

Polyaromatic amines. Part 2. Synthesis of 4,4',4''-tris(*N*-aryl-*N*-phenylamino)triphenylamine, *N,N*-bis[4-(*N*-aryl-*N*-phenylamino)-phenyl]tolylamine and *N,N,N',N'*-tetraaryl-*o*-phenylenediamine derivatives

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The title compounds were synthesised and characterised as part of a study into new aromatic amines for charge transporting materials. Proton and carbon spectral data for compounds 1–6 were obtained in C₆D₆ as a consequence of their facile oxidation in CDCl₃. Each compound was characterised by cyclic voltammetry. An estimate of the intramolecular charge mobility was deduced from the difference between the first and second oxidation potentials.

Introduction

In a previous paper we reported the synthesis and full spectroscopic characterisation of a series of derivatives of 1,3,5-tris-(diarylamino)phenyl]benzene and 1,3,5-tris(diarylamino)-benzene.¹ These and related polyaromatic amines are of interest owing to their potential applications in electrophotography and electroluminescent devices.^{2–4} In these devices positive holes are injected into a thin film of the aromatic amine loaded at high concentration into a binding resin. The charge is transported through the film by positive holes hopping between molecules. Efficient hole transporting ability is dependent upon their facile oxidation to stable radical cations. Ideally a good aromatic amine for a charge transport layer should form radical cations reversibly and that are therefore stable. In the search for new potential charge transport materials we have prepared and characterised some further series of aromatic amines using copper catalysed amine arylations. Methods now also exist for palladium catalysed aryl halide and triflate aminations.⁵

Results and discussion

Three series of amine derivatives are reported in this paper. Compounds 1–3 contain four nitrogen atoms, compounds 4–6 contain three and compounds 7–11 contain two. The compounds are listed in Table 1. Compounds 1–3 were prepared by a copper catalysed Ullmann coupling of 4,4',4''-triiodotriphenylamine 12 with an appropriate diarylamine.⁶ Diarylamines were prepared by the condensation of an aniline with an arenesulfonic acid.¹ 4,4',4''-Triiodotriphenylamine 12 was prepared by the iodination of triphenylamine using iodine and mercuric oxide.⁷ Compounds 4–6 were prepared by copper catalysed Ullmann coupling of *N,N*-bis(4-iodophenyl)-*p*-tolylamine 13 with an appropriate diarylamine.^{8–10} *N,N*-Bis(4-iodophenyl)tolylamine 13 was prepared by the iodination of *N,N*-diphenyl-4-tolylamine using iodine and mercuric oxide. Compounds 7–10 were prepared by copper catalysed arylation reactions of either *N*-phenyl-*o*-phenylenediamine, *o*-phenylenediamine or 4,5-dimethyl-*o*-phenylenediamine. Compound 11 was prepared by the copper catalysed arylation of *p*-phenylenediamine.^{6b,8,11}

Cyclic voltammetry

Measurements were made using a standard three electrode

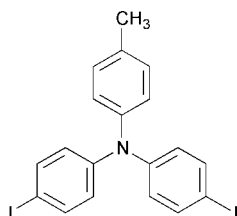
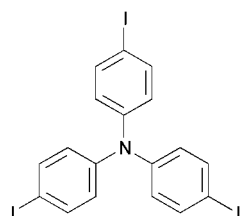
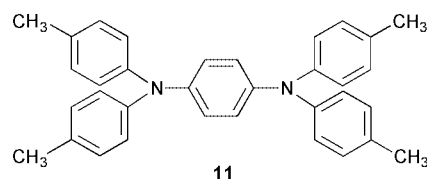
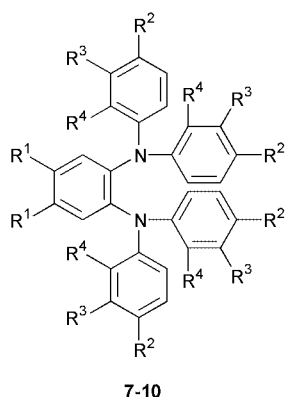
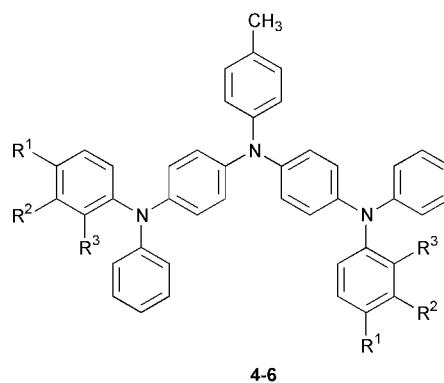
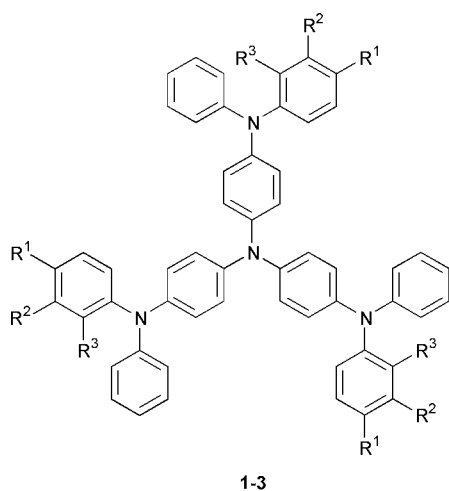
Table 1 Structures of compounds 1–10

