Poly(arylene amine)s from the Reduction of Aromatic Polyimines

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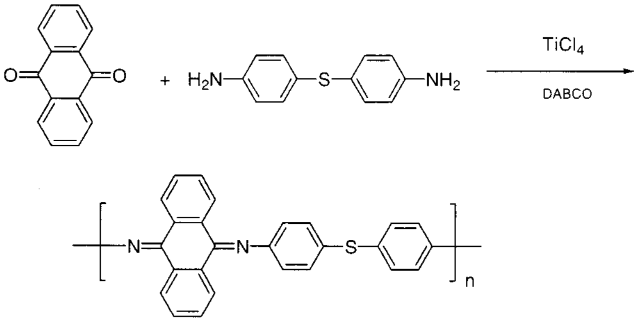
ABSTRACT: Poly(arylene amine)s were prepared from the reduction of aromatic poly(anthraquinone imines), which are readily available from the condensation reaction of arylene diamines and anthraquinones or 2,5-dimethylbenzoquinone. The reduction reaction was studied in detail with model diimines derived from anthraquinones. Simply stirring in hydrazine monohydrate at 70 °C readily reduced a polyimine derived from 2,5-dimethylbenzoquinone. Complete reduction of the polymers derived from anthraquinone or its derivatives was achieved by using hydrazine monohydrate in the presence of a palladium catalyst at 65 °C. These polymers have potential useful properties as photoconductors or antioxidants and extend the series of polyaniline analogues under very controlled structural and synthetic conditions.

Introduction

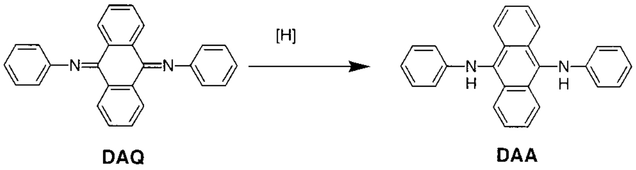
Poly(arylene amine)s have emerged as a class of very important materials because of their applications as electrically conducting materials,[1−4] hole transporting materials,[5,6] and antioxidants.[7−12] The synthesis of poly(quinone imine)s has recently been well established in this laboratory via the condensation of quinones with arylene diamines in the presence of anhydrous $TiCl_4$ and 1,4-diazabicyclo[2.2.2]octane (DABCO).[13−15] The reduction of poly(quinone imine)s would provide an efficient route to a variety of poly(arylene amine)s with different structures possessing potential interesting electronic and antioxidation properties for many applications, because their structure mimics polyaniline.



Herein we report our studies on the reduction of quinone diimine model compounds and poly(quinone imine)s. The reduction of the emeraldine and pernigraniline form of polyaniline itself has been reported in the literature by several authors.[16,17] An initial evaluation of the electric conductivities of poly(quinone imine)s and poly(arylene amine)s was also performed.

Results and Discussion

Reduction of Quinone Diimine Model Compounds. The oxidation/reduction chemistry of *N*,*N*′-diphenylquinone diimine has been thoroughly investigated due to interest in the outstanding antioxidant properties of *N*,*N*′-diphenyl-*p*-phenylenediamine.[18] However, the reduction of anthraquinone diimine and its derivatives is not described in the literature. The model compound *N*,*N*′-diphenylanthraquinone diimine (DAQ)[13] was subjected to varying reduction conditions to investigate which procedure would work best for the corresponding polymers. Catalytic hydrogenation over Pd catalyst at 60 and 30 psi of H_2 was first attempted and led to the correct diamine, but only in 30% yield. The remaining material, characterized by mass spectrometry, IR, and ^{1}H NMR, was a mixture of unreacted starting material and overreduced products. Lowering the pressure led to a significant decrease in the amount of overreduced products but did not produce the desired diamine in an acceptable yield. Thus, hydrogenation was deemed to be an unacceptable method of reduction due to the incomplete reactions and long reaction times.



The use of hydride reducing agents $NaBH_4$ and $LiBH_4$ was then investigated. The reductions were performed in THF under argon. $NaBH_4$ reduction led to the correct product, but only in 5−10% yields after 4 days at reflux. The remaining amount was unreacted starting material. $LiBH_4$ reduction led to a series of products, none of which was the desired diamine.

