

Cu(II)-Mediated Generation of Triarylamine Radical Cations and Their Dimerization. An Easy Route to Tetraarylbenzidines

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Triphenylamine (TPA) derivatives react with Cu^{2+} in acetonitrile to give TPA radical cations which undergo dimerization and deprotonation reactions to yield tetraphenylbenzidines (TPB). Synthetic utility of this reaction is demonstrated using several triphenylamine derivatives, and yields in excess of 80% are obtained in most cases. Involvement of the amine radical cations in these reactions was confirmed by ESR and absorption spectroscopic studies. A mechanism consistent with all observations is proposed. This study also revealed a very good correlation between the free energy change for radical cation formation and product yields.

Introduction

Tetraphenylbenzidine (TPB) and its derivatives have received considerable attention because of their applications as photoconductors and hole-transporting layers in organic light-emitting diodes, organic solar cells, organic field effect transistors, and xerography.^{1–7} In each of these applications, materials of electronic grade purity are required for optimal device performance. At present, TPB derivatives are most generally prepared by the Ullmann condensation reaction between diphenylamine and an unactivated aryl halide in the presence of a copper catalyst (metal, alloy, or salt) as shown in Scheme 1.

High temperatures and extended reaction times are often required, and the yields are generally unpredictable because of side reactions such as dehalogenation and homocoupling. Several attempts were made to moderate the Ullmann reaction

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SCHEME 1. Ullmann Synthesis of TPB Derivatives



conditions. For example, Goodbrand et al.^{8a} and Lu et al.^{8b} employed 1,10-phenanthroline ligand along with cuprous chloride and KOH in aromatic hydrocarbon solvents (toluene or xylene) at refluxing temperatures to obtain good yields of TPB

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derivatives. Ligands such as 1,4-diazabuta-1,3-diene,8c 18crown-6,8d,e or tri-tert-butylphosphine8f along with Cu salts and a base (K₂CO₃ or *t*-BuOK) were employed by others. All these modifications could not eliminate the requirements of high reaction temperatures (125-150 °C) and long reaction times (3-45 h). Palladium-catalyzed aromatic amination reactions developed by Buchwald and Hartwig appear promising, but these have not been applied for the synthesis of TPB derivatives.9 In this context, new synthetic methodologies, which involve mild reaction conditions and cheap chemicals, are very desirable. Herein we report a simple and highly efficient method, which involves the dimerization of triarylamine radical cations, for the synthesis of TPB and several of its derivatives. It is to be mentioned here that dimerization of electrochemically generated triphenylamine radical cations to TPB derivatives were studied previously by several groups,¹⁰ but the electrochemical method has not yet evolved as synthetically useful for the preparation of TPB derivatives.

Results and Discussion

Recently, we have introduced a very simple and effective method for the generation of aromatic amine radical cations.¹¹ The reaction involved mixing of the aromatic amines with 1 equiv of $Cu(ClO_4)_2$ in acetonitrile (ACN) solution. The amine radical cation is generated as a result of single electron transfer from the amine to Cu^{2+} as in eq 1.

amine +
$$Cu^{2+} \rightarrow amine^{+} + Cu^{+}$$
 (1)

We have shown that a large number of aromatic amines undergo this reaction. Taking *N*,*N*-dialkylanilines as examples, we have recently shown that this method can be effectively explored for generating the amine radical cations and studying their reactivity patterns.¹² In the present paper, we demonstrate that several triphenylamine derivatives are capable of generating their radical cations upon reaction with Cu^{2+} in acetonitrile and that this reaction is synthetically useful for the preparation of tetraphenylbenzidine derivatives. The reaction conditions are shown in Scheme 2.





In a typical experiment, the triarylamine was mixed with Cu- $(ClO_4)_2$ in acetonitrile and stirred at room temperature for 12 h. The solution turns deep blue upon addition of Cu($ClO_4)_2$, and completion of the reaction is indicated by change of color to pale yellow. Reaction mixture was worked up as described

in the experimental section to get good to excellent yields of tetraphenylbenzidines. Structures of the starting TPA and product TPB derivatives along with isolated yields are shown in Table 1.