Compound	R ¹	R ²	R ³	R ⁴
1	H	CH ₃	H	
2	CH ₃	CH ₃	H	
3	CH ₃	H	CH ₃	
4	H	CH ₃	H	
5	CH ₃	CH ₃	H	
6	CH ₃	H	CH ₃	
7	H	H	H	
8	H	CH ₃	H	CH ₃
9	H	CH ₃	H	H
10	CH ₃	CH ₃	H	H

configuration. Tetrabutylammonium perchlorate (0.1 M) in dichloromethane was used as the supporting electrolyte with platinum wire auxiliary and working electrodes. All measurements were carried out under an argon atmosphere and potentials were related to a saturated calomel reference electrode (SCE). The aromatic amines listed in Table 2 are deemed to undergo chemically reversible oxidation if the peak current ratios of the redox couples, i_{pc}/i_{pa} , are equal to 1, or pseudo-reversible oxidation if greater than 0.85.^{11,12} Data for triphenylamine (TPA) 14 and 4,4'-bis[*N*-(2,4-dimethylphenyl-*N*-phenylamino)]biphenyl (TPD) 15 were obtained for comparison. TPA shows a non-reversible redox couple. However, after repeated scans the voltammogram changes completely to resemble that of TPD, suggesting that the radical cation of TPA dimerises or reacts with neutral TPA to form molecules of TPD. The oxidative dimerisation of TPA has been reported previously.¹³ Polyamines 1–3 and 4–6 readily undergo four and three reversible redox couples respectively, which is in agreement with the reported results for these types of compounds.^{6b,8} They readily undergo autooxidation in organic solvents giving green solutions which made acquisition of NMR data difficult at first. In CDCl₃ it was not possible to obtain proton or carbon spectra since all peak resonances were absent. Satisfactory spectra were obtained in C₆D₆ presumably owing to the absence of minute traces of acid. The tetramers 1–3 show lower oxidation potentials than the trimers 4–6. The fourth oxidations of compounds 2 and 3 were only reversible at faster scan rates and the third oxidation of compound 6 was not reversible. The more highly oxidised the amine is, the greater its reactivity, making it less likely to show a reversible redox couple. The unsubstituted 1,2-phenylenediamine compound 7

Table 2 Summary of electrochemical analyses. Oxidation potentials, E_{pa} , reduction potentials, E_{pc} (in V), and peak current density ratios i_{pc}/i_{pa} of triarylamines versus SCE

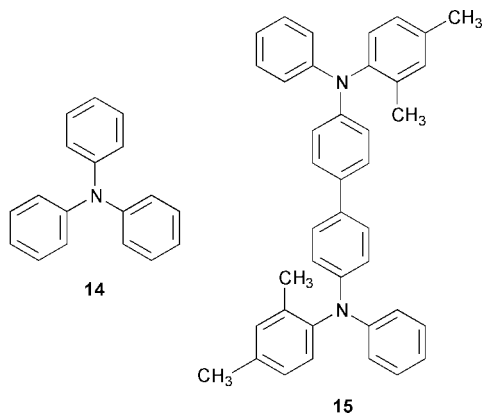
Compound	1st redox			2nd redox			3rd redox			4th redox		
	E_{pa}	E_{pc}	i_{pc}/i_{pa}	E_{pa}	E_{pc}	i_{pc}/i_{pa}	E_{pa}	E_{pc}	i_{pc}/i_{pa}	E_{pa}	E_{pc}	i_{pc}/i_{pa}
TPA	1.21	0.91	0.57									
TPD	0.81	0.70	1	1.03	0.93							
1	0.40	0.36	1	0.73	0.63	0.95	1.37	1.13	0.98	1.54	1.32	0.97
2	0.35	0.27	1	0.68	0.61	1	1.26	1.17	0.93	1.50	1.37	0.77
3	0.34	0.27	1	0.71	0.64	1	1.38	1.32	0.88	1.58	1.44	0.69
4	0.46	0.39	1	0.82	0.73	1	1.53	1.34	0.87			
5	0.43	0.35	1	0.78	0.71	1	1.45	1.36	0.91			
6	0.42	0.35	1	0.81	0.74	1	1.56	1.42	0.56			
7	0.99	0.87	0.84									
8	0.81	0.72	1	1.34	1.27	1						
9	0.82	0.74	1	1.32	1.24	0.87						
10	0.74	0.64	1	1.24	1.14	0.93						
11	0.51	0.40	1	0.99	0.88	1						



undergoes one reversible redox couple which degrades on repeated scans. The alkyl substituted derivatives **8–10** display two reversible oxidation states, although for compound **9** this required a faster scan rate of 400 mV s^{-1} . This demonstrates that alkyl substituents will stabilise the radical cations through steric hindrance.