Hydrazine reduction over Pd catalyst has previously been described in the literature for the reduction of polyaniline.[17] Modifying this procedure gave the desired *N*,*N*′-diphenylanthracene-9,10-diamine (DAA) in excellent yields (∼95%) in a reasonable time (∼2 h). A yellow solid precipitated from the reaction mixture within 30 min of addition of the hydrazine monohydrate. The precipitate was redissolved in hot THF, then isolated, and characterized.

The diimine DAQ possesses a nonplanar central ring system; it is buckled 26° to a butterfly conformation, as shown in the X-ray structure in Figure 1.[19] We postulated that, if the diimine were reduced to DAA, the central ring system would once again become a planar anthracene type system. ^{1}H NMR analysis revealed that

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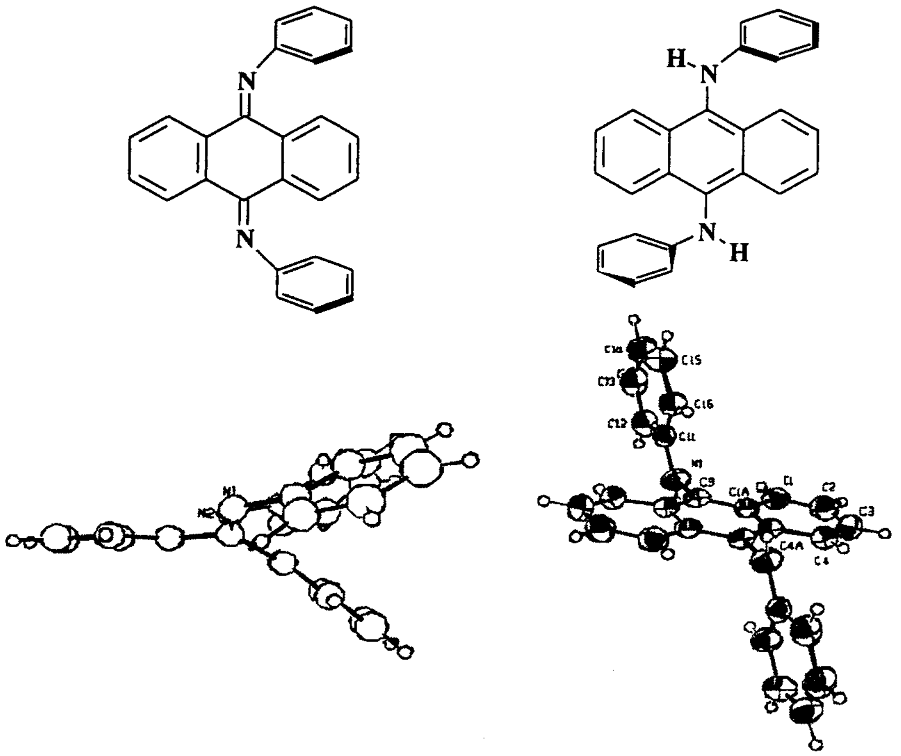


Figure 1. X-ray structures of *N*,*N*′-diphenylanthraquinonediimine and *N*,*N*′-diphenyl-9,10-anthracenediamine.

Table 1. Physical Properties of Model Compounds and Polymers

quinone diamine[a]	mp (°C) diimine	mp (°C) diamine	λ_{max}(UV) (nm) diimine	λ_{max}(UV) (nm) diamine	ϵ (UV) diamine
DAA	195−197	303−308	398	425	6 110
BDAA		242−245		421	
DDAD	236−237	273−275	368	431	10 100
DDEAD	158	245−250	374	438	12 200
DDEEAD	88−92	197−200	370		
DASQ	296−298	262−265	424	368	10 400
polymer **1**			486	357	
polymer **3a**−**4a**			428	430	
polymer **3b**−**4b**			586	545	

[a] *N*,*N*′-Diphenylanthracene-9,10-diamine (DAA); 2-*tert*-butyl-(*N*,*N*′-diphenyl)anthracene-9,10-diamine (BDAA); *N*,*N*′-diphenyl-(1,5-dimethoxyanthracene)-9,10-diamine (DDAD); *N*,*N*′-diphenyl)-1,5-di(2-methoxyethoxy)anthracene-9,10-diamine (DDEAD); *N*,*N*′-diphenyl(1,5-di(2-(2-methoxyethoxy)ethoxy)anthracene)-9,10-diamine (DDEEAD); *N*,*N*′-diphenylbenzo[1,2-*b*:4,5-*b*′]dithiophenene-4,8-diamine (DASQ).