TABLE 1. Starting Amines, Products, and Yields of Cu^{2+} -InitiatedTriarylamine Dimerizations



^a Yields based on reacted starting material.

It can be seen from Table 1 that the reaction gives good yields even when sensitive groups such as -CHO, $-COOCH_3$, or -SCN are present in the substrate. As mentioned previously, TPB derivatives of the type shown in Table 1 are generally prepared by Ullmann reaction, which generally fails with sensitive substrates. The method presented here is obviously better than the above approaches. It may, however, be noted that electron-withdrawing substituents such as -CHO and

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 $-NO_2$ exert a negative effect on this reaction. When the TPA contains one -CHO or $-NO_2$ group the reactions did not go to completion. Nearly 30% of the starting materials were recovered, and the yields reported in Table 1 are based on the amount of starting materials reacted. When two -CHO or $-NO_2$ groups were present, TPB formation did not take place, and most of the starting materials were recovered unchanged.

Dimerization of electrochemically generated TPA radical cation was studied in great detail and a mechanism for the dimerization was proposed previously.10 Using cyclic voltammetry and spectroelectrochemical measurements (ESR, UV/vis/ NIR), Dunsch and co-workers have clearly established the reaction pathways of several closely related, electrochemically generated triarylamine radical cations.¹³ Electrochemical behaviors of several amino substituted TPA derivatives were recently studied by Chiu et al.¹⁴ In Scheme 3 we have proposed a mechanism in line with those proposed in the electrochemical work. The first step in Scheme 3 is the formation of TPA radical cation by reaction with Cu²⁺. Dimerization of the radical cation would lead to the dication H₂TPB²⁺, which undergoes elimination of two protons to give TPB. The TPB generated is a better electron donor compared to TPA and hence it can donate an electron either to TPA^{•+} or to Cu²⁺ and generate TPB^{•+}, which is the end product of the reaction. Steps 2 and 3 in Scheme 3 are identical to those in electrochemical dimerization. In the electrochemical reaction, oxidation of TPB to TPB^{•+} (step 4) occurs at the electrode, which is kept at a higher potential. In the electrochemical reaction as well as in the chemical oxidation by Cu²⁺ reported here, the end product of is TPB⁺⁺. We observed that TPB^{•+} can be neutralized by triethylamine (TEA) or potassium carbonate during workup to give good yields of TPB.

SCHEME 3. Mechanism Showing the Formation of TPB++ from TPA



According to Scheme 3, the product TPB inhibits the reaction by reducing part of Cu^{2+} to Cu^+ or converting part of $TPA^{\bullet+}$ back to TPA. This means that more than one equivalent of Cu^{2+} is required to drive the reaction to completion. In order to identify the optimum amount of Cu^{2+} , we have carried out the dimerization of TPA at different concentrations of Cu^{2+} . As shown in Figure 1, the product yield reached a maximum at 1.5 equiv of Cu^{2+} . Optimum concentrations of Cu^{2+} were not



FIGURE 1. Plot of product yield vs Cu^{2+} concentration for TPA/ Cu^{2+} system.

determined for other TPA derivatives in Table 1, and we simply used 1.5 equiv of Cu^{2+} in all these cases.

In order to clearly establish the similarity between the electrochemical and Cu^{2+} mediated dimerization reactions, we have carried out spectroscopic and kinetic investigations on the TPA/Cu(ClO₄)₂ system in acetonitrile. The first step is to identify if radical cations are involved in these reactions and this is best done using ESR spectroscopy. We have recorded ESR spectra of all the TPA derivatives listed in Table 1 in the presence of Cu²⁺. All TPA derivatives which gave benzidines as products in this reaction exhibited ESR signals, and some examples are given in Figure 2 (see the Supporting Information (SI) for remaining ESR spectra).