It has been postulated that good intramolecular charge mobility in charge transport materials (CTM's) will improve

the hole hopping efficiency when the CTM is part of a polymeric binder.¹⁴ An estimate of intramolecular charge mobility or charge delocalisation can be deduced from the size of the separation of the first and second oxidation events. A larger gap indicates greater charge delocalisation because the positive charge is having a more pronounced effect on the second nitrogen making it harder to oxidise. TPD shows a potential gap of 220 mV indicating electronic communication between the two nitrogens after the first oxidation. Had only one oxidation couple been present, this would have indicated isolation of the charges because the first had no influence on formation of the second, and both occurred at the same potential. The potential gaps of compounds **1–6** are in the range 330–390 mV which is greater than the value for TPD. This is probably because in TPD the nitrogens are separated by a biphenyl group which holds the nitrogens further apart than the aryl ring in compounds **1–6**. The potential gap for the *p*-phenylenediamine **11**^{6b,8,11a} of 480 mV is larger than the values for compounds



1–6 because although the nitrogens are conjugated *para* to each other, there are only two of them. The radical cation of compound **11** cannot be delocalised as much as the radical cations might be for compounds **1–6** and therefore the next oxidation is relatively harder for compound **11**. The dication would have the two positive charges in close proximity to each other whereas for compounds **1–6** the two charges might be further apart on the peripheral nitrogen atoms. The potential gaps for compounds **8–10** are larger still in the range 500–530 mV. This might be a consequence of the close proximity in space of the *ortho* related nitrogens leading to electrostatic repulsion between the positive charges. *m*-Phenylenediamines show a potential gap of about 190 mV which is less, as expected, because the nitrogens are not conjugated to each other.^{11b}

Experimental

For general details, see preceding paper in this series.¹

4,4',4''-Triiodotriphenylamine **12**

Triphenylamine (1.00 g, 4.10 mmol) was dissolved in hot EtOH (50 ml) to which red mercuric oxide (5.0 g, 23.0 mmol) was added with vigorous stirring in order to maintain a suspension. Iodine (8.00 g, 31.0 mmol) was added and the reaction heated to reflux at 78 °C for 4 h. The mixture was cooled, concentrated *in vacuo* and filtered. The solids were transferred to a Soxhlet extractor and organic material was extracted with benzene. After 6 h the benzene solution was passed through silica and the excess iodine removed by washing with aqueous Na₂S₂O₃. After drying over MgSO₄ the benzene solution was concentrated *in vacuo* and the resulting solids recrystallised from dichloromethane–light petroleum to yield the *title compound* (1.25 g, 51%) as a yellow crystalline solid, mp 169–170 °C (lit.⁷ 188–189 °C) (Found: C, 34.8; H, 1.7; N, 2.4. C₁₈H₁₂N₃I₃ requires C, 34.7; H, 1.9; N, 2.4%); ν_{\max} (KBr)/cm⁻¹ 3051w, 1574s, 1483s, 1312s, 1282s, 1175m, 1058m, 1001s, 816s, 707s and 508s; δ_{H} (250 MHz; CDCl₃) 6.83 (6H, d, *J* 8.2, Ar) and 7.52 (6H, d, *J* 8.2, Ar); δ_{C} (62.9 MHz; CDCl₃) 86.6, 126.1, 138.5 and 146.6; *m/z* 623 (M⁺, 100%).

4,4',4''-Tris[*N*-(3-methylphenyl)-*N*-phenylamino]triphenylamine **1**. General procedure

4,4',4''-Triiodotriphenylamine **12** (2.00 g, 3.20 mmol), *N*-(3-methylphenyl)-*N*-phenylamine (2.60 g, 15.0 mmol), copper powder (1.26 g, 20.0 mmol), K₂CO₃ (2.24 g, 4.0 mmol) and *n*-decane (10.0 g) were refluxed at 173 °C for 24 h. The mixture was allowed to cool, then slurried with CH₂Cl₂ and filtered. The filtrate was washed with distilled H₂O (×2) and dried over MgSO₄. Solvents were removed under reduced pressure to leave a yellow–brown solid. Column chromatography, eluting with dichloromethane–light petroleum (10 : 90), gave the *title compound* as a colourless solid (75%), mp 207–209 °C (from cyclo-

hexane) (lit.^{6a} 209–210 °C); λ_{\max} (CH₂Cl₂)/nm 311 (log ϵ 5.54) and 343 (5.57); ν_{\max} (KBr)/cm⁻¹ 3035w, 2918m, 2848m, 1583s, 1527s, 1448w, 1311s, 1278s, 850m, 808m, 750m, 694s and 622m; δ_{H} (250 MHz; C₆D₆) 2.14 (9H, s, Me), 6.84–6.86 (3H, d, *J* 4.1, Ar), 6.94–7.01 (3H, t, *J* 7.1, Ar), 7.17–7.34 (33H, m, Ar); δ_{C} (62.9 MHz; C₆D₆) 21.8, 122.4, 123.0, 124.4, 124.5, 125.6, 125.7, 126.3, 130.0, 139.7, 143.7, 143.8, 148.9, 149.1 (one overlapping peak); *m/z* 788 (M⁺, 40%). Acc. mass: calc. 788.3879, found 788.3864.