DAA has a very symmetrical structure, suggesting a planar central ring system. X-ray structural analysis (Figure 1) confirmed that the central ring system is planar and fully aromatic with the *N*-phenyl rings rotated syn and out of the plane of the anthracene ring by 78°. DAA exhibits interesting and substantially different physical properties from DAQ. DAA is less soluble, has a higher melting point (306 °C) than the corresponding diimine DAQ, and exhibits a 24 nm bathochromic shift in the absorption spectrum, and a fluorescent emission at 529 nm compared to DAQ, consistent with DAA being an anthracene.

Substituted *N*,*N*′-diphenylanthraquinone diimines and related compounds were reduced in good yields (70−95% isolated yield) by the hydrazine-palladium method to the corresponding diamines. The reduction of these model compounds yielded the following diamines: 2-*tert*-butyl-(*N*,*N*′-diphenyl)anthracene-9,10-diamine (BDAA), *N*,*N*′-diphenyl(1,5-dimethoxyanthracene)-9,10-diamine (DDAD), *N*,*N*′-diphenyl-(1,5-di(2-methoxyethoxy-anthracene)-9,10-diamine (DDEAD), *N*,*N*′-diphenyl-(1,5-di(2-(2-methoxyethoxy)ethoxyanthracene)-9,10-diamine (DDEEAD), and *N*,*N*′-diphenylbenzo[1,2-*b*:4,5-*b*′]dithiophenene-4,8-diamine (DASQ). As shown in Table 1, these compounds exhibited similar physical behavior to DAA, namely increased melting point, bathochromic shift in the absorption spectrum, and reduced solubility compared to the diimine. Anthraquinones substituted with alkoxy groups in the peri position have been shown to give stereoregular diimines for both model compounds and polymers.[14] This was evidenced by a large upfield shift for the alkoxy substituent in the ^{1}H NMR spectrum and confirmed by X-ray crystal structure determination. The ^{1}H NMR spectra for the reduced diamines indicate that the *N*-phenyl rings have rotated out and away from the alkoxy substituents. The alkoxy NMR signals of the reduced diamine shift downfield, i.e., back to normal, indicating that they no longer lie within the *N*-phenyl ring shielding region. This is illustrated in the ^{1}H NMR spectrum of *N*,*N*′-diphenyl-(1,5-di(2-(2-methoxyethoxy)ethoxyanthraquinone diamine (DDEEAD) (Figure 2).

Looking at the data in Table 1, it is obvious that the melting points of all these model compounds increase

