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Polyaromatic amines. Part 4: Synthesis of poly(ethynyl) linked aromatic amines

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Abstract—The title compounds were synthesised and characterised as part of a study into new aromatic amines for charge transporting materials. Each compound was characterised by cyclic voltammetry. A qualitative estimate of the intramolecular charge mobility was deduced from the difference between the first and second oxidation potentials. © 2003 Elsevier Science Ltd. All rights reserved.

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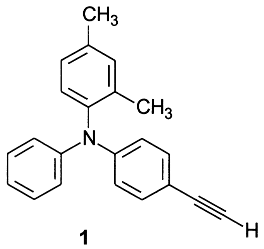
1. Introduction

Polyaromatic amines are of interest owing to their potential applications in electrophotography and electroluminescent devices.[1–6] In the search for new potential charge transport materials we have prepared and characterised some series of aromatic amines.[1–3] This paper reports compounds in which the aromatic amines are linked by ethynyl groups. The ethynyl group was of interest as a conjugating group because the two attached substituents can rotate and remain conjugated. This might facilitate intra-molecular charge mobility possibly aiding charge transport by lowering the overall oxidation potential.



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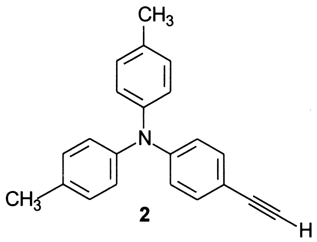

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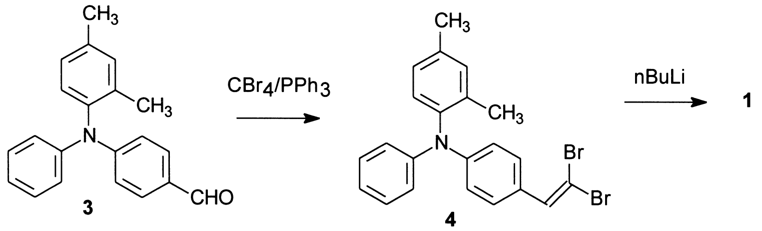
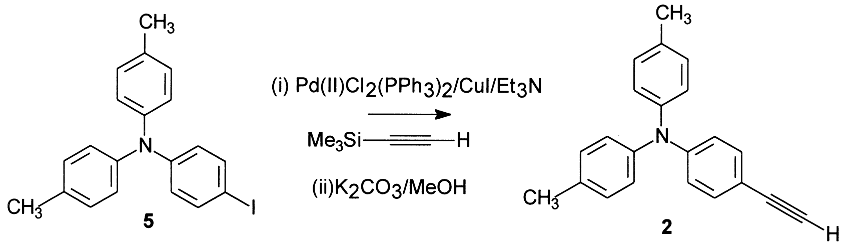


Scheme 1.



Scheme 2.

Keywords: aromatic amines; thiophene; anthracene; alkyne; acetylene.

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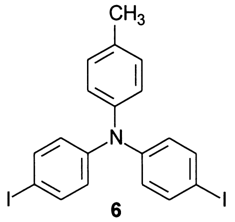
2. Results and discussion

The ethynyl linked amines **8**–**12** and **15**,**16** have been prepared via palladium catalysed coupling reactions of the ethynyl building blocks **1** and **2**. Alkyne **1** was prepared by treatment of aromatic aldehyde **3** with CBr_4 and PPh_3 followed by *n*BuLi (Scheme 1). Alkyne **2** was prepared by palladium catalysed coupling of mono-iodoarylamine **5** with trimethylsilylacetylene followed by deprotection (Scheme 2). Amine **5** was prepared by iodination of *N*,*N*-di(tolyl)phenylamine using iodine and mercuric oxide.[7] The bis- and tris-iodinated amine precursors **6** and **7** have been described previously.[2] Dimer **8** was obtained by oxidative coupling of acetylene **1** using $Pd(0)(PPh_3)_4$ and CuI (Scheme 3). Compound **9** was obtained by palladium catalysed coupling of acetylene **1** with 1,4-diiodobenzene (Scheme 4). Compound **10**, containing three amines, was prepared by palladium catalysed coupling of acetylene **1** with bis-iodinated precursor **6** (Scheme 5). Compound **11** was obtained in a similar manner but using acetylene **2**. Compound **12** containing four amines was prepared from tris-iodinated amine **7** and acetylene **2**. Compounds **15** and **16** were prepared from acetylene **2** and diiodoanthracene **13**[8] or thiophene **14**, respectively (Scheme 6).