4,4',4''-Tris[*N*-(3,4-dimethylphenyl)-*N*-phenylamino]triphenylamine **2**

General procedure as for compound **1**. 4,4',4''-Triiodotriphenylamine **12** (2.00 g, 3.20 mmol), *N*-(3,4-dimethylphenyl)-*N*-phenylamine (2.14 g, 10.9 mmol), copper powder (1.00 g, 16.0 mmol), K₂CO₃ (4.42 g, 32.0 mmol), 18-crown-6 (0.50 g) and *o*-dichlorobenzene (10 ml) were heated to 180 °C for 48 h. Yield 35%; yellow crystalline solid, mp 263–265 °C (from cyclohexane) (Found: C, 87.0; H, 6.9; N, 6.4. C₆₀H₅₄N₄ requires C, 86.7; H, 6.7; N, 6.4%); λ_{\max} (CH₂Cl₂)/nm 311 (log ϵ 6.64) and 343 (6.62); ν_{\max} (KBr)/cm⁻¹ 3033w, 2923m, 2850m, 1592s, 1502s, 1450m, 1303s, 1267s, 1218m, 825m, 750m and 694s; δ_{H} (250 MHz; C₆D₆) 2.03 (9H, s, Me), 2.14 (9H, s, Me), 7.19–7.25 (18H, m, Ar) and 7.31–7.36 (18H, m, Ar); δ_{C} (62.9 MHz; C₆D₆) 18.8, 19.5, 121.8, 122.9, 123.1, 124.9, 125.2, 126.5, 129.2, 130.7, 131.3, 137.5, 143.0, 143.1, 146.0 and 148.7; *m/z* 831 (M⁺, 20%).

4,4',4''-Tris[*N*-(2,4-dimethylphenyl)-*N*-phenylamino]triphenylamine **3**

General procedure as for compound **1**. 4,4',4''-Triiodotriphenylamine **12** (1.00 g, 1.62 mmol), *N*-(2,4-dimethylphenyl)-*N*-phenylamine (1.00 g, 5.1 mmol), copper powder (0.15 g, 2.31 mmol), K₂CO₃ (0.70 g, 5.10 mol), 18-crown-6 (0.40 g) and *o*-dichlorobenzene (10.0 g) were heated to 180 °C for 72 h. Yield 35%; yellow crystalline solid, mp 216–218 °C (from cyclohexanol–methanol); λ_{\max} (CH₂Cl₂)/nm 311 (log ϵ 5.90) and 344 (6.10); ν_{\max} (KBr)/cm⁻¹ 3033m, 2919m, 1593s, 1494s, 1304m, 1262s, 1231m, 828m, 752m and 694m; δ_{H} (250 MHz; C₆D₆) 2.21 (9H, s, Me), 2.28 (9H, s, Me), 6.96–7.01 (5H, m, Ar), 7.11–7.22 (19H, m, Ar) and 7.31 (12H, s, Ar); δ_{C} (62.9 MHz; C₆D₆) 19.1, 21.4, 121.2, 121.4, 124.0, 125.4, 130.2, 130.4, 133.2, 136.0, 136.9, 143.2, 143.8 and 148.8 (two overlapping peaks); *m/z* 831 (M⁺, 100%). Acc. mass: calc. 831.4427, found 831.4435.

N,N-Bis(4-iodophenyl)tolylamine **13**

N,N-Diphenyl-4-tolylamine (20.0 g, 7.70 mmol) was dissolved in hot ethanol (250 ml). To this red mercuric oxide (50.0 g, 231 mmol) was added with stirring to maintain a suspension. Iodine (64.0 g, 250 mmol) was added and the reaction mixture heated to reflux at 78 °C for 3 h. The mixture was cooled, slurried with CH₂Cl₂ and filtered to remove solids. The solvents were removed under reduced pressure to leave a dark viscous residue. The residue, dissolved in dichloromethane–light petroleum (30 : 70), was filtered through silica to give a thick yellow oil. Column chromatography, eluting with dichloromethane–light petroleum (30 : 70), gave an off-white solid which was recrystallised from dichloromethane–methanol to yield the *title compound* (21.3 g, 55%) as a white crystalline powder, mp 140–141 °C (Found: C, 44.3; H, 2.6; N, 2.9. C₁₉H₁₅Ni₂ requires C, 44.6; H, 2.9; N, 2.7%); ν_{\max} (KBr)/cm⁻¹ 3024, 2910, 1572, 1482, 1313, 1266, 1176, 1061, 1003, 815, 714, 574 and 498; δ_{H} (250 MHz; CDCl₃) 2.32 (3H, s, Me), 6.77–6.81 (4H, d, *J* 8.5, Ar), 6.94–6.97 (2H, d, *J* 8.3, Ar), 7.06–7.10 (2H, d, *J* 8.3, Ar) and 7.47–7.50 (4H, d, *J* 8.5, Ar); δ_{C} (62.9 MHz; CDCl₃) 20.9, 85.2, 125.3, 125.4, 130.3, 134.1, 138.2, 144.1 and 147.3; *m/z* 511 (M⁺, 100%).