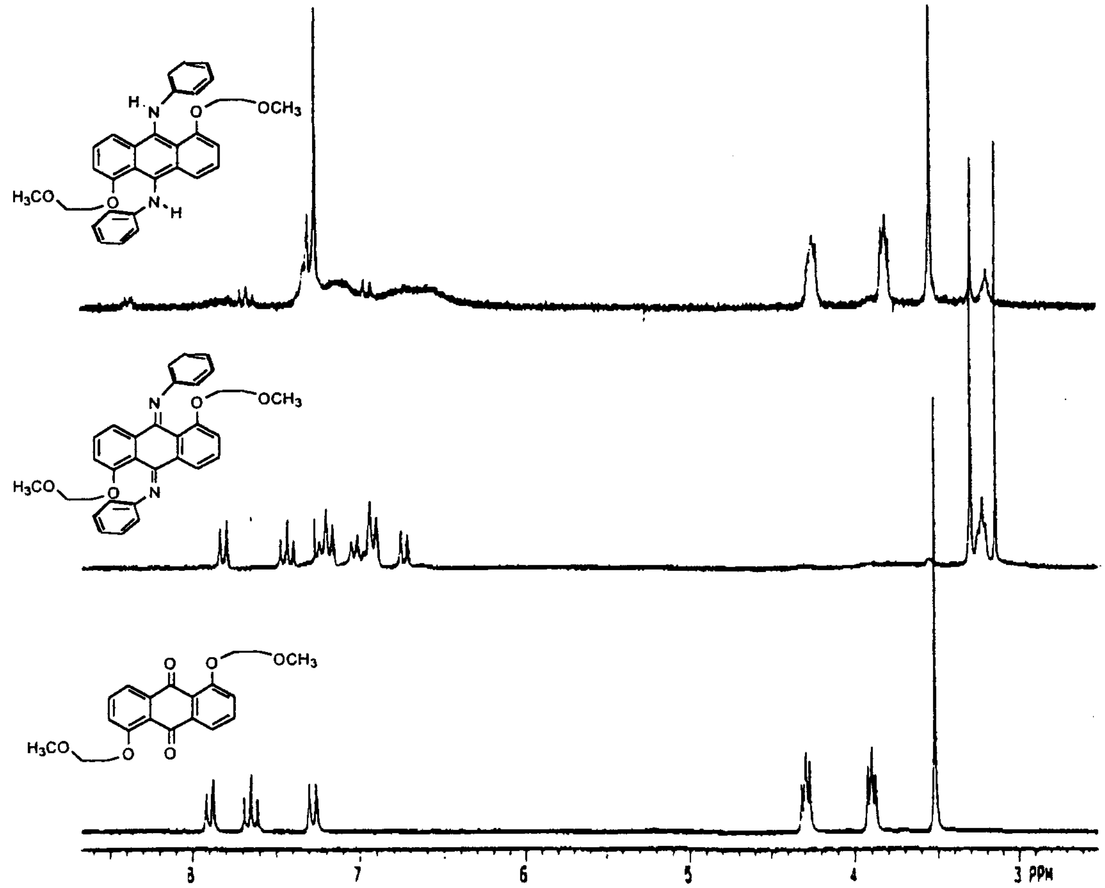


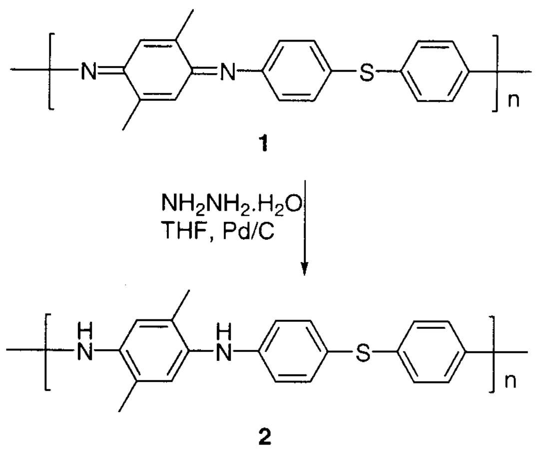
Figure 2. Comparison of ^{1}H NMR spectra of an anthraquinone, its diimine derivative, and its diamine derivative ($CDCl_3$).

upon reduction, except for DASQ. Upon reduction the aromatic system of anthracene is reestablished, the molecule can flatten out, and therefore the melting point increases. The case of the bis(thiophene)benzoquinone diamine (DASQ) is somewhat different because the corresponding diimine is locked in the anti conformation, and the phenyls are "locked" over the sulfur atom; the diimine is therefore pretty rigid and flat except for the *N*-phenyl groups.[21] We propose that the lower melting point in this case is due to the increased flexibility in the diamine.

As far as the UV data for the diimines and diamines are concerned, the λ_{max} increases upon reduction. Interestingly, all the λ_{max} values for the anthracene diamines are in the same range independent of the substitution pattern, namely 435–440 nm. This is because the 9,10-diaminoanthracene system is reestablished. The bis(thiophene)benzoquinone derivatives again have anomalous values, which again can be explained by the more coplanar structure of the diimine compared to the diamine.

Reduction of Poly(quinone imine)s. a. Reduction of a Polybenzoquinone Imine. Polyimine **1** was synthesized from 2,5-dimethylbenzoquinone and 4,4′-thiodianiline in 76% yield.[15] It is an intensely red solid with a weight-average molecular weight of 8900 and a number-average molecular weight of 5000, as determined by GPC. The reduction of this polymer was carried out by two methods, and both of them offered the desired products. First, stirring the solid polyimine in hydrazine monohydrate at 70 °C accomplished the reduction. The intense red color gradually disappeared, and white polymer was formed after 10 h. The reaction mixture was stirred for 24 h to ensure the completion of the reduction. The reduction was much faster in the presence of palladium catalyst. The intense red color disappeared within 2 h, indicating the completion of the reduction.

In the ^{1}H NMR of the polyamine **2** a new peak corresponding to the NH group was observed at 7.44 ppm. The doublet peaks corresponding to the CH in the benzoquinone ring in polyimine **1** changed to a singlet peak and shifted to downfield at 6.98 ppm. The FT-IR spectrum showed a very sharp peak at 3383 cm^{-1}, which is assigned to the NH group. Another characteristic change is that the strong peak at 1580 cm^{-1} corresponding to the C=N group disappeared.