The paramgnetic Cu²⁺ shows a ESR signal around 3000 G. When 1 equiv of a TPA derivative was added, the ESR signal at 3000 G completely disappeared and new signals corresponding to radical cations of the TPA appeared immediately near 3250 G. This clearly indicates that radical cations of the TPAs are formed as a result of electron transfer from the amine to the paramagnetic Cu²⁺. The ESR signals decayed with time and the spectra presented in Figure 2 were collected during the first 3 min of mixing. In all cases, we got almost identical single line ESR spectra. Stamires and Turkevich have previously observed unresolved single line ESR spectrum for TPA++ at relatively high concentrations.¹⁵ The lack of hyperfine structure was attributed to interactions of the radical cations with each other. In the case of the diformyl and dinitro derivatives (entries 9 and 10 in Table 1), ESR spectra corresponding to amine radical cations were not observed and the signal due to Cu²⁺ did not disappear.

We have monitored the dimerization reaction using absorption spectroscopy. TPA do not absorb above 370 nm in acetonitrile solution. Upon addition of 1.5 equiv of Cu(ClO₄)₂, an intense absorption band in the 600–800 nm region is formed and as a result the solution turned blue. Absorption spectrum of TPA/ Cu²⁺ system in acetonitrile immediately after mixing is shown in Figure 3a ($\lambda_{max} = 680$ nm). Lewis and Lipkin had generated TPA⁺⁺ by photoionization of TPA in rigid matrix at low temperature.¹⁶ TPA⁺⁺ thus generated exhibited absorption maximum at 660 nm. Hasegawa had shown that TPA⁺⁺ generated by the chemical oxidation of TPA with acid zeolites absorbed at 678 nm.¹⁷ Hall obtained TPA⁺⁺ by reacting TPA with silica–alumina catalyst and reported its absorption maxi-

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FIGURE 2. (a) ESR spectrum of 0.1 M solution of $Cu(ClO_4)_2$ in ACN; (b-d) ESR spectra of 1 mmol of triarylamine with 1 mmol of $Cu(ClO_4)_2$ in ACN.



FIGURE 3. Time-dependent changes in the absorption spectrum of a solution containing TPA (1×10^{-4} M) and Cu(ClO₄)₂ (1.5×10^{-4} M) in ACN. Spectrum "n" was taken after 24 h. Insets show the time dependences of absorptions at 680 and 1270 nm.

mum as 660 nm.¹⁸ Dollish and Hall generated TPA^{•+} by reacting TPA with iodine and showed that this species absorbs around 660 nm.¹⁹ Based on these reports and our own previous findings,^{10,11} we assign the 680 nm band in Figure 2a to TPA^{•+}.

The absorption due to TPA^{•+} was monitored as a function of time and this is shown in Figure 3b–n. It can be seen that the absorption due to TPA^{•+} decreased with time along with concomitant increase in the absorptions in the 400–580 nm and 900–1600 nm regions. Presence of the isosbestic points in Figure 3 suggest that the species responsible for the new absorptions originate from TPA^{•+}. This is also clear from the decay at 680 nm and the matching growth at 1270 nm, shown as insets in Figure 2. The final spectrum (Figure 3n) was very stable (more than 24 h) and is assigned to TPB^{•+} based on literature reports and our own results.^{10,11,15–20} For example, Seo et al. observed that electrolysis of TPA or TPB solutions at +1.15 V gave the same species having absorption at 480 nm, and this was identified as TPB^{•+}.^{10a} Dollish and Hall¹⁹ generated TPA^{•+} by oxidizing TPA with silica–alumina catalyst and observed that the initial absorption band at 660 nm assignable to TPA^{•+} decreased with time leading to the formation a new band at 480 nm. This band was assigned to TPB^{•+}, arising from a $\pi - \pi^*$ transition. Recent studies have also established the existence of a long wavelength band in the

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FIGURE 4. Effect of addition of increasing amounts of TEA to solution of spectrum "n" in Figure 3.

1000–1600 nm region for TPB^{•+}, which is assigned to the intervalence charge-transfer excitation.²¹ TPB^{•+} consists of a neutral TPA unit and a TPA^{•+} unit. The intervalence charge-transfer band arises as a result of photoexcited electron transfer from the neutral TPA moiety to the TPA^{•+}. These reports are in agreement with the assignments made here. We observed that TPB^{•+} could also be generated by the reaction of Cu²⁺ with TPB and the spectrum obtained was identical to Figure 3n, which further confirms the assignment.

