.03. FAB mass spectrum for macrocyclic oligomers: *m/e* (% relative intensity) 1942 (3, pentamer), 1554 (13, tetramer), 1166 (44, trimer), 777 (100, dimer).

Polymerization of 4,4′-Thiodianiline and Anthraquinone. Yield: 92%. ^{1}H NMR (C$_6$D$_6$): δ 6.43 (m), 6.72 (m), 7.01 (m), 7.30 (m), 8.45 (m). IR: 1619 cm^{-1} (C=N). UV–vis: λ_{max} 424 nm, ε 8000 M^{-1} cm^{-1}. η_{inh} = 0.12 dL/g. Elem. Anal. Calcd for $C_{26}H_{16}N_2S$: C, 80.39; H, 4.15; N, 7.21; S, 8.25. Found: C, 78.81; H, 3.99; N, 7.06; S, 7.75.

Polymerization of 4,4′-Oxydianiline and Anthraquinone. Yield: 64%. ^{1}H NMR (CDCl$_3$): δ 8.35 (t), 7.84 (t), 6.81 (m), 6.68 (m). IR: 1619 cm^{-1} (C=N). UV–vis: λ_{max} 432 nm, ε 11 500 M^{-1} cm^{-1}. η_{inh} = 0.19 dL/g. Elem. Anal. Calcd for $C_{26}H_{16}N_2O$: C, 83.85; H, 4.33; N, 7.52. Found: C, 84.85; H, 5.02; N, 7.57.

Polymerization of *p*-Phenylenediamine and Anthraquinone. Yield: 88%. ^{1}H NMR (CDCl$_3$): δ 7.02 (m), 7.33 (m), 7.55 (m), 8.38 (m). ^{13}C NMR (CDCl$_3$): δ 119.3*, 120.9*, 121.4*, 122.8* (t, C2′), 125.4*, 126.7*, 128.5* (t, C1–8), 128.9 (q, C11–14 asym), 129.4*, 130.4* (t, C1–8), 131.4 (q, C11–14 sym), 131.9 (q, C11–14 asym), 136.0 (q, C11–14 asym), 138.9 (q, C11–14 asym), 147.4 (q, C1′), 156.5* (q, C9, C10) 156.8* (C9, C10) (an asterisk indicates that no assignment to a specific isomer was possible). IR (KBr): 1619 cm^{-1} (C=N). UV–vis: λ_{max} 468 nm, ε 6200 M^{-1} cm^{-1}. Film UV–vis: λ_{max} 474 nm. Elem. Anal. Calcd for $C_{20}H_{12}N_2$: C, 85.69; H, 4.32; N, 9.90. Found: C, 84.74; H, 4.32; N, 9.82.

Polymerization of 4,4′-Methylenedianiline with 2-*tert*-Butylanthraquinone. This polymerization was run using 1.5 mol equiv of TiCl$_4$ in refluxing toluene and triethylamine as the base. Yield: 41%. IR (KBr): 1619 cm^{-1} (C=N). UV–vis: λ_{max} 406 nm. SEC: M_w 22 400. Elem. Anal. Calcd for $C_{31}H_{26}N_2$: C, 87.29; H, 6.14; N, 6.57. Found: C, 86.91; H, 6.04; N, 6.60.

Polymerization of 4,4′-Oxydianiline with 2-*tert*-Butylanthraquinone. This polymerization was run using 1.5 mol equiv of TiCl$_4$ in refluxing toluene and triethylamine as the base. Yield: 44%. IR (KBr): 1619 cm^{-1} (C=N). UV–vis: λ_{max} 418 nm. SEC: M_w 16 000. Elem. Anal. Calcd for $C_{30}H_{24}N_2O$: C, 84.08; H, 5.65; N, 6.54. Found: C, 84.17; H, 5.56; N, 6.19.

Polymerization of 4,4′-Thiodianiline with 2-*tert*-Butylanthraquinone. This polymerization was run using 1.5 mol equiv of TiCl$_4$ in refluxing toluene and triethylamine as the base. Yield: 43%. IR (KBr): 1620 cm^{-1} (C=N). UV–vis: λ_{max} 428 nm. SEC: M_w 9700. Elem. Anal. Calcd for $C_{30}H_{24}N_2S$: C, 81.05; H, 5.44; N, 6.30. Found: C, 80.88; H, 5.44; N, 6.18.

Polymerization of *p*-Phenylenediamine and 2-*tert*-Butylanthraquinone. Yield: 97%. ^{1}H NMR ($CDCl_3$): δ 1.03 (m), 1.09 (m), 1.35 (m), 1.42 (m), 7.01 (m), 7.45 (m), 7.55 (m), 8.38 (m). IR (KBr): 1619 cm^{-1} (C=N). UV−vis: λ_{max} 470 nm, ϵ 1800 M^{-1} cm^{-1}. Elem. Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 83.41; H, 5.90; N, 8.47.

Polymerization of 4,4′-Methylenedianiline and Bisthiophenobenzoquinone. Yield: 19%. ^{1}H NMR (DMSO-d_6): δ 7.6 (m), 7.4 (m), 6.76 (m), 6.45 (m). IR (KBr): 1597 (C=N), 1643 (C=O), 3300 (NH_2) cm^{-1}. UV−vis: λ_{max} 450 nm, ϵ 340 M^{-1} cm^{-1}.

Polymerization of BIBQ with 4,4′-Methylenedianiline. Yield: 65%. ^{1}H NMR ($CDCl_3$): δ 7.15, 6.8 (2 m, 4H, aromatic H), 4.3 (br s, 4H, α-CH_2 in Bu), 4.0 (s, 2H, $ArCH_2Ar$), 2.3 (s, 6H, Me), 1.7, 1.3 (2s, 4H, CH_2CH_2), 0.8 (s, 6H, Me in Bu). IR (KBr): 1657 (w, C=O), 1605 (C=N) cm^{-1}. UV (THF): λ_{max} 454 nm. SEC: M_w 4350; M_n 2160.

Polymerization of BIBQ with 4,4′-Thiodianiline. Yield: 51%. ^{1}H NMR ($CDCl_3$): δ 7.4, 6.9 (2 d, 4H, aromatic H), 4.3 (br s, 4H, α-CH_2 in Bu), 2.1 (s, 6H, Me), 1.7, 1.3 (2s, 4H, CH_2CH_2), 0.8 (s, 6H, Me in Bu). IR (KBr): 1650 (w, C=O), 1605 (C=N) cm^{-1}. UV (THF): λ_{max} 470 nm. SEC: M_w 2800; M_n 1700.

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Supplementary Material Available: Structure of BIBQ and tables of experimental details, positional parameters, displacement coefficients, torsional angles, bond distances and angles, least-squares planes, and dihedral angles between planes and X-ray structures of BIBQ (16 pages). Ordering information is given on any current masthead page.

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