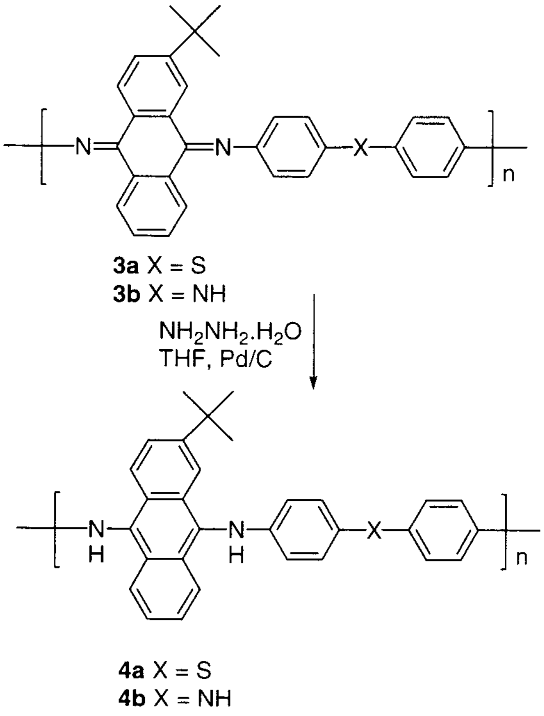


Both polyimine **1** and polyamine **2** are highly soluble in common organic solvents, such as tetrahydrofuran, chloroform, dimethylacetamide, dimethyl sulfoxide, etc. Polyamine **2** has a weight-average molecular weight of 8000 and a number-average molecular weight of 5100 as determined by GPC, which is lower than its precursor's. This could be due to the more flexible chain of the polyamine compared to that of the polyimine.

Polyamine **2** is not stable in air, even at room temperature. By exposure to air, it gradually oxidizes back to its precursor, as indicated by the reappearance of the red color and in analogy to the antioxidant properties of the parent compound *N*,*N′*-diphenyl-*p*-phenylenediamine. The partly oxidized polymer readily turned green in color by exposure to aqueous HCl solution, which is similar to polyaniline.

The almost identical polymer with alternating amine and thioether functionalities has been synthesized by Müllen et al.[20] The monomer synthesis for this polymer involves several steps. In contrast, the present procedure readily led to a variety of thioether and amine hybrid polymers.

b. Reduction of Polyanthraquinonimines. The reduction of polyimines derived from anthraquinones was much more difficult than that of polyimines derived from 2,5-dimethylbenzoquinone. Stirring polyimine **3a** in hydrazine monohydrate at 70 °C for 3 days only offered partially reduced products as evidenced from FT-IR analysis. Complete reduction was obtained in the presence of palladium catalyst and using THF as the solvent after stirring for 24 h at reflux. Unlike polyamine **2**, which is white, polymers **4a**−**b** are still colored, although they are much lighter than their precursors.



Polyamine **4a** showed a peak at 5.9 ppm in its ^{1}H NMR with $CDCl_3$ as the solvent, which corresponds to the secondary aromatic amine. Two singlet peaks, δ 5.75 and 5.31 ppm, appeared in the ^{1}H NMR of polyamine **4b**. This is due to the presence of two types of different NH group. In the FT-IR spectra both polyamines **4a** and **4b** showed a sharp and strong absorptions at 3383 cm^{-1} due to the NH group. The absence of peaks at 1627 cm^{-1} in FT-IR indicated the complete reduction for both polyimines.

In contrast to the model compounds, polyamines **4a** and **4b** had very different solubility from their precursor polyimines. Polyamines **4a** and **4b** were more soluble in tetrahydrofuran and dimethyl sulfoxide, while their precursor polyimines **3a**−**b** were much less soluble in these solvents. Polyimines **3a** and **3b** were very soluble in chloroform, while polyamines **4a** and **4b** were much less soluble in chloroform.

Polyimines **3a** and **3b** resemble rigid-rod polymers more than polyamines **4a** and **4b** in their main chains, as reflected by their apparent molecular weights determined from GPC analysis. The M_w for polymer **3a** was 35 000 and M_n was 14 000. In contrast, M_w for polymer **4a** was 11 000 and M_n was 6900. The same trend was true for polymers **3b** and **4b**. M_w for polymer **3b** was 21 000 and M_n was 11 000. In comparison, M_w for polymer **4b** was 9400 and M_n was 5300.