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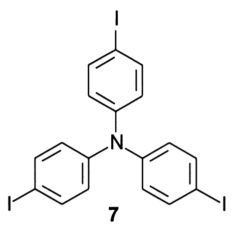

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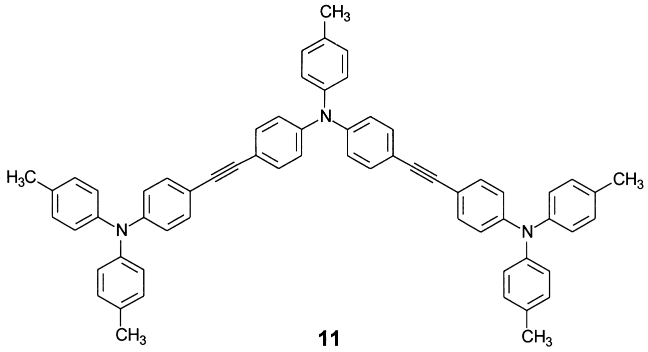

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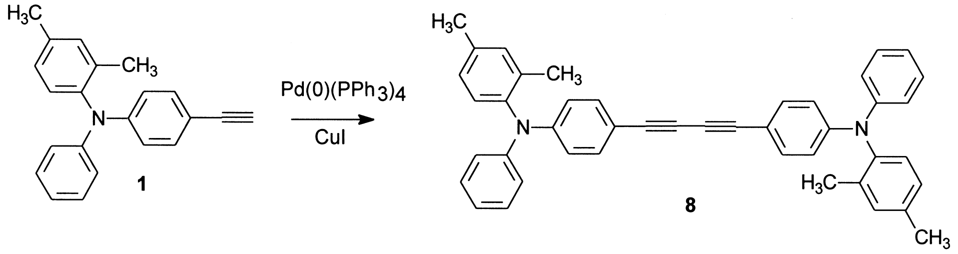
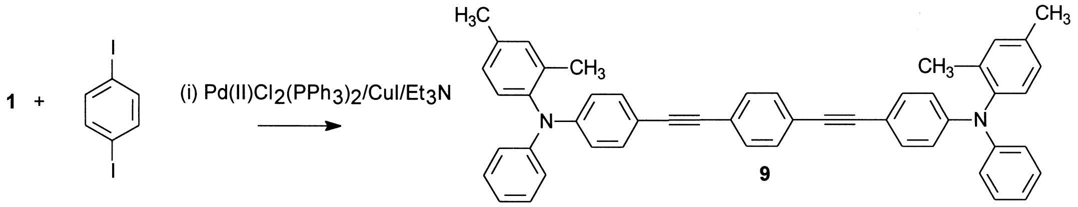
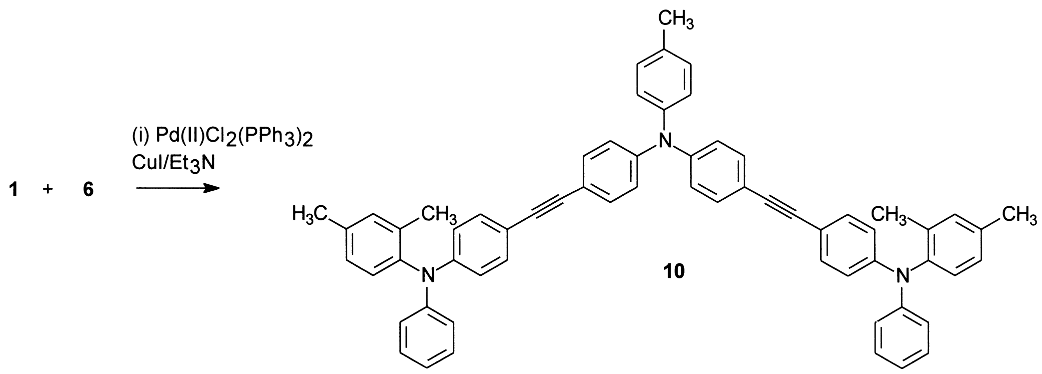