The absorptions due to TPB⁺⁺ at 400–580 nm and at 900– 1600 nm were very stable for several hours. Upon addition of excess TEA these bands disappeared leading to the formation of a new absorption below 400 nm (Figure 4). Based on a comparison with authentic sample, the new band was assigned to TPB. We observed that TPB⁺⁺ can also be quenched by aqueous K₂CO₃, although the mechanism of quenching is not very clear. Thus, K₂CO₃ was employed in the workup procedure.

Although we have proposed a few intermediates for the reaction in Scheme 3, the spectroscopic studies (Figures 2 and 3) could identify only TPA⁺⁺ and TPB⁺⁺. The isosbestic points in Figure 3 suggest that TPA++ is converted smoothly into TPB^{•+}, and there are no observable intermediates in this transformation. Formation of TPB^{•+} from TPA^{•+}, however, has to involve dimerization of the radical cation (radical-radical coupling) to the dicationic species H_2TPB^{2+} , deprotonation of H_2TPB^{2+} to TPB and oxidation of TPB to TPB⁺ as shown in Scheme 3. Most probably, H₂TPM²⁺ and TPB are not observed in Figure 3 because the deprotonation and electron-transfer reactions are very fast compared to the dimerization reaction. In general, radical cations and dications are highly acidic compared to neutral molecules, and hence deprotonation of H2- TPB^{2+} to neutral TPB molecule is expected to be very fast. The TPB thus formed is a better electron donor ($E_{ox} = 0.69V$ vs SCE) than TPA ($E_{ox} = 0.92$ V vs SCE). Hence, a spontaneous electron exchange reaction between the two can take place, leading to the formation of TPB+.10a If Cu2+ is present in excess, electron transfer from TPB to Cu²⁺ can also occur spontaneously, leading to the formation of TPB^{•+}.



FIGURE 5. Plot of $1/A_t - 1/A_0$ vs time for TPA/Cu²⁺ system.

The mechanism presented in Scheme 3 is based on the reports dealing with the electrochemical oxidations of triphenylamine. In electrochemical reactions, high concentrations of the radical species are generated at the electrodes and radical-radical coupling is the preferred pathway.^{10b} In the present case, where the reaction occurs in bulk solution another mechanism involving addition of TPA^{•+} to TPA (radical-parent coupling) also needs to be considered. The coupled product can undergo electron transfer with Cu²⁺ to generate H₂TPB²⁺. A distinction between the two reaction pathways could be made using kinetic experiments. The radical-radical coupling is second order with respect to TPA⁺⁺ whereas the radical-parent pathway is firstorder each in TPA^{•+} and TPA. The absorption due to TPA^{•+} occurs in a region where TPA or other intermediates in Scheme 3 do not interfere. This gives us an opportunity to determine the order of the reaction by monitoring the absorption due to TPA^{•+}. The time dependence of the absorbance due to TPA^{•+} at 680 nm plotted as per second-order kinetics is shown in Figure 5. The straight line is a fit to second-order kinetics. Good match of the data to the fit strongly supported the radical-radical coupling mechanism shown in Scheme 3. The rate constant obtained for the dimerization of TPA was $9.3 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$. The value obtained is several orders smaller than that reported by Creason et al.^{10b} ($k = 1.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) for the electrochemical dimerization. The large value in the electrochemical work is due to the large concentration of the ion radicals at the electrode surface. It is to be mentioned here that the kinetic experiments were carried out only in the case of TPA. For other derivatives shown in Table 1, particularly those with electron-withdrawing substituents, reaction of the amines with Cu²⁺ was slow. Thus, formation of radical cations interfered with its decay and determination of dimerization rate constants required prior knowledge about the rate of formation of the amine radical cations. Stopped-flow experiments to determine these rates are being planned.