The UV data for the polymers are also included in Table 1. Polymer **1** is derived from dimethylbenzoquinone, and the ring structure does not buckle upon diimine formation and the backbone is conjugated. The λ_{max} value of the diimine polymer **1** speaks for substantial delocalization along the backbone. Reduction reduces the length of the conjugation and therefore lowers the λ_{max} value. Polymer **3a**, the diimine derived from *tert*-butylanthraquinone and thiodianiline, is more highly conjugated than the corresponding model compound due to the contribution of the sulfur, but the λ_{max} value is indicative of more limited delocalization than in polymer **1**. Upon reduction, the λ_{max} value does not really change and reverts back to the λ_{max} observed for the reduced model compounds, i.e., the anthracene system. The λ_{max} values for polymers **3b** and **4b** derived from *tert*-butylanthraquinone and aminodianiline are extremely high, corresponding to the larger contribution of the nitrogen lone pair to delocalization along the backbone.

Initial Conductivity Measurements. Thin films of polyimines were prepared by spin-coating their chloroform solutions on small pieces of glass. Thin films of polyamines were spin-coated from their THF solutions. All of these films were placed in a desiccator full of dry HCl gas for doping. Instant color changes were observed for polyimine **1a**, which turned green. The red colors of polyimines **3a** and **3b** gradually changed to light green. All of the thin films were nonconductive as evaluated by the four-probe procedure. This is not surprising because it is well-known that polyaniline in its fully reduced form or oxidized form is not conducting.[1,2] All the polymers evaluated so far were either in their fully reduced form or their fully oxidized form.

Conclusion

A convenient reduction procedure, namely hydrazine catalyzed by palladium, has been shown to convert aromatic polyquinonimines into polyarylene amines. These products have been thoroughly characterized by spectroscopic methods. Though not electrically conducting, they may have useful photoconducting and antioxidant properties. This procedure constitutes another component of formally clean syntheses of polyaniline analogues. It remains to be established how the physical properties of these new polymers correspond to or differ from the polyaniline series.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR were performed on a Varian Unity 300 NMR machine. GPC analysis was performed using Phenomenex Phenogel columns and a Beckman 160 UV detector. THF was used as the eluent, and polystyrenes were used as standards. UV−vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. FT-IR spectra were recorded on a Perkin-Elmer 983 spectrometer. X-ray structure analyses were performed by the Molecular Structure Laboratory of The University of Arizona. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Samples for electron conductivity evaluation were prepared as follows. Thin films, obtained by spin-coating the free base polymer solutions (100 mg in 20 mL of solvent), were protonated by placing them in a desiccator full of HCl gas for 24 h. Conductivity measurements were tested by the standard four-probe procedure.

Hydrazine monohydrate, THF, and 10% Pd/C were purchased from Aldrich Chemical Inc. and used as received.

Purification of 4,4′-Diaminodiphenylamine. The technical grade 4,4′-diaminodiphenylamine sulfate (15.0 g) purchased from Aldrich Chemical Inc. was stirred in 50 mL of concentrated HCl and 200 mL of water at 50 °C for 3 h. The solution was filtered while hot, and the solid was washed with 100 mL of water. Adding concentrated NaOH aqueous solution to the filtrate while passing Ar through the solution precipitated the free 4,4′-diaminodiphenylamine, which was collected by filtration and recrystallized again with distilled water under Ar atmosphere.

Anthraquinone diimines were synthesized according to previously reported procedures.[13−15]

Reduction of *N,N′*-Diphenylquinone Diimine Model Compounds. The experiments were carried out by a modified literature procedure.[17] The general procedure is as follows: Hydrazine monohydrate (8.4 mmol) was added dropwise into a stirred solution of *N,N′*-diphenylquinone diimine (0.42 mmol) and 10 wt % of palladium on carbon (10% w/w) in 25 mL of THF at room temperature. Ethanol (10 mL) was added to the reaction mixture to form a homogeneous mixture if a biphasic mixture formed upon addition of hydrazine. The reaction mixture was stirred for 20 h at room temperature and then filtered through a thin layer of Celite. The solid phase was washed with 50 mL of hot THF, and the solvent in the filtrate was removed by rotary evaporator in vacuo. The product was purified by multiple recrystallization from ethyl acetate.