N,N-Bis{4-[*N*-(3-methylphenyl)-*N*-phenylamino]phenyl}tolylamine 4

General procedure as for compound 1. *N,N*-Bis(4-iodophenyl)tolylamine 13 (12.0 g, 23.5 mmol), *N*-(3-methylphenyl)-*N*-phenylamine (13.0 g, 70.5 mmol), copper powder (5.36 g, 85.0 mmol), KOH (9.52 g, 238 mmol) and *n*-decane (5.00 g) were refluxed at 173 °C for 24 h. Yield 63%, as a yellow crystalline solid, mp 237–238 °C (from cyclohexane) (Found: C, 86.6; H, 6.2; N, 6.55. C₄₅H₃₉N₃ requires C, 86.9; H, 6.3; N, 6.8%); λ_{max} (CH₂Cl₂)/nm 317 (log ε 6.04); ν_{max} (KBr)/cm⁻¹ 3033m, 1583s, 1504s, 1483s, 1310s, 1268s, 835m, 819m, 777m, 750s, 695s, 560m and 526s; δ_H (250 MHz; C₆D₆) 2.15 (6H, s, Me), 2.23 (3H, s, Me), 6.83–7.04 (5H, m, Ar) and 7.18–7.34 (25H, m, Ar); δ_C (62.9 MHz; C₆D₆) 21.2, 21.8, 122.3, 122.9, 124.3, 124.4, 125.3, 125.4, 125.6, 126.4, 130.0, 130.8, 132.9, 139.7, 143.4, 144.2, 146.3, 148.9 and 149.2 (one overlapping peak); *m/z* 621 (M⁺, 100%).

N,N-Bis{4-[*N*-(3,4-dimethylphenyl)-*N*-phenylamino]phenyl}tolylamine 5

General procedure as for compound 1. *N,N*-Bis(4-iodophenyl)tolylamine 13 (2.00 g, 3.91 mmol), *N*-(3,4-dimethylphenyl)-*N*-phenylamine (2.50 g, 11.7 mmol), copper powder (1.30 g, 20.0 mmol), KOH (2.25 g, 56.2 mmol) and *n*-decane (10 ml) were refluxed at 173 °C for 24 h. Yield 51%; yellow crystalline solid, mp 248–249 °C (from cyclohexane–dichloromethane) (Found: C, 87.0; H, 6.7; N, 6.3. C₄₇H₄₃N₃ requires C, 86.9; H, 6.7; N, 6.5%); λ_{max} (CH₂Cl₂)/nm 319 (log ε 6.91); ν_{max} (KBr)/cm⁻¹ 3030m, 2918m, 2851m, 1592s, 1503s, 1450m, 1308s, 1268s, 1218m, 824m, 749m, 695s, 568m and 514m; δ_H (250 MHz; C₆D₆) 2.03 (6H, s, Me), 2.12 (6H, s, Me), 2.14 (3H, s, Me), 6.94–7.06 (5H, m, Ar) and 7.19–7.37 (23H, m, Ar); δ_C (62.9 MHz; C₆D₆) 19.5, 20.2, 21.2, 122.4, 123.5, 123.7, 125.2, 125.4, 125.9, 127.2, 129.9, 130.7, 131.3, 132.0, 132.6, 138.2, 143.7, 143.9, 146.4, 146.7 and 149.4; *m/z* 649 (M⁺, 100%).