An examination of Table 1 shows that the dimerization reaction is slow or incomplete when the TPAs contain electronwithdrawing groups. In the case of the dinitro derivative, the radical cation was not formed and the reaction did not proceed at all. These factors can be attributed to the free energy changes associated with the radical cation formation. Free energy change for the electron-transfer reaction (1) can be calculated using the standard expression

$$\Delta G^{\circ} = E_{\rm ox} - E_{\rm red} - e^2/d\epsilon \qquad (2)$$

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TABLE 2. $E_{\rm ox}$ for TPA Derivatives and ΔG^0 Associated with Radical Cation Formation

triarylamine ^a	$E_{\rm ox}$ vs SCE	ΔG^0
$R_1 = H, R_2 = H$	0.92	-0.210
$R_1 = H, R_2 = CH_3$	0.90	-0.230
$R_1 = CH_3, R_2 = CH_3$	0.88	-0.250
$R_1 = OCH_3, R_2 = OCH_3$	0.76	-0.370
$R_1 = H, R_2 = SCN$	1.02	-0.101
$R_1 = H, R_2 = COOCH_3$	1.05	-0.080
$R_1 = H, R_2 = CHO$	1.08	-0.050
$R_1 = H, R_2 = NO_2$	1.16	+0.030
$R_1 = CHO, R_2 = CHO$	1.21	+0.080
$R_1 = NO_2, R_2 = NO_2$	1.35	+0.220
a R ₁ and R ₂ as in Scheme 2.		

where $E_{\rm ox}$ is the oxidation potential of the TPA derivatives, $E_{\rm red}$ is the reduction potential of Cu²⁺, *d* is the center-to-center distance between TPA and Cu(ClO₄)₂ hexahydrate in the collision complex, and ϵ is the dielectric constant (= 37) of ACN. $E_{\rm ox}$ values for all the TPA derivatives were measured using cyclic voltammetry and these are given in Table 2. $E_{\rm red}$ of Cu²⁺ in ACN is + 0.952 V vs SCE. In fact, this value is approximately 1 V more positive than $E_{\rm red}$ in water, and the gain in energy by changing the solvent to ACN is attributed to formation of the stable tetrakis(acetonitrile)copper(I) complex immediately following the reduction of Cu²⁺ to Cu⁺.²² Reaction (1) takes place only in acetonitrile, and part of the driving force for the reaction comes form the free energy of formation of [Cu(CH₃CN)₄]⁺ complex. Hence, reaction (1) should be modified as shown in (3).

amine +
$$\operatorname{Cu}^{2+} \xrightarrow{\operatorname{CH}_3\operatorname{CN}} \operatorname{amine}^{\bullet+} + \left[\operatorname{Cu}(\operatorname{CH}_3\operatorname{CN})_4\right]^+$$
 (3)

Under these conditions, it is advisable to replace $E_{\rm red}$ in eq 2 with the reduction peak potential (E_p) obtained by linear sweep voltammetry. For the reduction of Cu²⁺ in ACN, we obtained E_p as +1.082. The Coulombic term in eq 2 was calculated assuming d = 8 Å. Using these values, the ΔG° associated with the radical cation formation was calculated for all TPA derivatives shown in Table 1 and the values are presented in Table 2.

Analysis of Tables 1 and 2 showed that there is good correlation between the ΔG° values and product yields. For the first six entries in Table 2, ΔG° values are negative and yields of TPB are very good. For the mononitro derivative (entry 7), the ΔG° value is slightly positive and the reaction did not go to completion. In the case of diformyl and dinitro derivatives, TPB derivatives were not formed because the ΔG° for formation of radical cations were positive. This shows that a correlation exists between ΔG° of radical cation fromation and yields of TPB in the systems studied.

Conclusion

In summary, we have shown that the reaction of triphenylamine derivatives with Cu^{2+} in ACN generates radical cations of the amines and that this reaction can be exploited for the synthesis of tetraphenylbenzidine derivatives. A mechanism for the formation of TPB derivatives is also proposed. The mechanism is confirmed by spectroscopic and kinetic studies. Finally, the yields of the TPB derivatives are correlated to the free energy change associated with the formation of radical cations.