N,N′-Diphenylanthracene-9,10-diamine (DAA). Yield: 88.3%; mp: 303−308 °C. ^{1}H NMR (DMSO-d_6) δ (ppm): 6.45 (d,4H), 6.63 (t, 2H), 7.05 (t, 4H), 7.50 (dd, 4H), 8.22 (dd, 4H), 8.45 (s, NH). IR (KBr, cm^{-1}): 3394 (NH), 3045, 1600 (C═C), 1497, 1380, 1084, 740. MS (*m/z*): 360 (M$^+$, 100%), 283, 254, 205, 77, 51. UV−vis: $\lambda_{\max}$ (THF) 425 nm, $\epsilon = 6110$ M^{-1} cm^{-1}. Elem. Anal. (%): Calcd for $C_{26}H_{20}N_2$: C, 86.63; H, 5.60; N, 7.77. Found: C, 86.73; H, 5.49; N, 7.65.

2-tert-Butyl-(N,N′-diphenyl)anthracene-9,10-diamine (BDAA). Yield: 94.0%; mp: 242−245 °C. ^{1}H NMR (CDCl$_3$) δ (ppm): 1.33 (s, 9H), 5.98 (d, 2H), 6.62 (d, 4H), 6.75 (t, 2H), 7.15 (t, 4H), 7.41 (dd, 2H), 7.51 (dd, 1H), 8.10 (s, 1H), 8.15 (s, 1H), 8.25 (dd, 2H). IR (KBr, cm^{-1}): 3379 (NH), 1600 (C═C), 1496, 1350, 1225, 1150, 750. MS (*m/z*): 416 (M$^+$, 100%), 386, 339, 309, 208, 178, 92, 77, 51. UV−vis: $\lambda_{\max}$ (THF) 421 nm, $\epsilon = 6000$ M^{-1} cm^{-1}. Elem. Anal. (%): Calcd for $C_{30}H_{28}N_2$: C, 86.49; H, 6.79; N, 6.77. Found: C, 85.61; H, 6.65; N, 6.77.

N,N′-Diphenyl-(1,5-dimethoxyanthracene)-9,10-diamine(DDAD). Yield: 50%; mp 273−275 °C. ^{1}H NMR (CDCl$_3$, 25 °C) δ (ppm): 4.02 (s, 6H), 6.56 (d, 4H), 6.80 (t, 2H), 7.11 (t, 4H), 7.20 (d, 3H), 7.95 (dd, 3H). IR (KBr, cm^{-1}): 3395 (NH), 2936, 1600 (C═C), 1251, 1046, 750. MS (*m/z*): 420 (M$^+$, 100%), 389, 361, 326, 284, 210, 93, 77, 51. UV−vis: $\lambda_{\max}$ (THF) 431 nm, $\epsilon = 10\,100$ M^{-1} cm^{-1}.

N,N′-Diphenyl-1,5-di(2-methoxyethoxy)anthracene-9,10-diamine (DDEAD). Yield: 89%; mp 245−250 °C (dec). ^{1}H NMR (CDCl$_3$, 25 °C) δ (ppm): 3.54 (s, 6H), 3.81 (t, 4H), 4.24 (t, 4H), 6.54 (d, 4H), 6.73 (t, 2H), 7.12 (m, 8H), 7.85 (d, 2H). IR (KBr, cm^{-1}): 3378 (NH), 2950, 1600 (C═C), 1500, 900, 720. MS (*m/z*): 508 (M$^+$), 449, 389, 361, 298, 241, 77, 51, 29 (100%). UV−vis: $\lambda_{\max}$ (THF) 438 nm, $\epsilon = 12\,200$ M^{-1} cm $^{-1}$.

N,N′-Diphenyl-(1,5-di(2-(2-methoxyethoxy)ethoxy)anthracene)-9,10-diamine (DDEEAD). Yield: 70%; mp: 197−200 °C. ^{1}H NMR (CDCl$_3$) δ (ppm): 1.54 (s, 2H, NH), 3.10 (s, 3H), 3.36 (, H), 3.61 (t, 4H), 3.76 (t, 4H), 3.91 (t, 4H), 4.27 (t, 4H), 6.52 (d, 4H), 6.74 (dd, 2H), 7.07 (t, 4H), 7.18 (t, 4H), 7.83 (d, 2H), 8.31 (s, 2H). IR (KBr, cm^{-1}): 3401 (NH), 3050, 2893, 1601 (C═C), 1506, 1350, 774. MS (*m/z*): 596 (M$^+$), 505, 426, 390, 270, 241, 93, 59 (100%). Elem. Anal. (%): Calcd for $C_{36}H_{40}N_2O_6$: C, 72.45; H, 6.76; N, 4.69. Found: C, 71.39; H, 6.56; N, 4.65.