N,N-Bis{4-[*N*-(2,4-dimethylphenyl)-*N*-phenylamino]phenyl}tolylamine 6

General procedure as for compound 1. *N,N*-Bis(4-iodophenyl)tolylamine 13 (1.20 g, 2.31 mmol), *N*-(2,4-dimethylphenyl)-*N*-phenylamine (1.00 g, 5.10 mmol), copper powder (0.14 g, 2.30 mmol), K₂CO₃ (0.70 g, 5.10 mmol), 18-crown-6 (0.40 g) and *o*-dichlorobenzene (30 ml) were heated at 180 °C for 72 h. Yield 43%; yellow crystalline solid, mp 263–264 °C (from cyclohexane); λ_{max} (CH₂Cl₂)/nm 327 (log ε 6.19); ν_{max} (KBr)/cm⁻¹ 3094w, 3034m, 2915m, 2855w, 1594m, 1502s, 1383w, 1309m, 1265s, 1232m, 1110w, 879w, 816m, 749m, 693m, 587w, 549w and 512m; δ_H (250 MHz; C₆D₆) 2.21 (6H, s, Me), 2.24 (3H, s, Me), 2.28 (6H, s, Me), 6.89–7.11 (6H, m, Ar) and 7.18 (22H, m, Ar); δ_C (62.9 MHz; C₆D₆) 19.1, 21.2, 21.4, 121.2, 121.4, 124.0, 124.6, 125.5, 129.8, 130.2, 130.6, 132.2, 133.2, 136.0, 136.8, 143.2, 143.3, 143.8, 146.7 and 148.8 (one overlapping peak); *m/z* 649 (M⁺, 100%). Acc. mass: calc. 649.3457, found 649.3450.

N,N,N',N'-Tetraphenyl-*o*-phenylenediamine 7

General procedure as for compound 1. *N*-Phenyl-*o*-phenylenediamine (5.00 g, 27.3 mmol), iodobenzene (100 g, 480 mmol), copper powder (5.00 g, 82.0 mmol), K₂CO₃ (20.0 g, 164 mmol) and 18-crown-6 (0.50 g) were refluxed at 188 °C for 6 h. Yield 63%, as a colourless solid, mp 175–176 °C (from dichloromethane–light petroleum) (lit.^{11c} 168 °C) (Found: C, 87.1; H, 5.65; N, 6.6. C₃₀H₂₄N₂ requires C, 87.35; H, 5.9; N, 6.8%); λ_{max} (CH₂Cl₂)/nm 299 (log ε 5.97); ν_{max} (KBr)/cm⁻¹ 3063m, 3033m, 1586s, 1518w, 1487s, 1438m, 1313s, 1266s, 1169m, 1075m, 1026w, 833w, 831w, 749s, 692s, 632m, 546w and 499m; δ_H (250 MHz; CDCl₃) 6.72–7.29 (24H, m, Ar); δ_C (62.9 MHz; CDCl₃) 122.3, 123.0, 125.3, 128.5, 129.5, 143.7 and 147.4; *m/z* 412 (M⁺, 100%).

N,N,N',N'-Tetrakis(2,4-dimethylphenyl)-*o*-phenylenediamine 8

General procedure as for compound 1. 1,2-Phenylenediamine (2.50 g, 23.1 mmol), 2,4-dimethyl-1-iodobenzene (60.0 g, 256 mmol), copper powder (2.91 g, 46.2 mmol), K₂CO₃ (12.8 g, 924 mmol) and 18-crown-6 (0.50 g) were heated to 180 °C for 24 h. Yield 42%; colourless solid, mp 271–272 °C (from dichloromethane–light petroleum) (Found: C, 86.6; H, 7.35; N, 5.1. C₃₈H₄₀N₂ requires C, 87.0; H, 7.7; N, 5.3%); λ_{max} (CH₂Cl₂)/nm 291 (log ε 5.35); ν_{max} (KBr)/cm⁻¹ 3006m, 2948m, 2915m, 2858m, 1590m, 1494s, 1444m, 1378w, 1294m, 1270m, 1253m, 1221s, 1157w, 1127m, 1036m, 872w, 821m and 754m; *m/z* 524 (M⁺, 30%).

N,N,N',N'-Tetra-4-tolyl-*o*-phenylenediamine 9

General procedure as for compound 1. 1,2-Phenylenediamine (1.00 g, 9.26 mmol), 4-iodotoluene (16.2 g, 74.0 mmol), copper powder (2.33 g, 37.0 mmol), K₂CO₃ (10.2 g, 74.0 mmol), 18-crown-6 (0.50 g) and *o*-dichlorobenzene (20 ml) were heated to 180 °C for 18 h. Yield 69%; colourless solid, mp 144–145 °C (from dichloromethane–light petroleum) (Found: C, 87.0; H, 6.5; N, 5.5. C₃₄H₃₂N₂ requires C, 87.1; H, 6.9; N, 6.0%); λ_{max} (CH₂Cl₂)/nm 301 (log ε 4.86); ν_{max} (KBr)/cm⁻¹ 3026m, 2916m, 2858m, 1606s, 1590m, 1548w, 1506s, 1487s, 1446s, 1348w, 1315s, 1291s, 1265s, 1109m, 1048m, 1016m, 811s, 754s and 708m; δ_H (250 MHz; CDCl₃) 2.22 (12H, s, Me), 6.60–6.64 (8H, d, *J* 8.0, Ar), 6.87–6.90 (8H, d, *J* 8.0, Ar) and 6.97–7.06 (4H, m, Ar); δ_C (62.9 MHz; CDCl₃) 20.8, 123.1, 124.6, 128.9, 129.0, 131.4, 143.8 and 145.5; *m/z* 468 (M⁺, 100%).