Experimental Section

1. General Methods. Absorption spectra were recorded on a UV-vis-NIR spectrophotometer. The ¹H and ¹³C NMR spectra were recorded in CDCl₃ on a FT-NMR (300 MHz) spectrometer, and the chemical shifts, δ , are referred to TMS. The FAB mass spectra were recorded on a spectrometer. Redox potentials of Cu-(II) and all the TPA derivatives were measured using a cyclic voltammetric analyzer, with a conventional three-electrode system. The ESR spectra were recorded using an ESR spectrometer operating at X-band frequencies and having a 100 kHz field modulation. Cu(ClO₄)₂ and triphenylamine were commercial samples. Other triphenylamine derivatives were prepared by the reactions of primary or secondary amines with aryl halides as per reported procedures.⁸ All experiments were carried out at room temperature (25 ± 1 °C), unless otherwise mentioned.

2. General Procedure for Preparation of Tetraphenylbenzidines. A solution of $Cu(ClO_4)_2$ hexahydrate (222 mg, 0.60 mmol) in ACN (10 mL) was added to a solution of the triarylamine (0.4 mmol) in ACN (20 mL) at room temperature, and the mixture was stirred for 12 h. Solid K₂CO₃ (500 mg) and water (1 mL) were added, and stirring was continued for 0.5 h. Filtered and the solids were washed twice with chloroform. The combined organic extracts were filtered through a short pad of alumina. The solvent was removed and the residue so obtained was recrystallized form dichloromethane-hexane mixture to give pure products. Yields shown in Table 1 are those of pure products. For entries 6–8 in Table 1, the organic residues were chromatographed over neutral alumina. Elusion with a mixture of chloroform—hexane (1:9) gave the unreacted starting materials. Further elution with chloroform hexane (1:4) gave the pure products.

N,N,N',N'-**Tetraphenylbiphenyl-4,4'-diamine(1)**:^{8c} yield 81%; ¹H NMR (CDCl₃) δ 6.99–7.45 (m, 28H); ¹³C NMR (CDCl₃) δ 122.76, 124.04, 124.24, 127.25, 129.21, 134.66, 146.66, 147.65; MS (FAB) *m*/*z* 488 (M⁺). Anal. Calcd for C₃₆H₂₈N₂: C, 88.49; H, 5.78; N, 5.73. Found: C, 88.02; H, 6.21; N, 5.87.

N,N'-**Diphenyl**-*N,N*'-**di**(*p*-tolyl)**biphenyl**-4,4'-**diamine**(2):^{8f} yield 86%; ¹H NMR (CDCl₃) δ 2.32 (s, 6H), 7.07–7.42 (m, 26H); ¹³C NMR (CDCl₃) δ 20.82, 122.33, 123.52, 123.72, 125.00, 127.15, 129.12, 129.93, 132.83, 134.36, 145.11, 146.82, 147.87; MS (FAB) *m*/*z* 516 (M⁺). Anal. Calcd for C₃₈H₃₂N₂: C, 88.34; H, 6.24; N, 5.42. Found: C, 88.08; H, 6.50; N, 5.32.

N,*N*,*N*',*N*'-**Tetra**(*p*-tolyl)biphenyl-4,4'-diamine(3):^{8d} yield 94%; ¹H NMR (CDCl₃) δ 2.15 (s, 12H), 6.83–6.94 (m, 20H), 7.25 (d, 4H); ¹³C NMR (CDCl₃) δ 21.01, 123.15, 124.68, 127.24, 130.05, 132.48, 134.15, 145.51, 147.17; MS (FAB) *m*/*z* 544 (M⁺). Anal. Calcd for C₄₀H₃₆N₂: C, 88.20; H, 6.66; N, 5.14. Found: C, 87.81; H, 7.16; N, 5.45.