N,N′-Diphenylbenzo[1,2-b:4,5-b′]dithiophenene-4,8-diamine (DASQ). Yield: 100%; mp 262−265 °C. ^{1}H NMR (CDCl$_3$, 25 °C) δ (ppm): 2.79 (s, NH), 6.75 (m, 6H), 7.15 (t, 4H), 7.38 (d, 2H), 7.54 (d, 2H). IR (KBr) 3353 (NH), 3097, 1604 (C═C), 1497, 1387, 1285, 751 cm^{-1}. MS (*m/z)*: 372 (M$^+$, 100%), 295, 261, 211, 77, 51. UV−vis: $\lambda_{\max}$ (THF) 368 nm, $\epsilon = 10\,400$ M^{-1} cm^{-1}.

Reduction of Poly(arylene imine)s by Hydrazine Monohydrate. A general procedure is as follows. Poly(arylene imine) **1** (0.3 g) was suspended in hydrazine monohydrate (7.0 mL) at 70 °C for 24 h. The deep-red polyimine gradually changed to white. The solution was diluted with 10 mL of water, the precipitate was filtered, washed with large amount of water, and dried at 60 °C for 24 h in vacuo.

Reduction of Poly(arylene imine)s by Hydrazine Monohydrate in the Presence of Pd/C Catalyst. A general procedure is as follows. Poly(arylene imine) **3a** (0.3 g) was dissolved in 6 mL of THF in the presence of 10 wt % Pd/C. Hydrazine monohydrate (2.0 mL) was added in one portion, and a suspension was formed which was brought to reflux. A clear solution was gradually formed as the reduction going on. After kept at reflux for 24 h, the solution was cooled and filtered. The filtrate was condensed by a rotary evaporator, and polymer was precipitated out by pouring into 100 mL of methanol. The resulting poly(arylene amine) was collected by filtration and drying at 60 °C for 24 h in vacuo.

For polymer **1**, the completion of reduction was within 2.0 h as suggested by the color change.

Poly(arylene amine) ***2***. White powder. Yield: 100%. ^{1}H NMR (DMSO-d_6) δ (ppm): 2.05 (s, 6H, $-CH_3$), 6.69 (d, 4H), 6.98 (s, 2H), 7.09 (d, 4H), 7.44 (s, 2H, −NH−). ^{13}C NMR (CDCl$_3$) δ (ppm): 17.6, 115.2, 123.0, 124.8, 129.6, 132.5, 135.7, 145.7. FT-IR (KBr, cm^{-1}): 3383, 3012, 1593, 1513, 1493, 1308, 1288, 1176, 812. UV−vis: $\lambda_{\max}$ (THF) 357 nm. GPC data vs polystyrene standards: M_w 8000, M_n 5100.

Poly(arylene amine) ***4a***. Light brown powder. Yield: 100%. ^{1}H NMR (CDCl$_3$) δ (ppm): 1.25 (m, 9H), 5.90 (s, 2H, −NH−), 6.45 (b, 4H), 6.80 (m, 2H), 7.07 (b, 4H), 7.28 (m, 3H), 8.15 (m, 2H). FT-IR (KBr, cm^{-1}): 3383, 3058, 2952, 1593, 1493, 1461, 1388, 824. UV−vis: $\lambda_{\max}$ (THF) 430 nm. GPC data vs polystyrene standards: M_w 11 000, M_n 6900.

Poly(arylene amine) ***4b***. Dark red powder. Yield: 100%. ^{1}H NMR (CDCl$_3$) δ (ppm): 1.25 (s, 9H), 5.31 (s, 1H, −NH−), 5.75 (s, 2H, −NH−), 6.44 (b, 4H), 6.71 (m, 7H), 7.28 (m, 2H), 8.15 (m, 2H). FT-IR (KBr, cm^{-1}): 3386, 3067, 2961, 2904, 2862, 1607, 1495, 1301, 832. UV−vis: $\lambda_{\max}$ (THF) 545 nm. GPC data vs polystyrene standards: M_w 9400, M_n 5300.

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