N,N,N',N'-Tetra-4-tolyl-4,5-dimethyl-*o*-phenylenediamine 10

General procedure as for compound 1. 4,5-Dimethyl-1,2-phenylenediamine (1.00 g, 7.35 mmol), 4-iodotoluene (14.4 g, 66.2 mmol), copper powder (2.12 g, 33.1 mmol), K₂CO₃ (9.13 g, 66.2 mmol), 18-crown-6 (0.50 g) and *o*-dichlorobenzene (20 ml) were heated to 180 °C for 18 h. Yield 63%; colourless solid, mp 219–220 °C (from dichloromethane–light petroleum) (Found: C, 86.9; H, 7.1; N, 5.4. C₃₆H₃₆N₂ requires C, 87.1; H, 7.3; N, 5.6%); λ_{max} (CH₂Cl₂)/nm 303 (log ε 4.69); ν_{max} (KBr)/cm⁻¹ 3019m, 2918m, 2859m, 1605s, 1579w, 1506s, 1450m, 1396m, 1313s, 1296m, 1262m, 1220m, 1108m, 1017w, 877w, 813s, 783w, 754w, 711m and 619w; δ_H (250 MHz; CDCl₃) 2.13 (6H, s, Me), 2.21 (12H, s, Me), 6.60–6.64 (8H, d, *J* 8.0, Ar) and 6.85–6.88 (10H, d, *J* 9.0, Ar); δ_C (62.9 MHz; CDCl₃) 19.8, 21.7, 122.8, 129.0, 130.1, 130.9, 133.4, 141.5 and 145.6; *m/z* 496 (M⁺, 100%).

N,N,N',N'-Tetra-4-tolyl-*p*-phenylenediamine 11

General procedure as for compound 1. 1,4-Phenylenediamine (1.00 g, 9.26 mmol), 4-iodotoluene (16.2 g, 74.0 mmol), copper powder (2.33 g, 37.0 mmol), K₂CO₃ (10.2 g, 74.0 mmol), 18-crown-6 (0.50 g) and *o*-dichlorobenzene (20 ml) were heated to 180 °C for 12 h. Yield 35%; colourless solid, mp 271–272 °C (from dichloromethane–light petroleum) (Found: C, 87.4; H, 6.7; N, 5.85. C₃₄H₃₂N₂ requires C, 87.1; H, 6.9; N, 6.0%); λ_{max} (CH₂Cl₂)/nm 313 (log ε 4.62); ν_{max} (KBr)/cm⁻¹ 3022m, 2915m, 2858w, 1607m, 1579w, 1501s, 1383w, 1318m, 1270s, 1110m, 838m, 815s and 713m; δ_H (250 MHz; C₆D₆) 2.24 (12H, s, Me), 7.03–7.07 (8H, d, *J* 8.0, Ar), 7.23–7.27 (8H, d, *J* 8.0, Ar) and 7.31 (4H, s, Ar); δ_C (62.9 MHz; C₆D₆) 21.2, 124.9, 125.5, 130.6, 132.4, 143.9 and 146.7; *m/z* 468 (M⁺, 100%).

4,4'-Bis[*N*-(2,4-dimethylphenyl)-*N*-phenylamino]biphenyl 15

N,N'-Diphenylbenzidine (78.0 g, 213 mmol), 2,4-dimethyl-iodobenzene (154.0 g, 664 mmol), copper powder (40.0 g, 635 mmol), K₂CO₃ (142 g, 1.02 mol) and 18-crown-6 (10.0 g) with *o*-dichlorobenzene (200 ml) as solvent were heated at

170 °C and stirred under nitrogen for 48 h with removal of residual H₂O. The mixture was cooled and slurried with CH₂Cl₂ and filtered. The filtrate was washed with distilled H₂O (×2) and the low boiling solvents removed under reduced pressure. The remaining brown residue was dissolved in THF and added slowly to MeOH with stirring. A brown solid precipitated. Column chromatography, eluting with dichloromethane–cyclohexane (3 : 1), gave a yellow solid. Crystallisation from dichloromethane–cyclohexane yielded the *title compound* (58.4 g, 50%) as a colourless solid, mp 108–109 °C (Found: C, 88.4; H, 6.8; N, 5.05. C₄₀H₃₆N₂ requires C, 88.2; H, 6.7; N, 5.1%); λ_{\max} (CH₂Cl₂)/nm 301 (log ϵ 4.96) and 349 (5.31); ν_{\max} (KBr)/cm⁻¹ 3029w, 2920m, 2847m, 1590s, 1492s, 1448m, 1315s, 1290m, 1231m, 1175m, 1028w, 816m, 749w, 697m, 620w, 577w and 542w; δ_{H} (250 MHz; CDCl₃) 2.01 (6H, s, Me), 2.33 (6H, s, Me), 6.86–7.06 (15H, m, Ar), 7.16–7.25 (5H, m, Ar) and 7.35–7.39 (4H, d, *J* 8.5, Ar); δ_{C} (62.9 MHz; CDCl₃) 18.5, 21.0, 121.2, 121.4, 127.0, 128.1, 129.0, 129.5, 132.4, 133.5, 135.8, 136.3, 142.6, 146.3 and 147.4 (one overlapping peak); *m/z* 544 (M⁺, 100%).