N,N,N',N'-Tetrakis(4-methoxyphenyl)biphenyl-4,4'-diamine (4):^{21a} yield 87%; ¹H NMR (CDCl₃) δ 3.78 (s, 12H), 6.81 (d, 8H), 6.96 (m, 4H), 7.05 (d, 8H), 7.34 (d, 4 H); ¹³C NMR (CDCl₃) δ 55.45, 114.62, 121.08, 126.37, 126.84, 132.99, 140.92, 147.35, 155.67; MS (FAB) *m/z* 608 (M⁺). Anal. Calcd for C₄₀H₃₆N₂O₄: C, 78.92; H, 5.96; N, 4.60. Found: C, 78.86; H, 6.45; N, 4.64.

N,*N*'-**Bis**(*p*-carbomethoxyphenyl)-*N*,*N*'-**di**(phenyl)**biphenyl**-**4**,**4**'-**diamine** (5): yield 83%; ¹H NMR (CDCl₃) δ 3.88 (s, 6H), 7.03 (d, 4H), 7.14–7.19 (m, 10H), 7.30–7.35 (m, 4H), 7.50 (d, 4H), 7.86 (d, 4H); ¹³C NMR (CDCl₃) δ 52.71, 119.34, 121.39, 122.35, 124.81, 126.71, 128.75, 130.71, 131.94, 136.24, 146.54, 145.77, 151.77, 166.86; MS (FAB) *m*/*z* 605 (M + 1). Anal. Calcd for C₄₀H₃₂N₂O₄: C, 79.45; H, 5.33; N, 4.63. Found: C, 79.01; H, 5.75; N, 4.90.

N,*N*'-**Bis**(4-nitrophenyl)-*N*,*N*'-diphenylbiphenyl-4,4'-diamine-(6). 30% starting amine was recovered: yield based on reacted SM

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81%; ¹H NMR (CDCl₃) δ 6.90 (d, 4H), 7.12–7.17 (m, 10H), 7.28–7.33 (m, 4H), 7.48 (d, 4H), 7.97 (d, 4H); ¹³C NMR (CDCl₃) δ 118.57, 125.45, 125.86, 126.41, 126.55, 128.16, 129.98, 137.10, 140.35, 144.98, 145.50, 153.23; MS (FAB) *m*/*z* 578 (M⁺). Anal. Calcd for C₃₆H₂₆N₂O₄: C, 74.73; H, 4.53; N, 9.68. Found: C, 74.31; H, 5.03; N, 9.51.

N,*N*'-**Bis**(*p*-formylphenyl)-*N*,*N*'-**diphenylbiphenyl-4**,4'-**di**amine (7). 20% starting amine was recovered: yield based on reacted SM 85%; ¹H NMR (CDCl₃) δ 7.07 (d, 4H), 7.16–7.25 (m,10H), 7.33–7.38 (m, 4H), 7.53 (d, 4H), 7.69 (d, 4H), 9.81(s, 2H); ¹³C NMR (CDCl₃) δ 119.75, 125.23, 126.16, 126.34, 127.92, 129.34, 129.77, 131.29, 136.62, 145.39, 146.02, 153.11, 190.38; MS (FAB) *m*/*z* 545 (M + 1). Anal. Calcd for C₃₈H₂₈N₂O₂: C, 83.80; H, 5.18; N, 5.14. Found: C, 83.43; H, 5.61; N, 5.34.

N,*N*'-**Diphenyl**-*N*,*N*'-**bis**(4-thiocyanatophenyl)biphenyl-4,4'-diamine (8). 10% starting amine was recovered: yield based on reacted SM 82%; ¹H NMR (CDCl₃) δ 7.01 (d, 4H), 7.08 (d, 10H), 7.23–7.33 (m, 8H), 7.42 (d, 4H); ¹³C NMR (CDCl₃) δ 113.73, 121.96, 122.91, 123.41, 125.50, 126.71, 128.64, 130.63, 134.02, 135.90, 145.67, 146.39, 149.65; MS (FAB) m/z 602 (M⁺). Anal. Calcd for C₃₈H₂₆N₄S₂: C, 75.72; H, 4.35; N, 9.29. Found: C, 75.49; H, 4.80; N, 9.14.

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Supporting Information Available: ¹H NMR and ¹³C NMR spectra for all compounds and ESR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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