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References

- 1 M. J. Plater, M. McKay and T. Jackson, *J. Chem. Soc., Perkin Trans. 1*, 2000, 2695.
- 2 (a) R. H. Young and J. J. Fitzgerald, *J. Phys. Chem.*, 1995, **99**, 4230; (b) M. Van der Auweraer, F. C. De Schryver, P. M. Borsenberger and J. J. Fitzgerald, *J. Phys. Chem.*, 1993, **97**, 8808; (c) G. Verbeek, M. Van der Auweraer, F. C. De Schryver, C. Geelen, D. Terrell and S. De Meuter, *Chem. Phys. Lett.*, 1992, **188**, 85.
- 3 H. Tanaka, S. Tokito, Y. Taga and A. Okada, *Chem. Commun.*, 1996, 2175.
- 4 Review: (a) Y. Shirota, *J. Mater. Chem.*, 2000, **10**, 1; (b) K. Yoshizawa, A. Chano, A. Ito, K. Tanaka, T. Yamabe, H. Fujita, J. Yamauchi and M. Shiro, *J. Am. Chem. Soc.*, 1992, **114**, 5994; (c) K. R. Stickley and S. C. Blackstock, *Tetrahedron Lett.*, 1995, **36**, 1585; (d) R. J. Bushby and K. M. Ng, *Chem. Commun.*, 1996, 659; (e) K. Sato, M. Yano, M. Furuichi, D. Shiomi, T. Takui, K. Abe, K. Itoh, A. Higuchi, K. Katsuma and Y. Shirota, *J. Am. Chem. Soc.*, 1997, **119**, 6607; (f) M. M. Wienk and R. A. J. Janssen, *J. Am. Chem. Soc.*, 1997, **119**, 4492; S. Tanaka, T. Iso and Y. Doke, *Chem. Commun.*, 1997, 2063.
- 5 (a) M. C. Harris and S. L. Buchwald, *J. Org. Chem.*, 2000, **65**, 5327; (b) review: J. F. Hartwig, *Angew. Chem., Int. Ed.*, 1998, **37**, 2046; (c) J. P. Wolfe, S. Wagaw and S. L. Buchwald, *J. Am. Chem. Soc.*, 1996, **118**, 7215; (d) M. S. Driver and J. F. Hartwig, *J. Am. Chem. Soc.*, 1996, **118**, 7217; (e) R. A. Singer, J. P. Sadighi and S. L. Buchwald, *J. Am. Chem. Soc.*, 1998, **120**, 213; (f) J. Louie and J. F. Hartwig, *J. Am. Chem. Soc.*, 1997, **119**, 11695; (g) K. Hori and M. Mori, *J. Am. Chem. Soc.*, 1998, **120**, 7651.
- 6 (a) Y. Shirota, T. Kobata and N. Noma, *Chem. Lett.*, 1989, 1145; (b) S. Sasaki and M. Iyoda, *Chem. Lett.*, 1995, 1011; K. Naito and A. Miura, *J. Phys. Chem.*, 1993, **97**, 6240.
- 7 T. N. Baker, W. P. Doherty, W. S. Kelley, W. Newmeyer, J. E. Rogers, R. E. Spalding and R. I. Walter, *J. Org. Chem.*, 1965, **30**, 3714.
- 8 P. Strohriegel, G. Jesberger, J. Heinze and T. Moll, *Makromol. Chem.*, 1992, **193**, 909.
- 9 H. Tanaka, Y. Yamaguchi and M. Yokoyama, *Denshi Shashin Gakkaishi*, 1990, **29**, 366.
- 10 R. G. Bacon and S. D. Hamilton, *J. Chem. Soc., Perkin Trans. 1*, 1972, **18**, 2391.
- 11 (a) S. Dapperheld, E. Steckhan, K. H. Brinkhaus and T. Esch, *Chem. Ber.*, 1991, **124**, 2557; (b) M. Yano, K. Sato, D. Shiomi, A. Ichimura, K. Abe, T. Takui and K. Itoh, *Tetrahedron Lett.*, 1996, **37**, 9207; (c) F. Welzel, *Chem. Ber.*, 1970, **103**, 1318.
- 12 D. Pletcher, *A First Course in Electrode Processes*, Alresford Press Ltd, Alresford, 1991.
- 13 E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy and R. N. Adams, *J. Am. Chem. Soc.*, 1966, 3498.
- 14 T. Kitamura and M. Yokoyama, *J. Appl. Phys.*, 1991, **69**, 821.