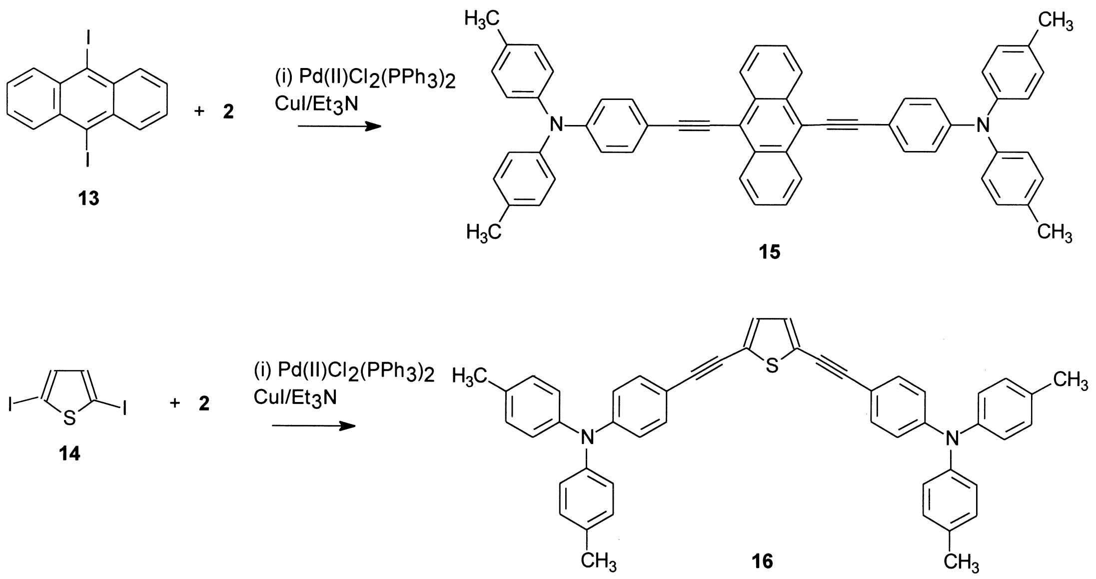
Scheme 3.



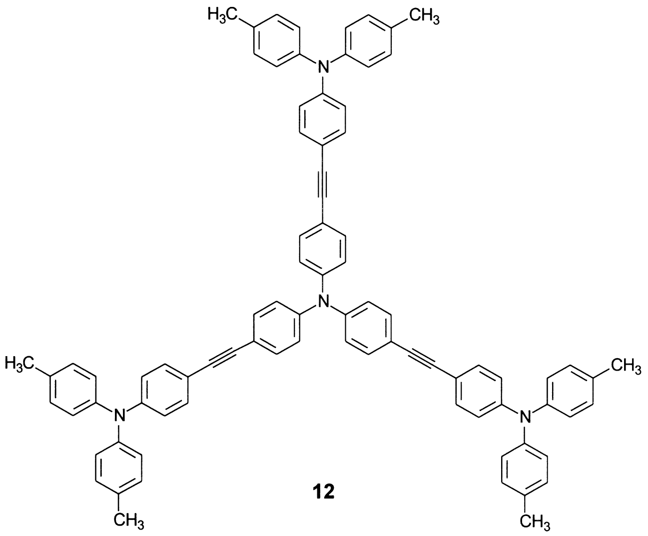
Scheme 4.



Scheme 5.



Scheme 6.



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3. Cyclic voltammetry

The electrochemical methods used have been described previously.[2] Data for triphenylamine (TPA) and 4,4′-bis-[*N*-(2,4-dimethylphenyl-*N*-phenylamino)]biphenyl (TPD) is included for comparison and has been described previously.[2] When a compound displays two reversible oxidation states, a large potential gap is indicative of good electronic communication between the charges. TPD shows a potential gap of 220 mV. The butadiyne compound **8** shows a potential gap of 100 mV indicating that the charges are more isolated from each other than in TPD. Compounds **9** and **16** only show one reversible oxidation state at 1.05 and 0.96 V, respectively. The absence of a second oxidation state suggests that the first positive charge is not delocalised over the molecule i.e. if a second oxidation occurs, it occurs at the same potential as the first one. Thiophene is the most aromatic of the π-excessive heterocycles with an aromaticity close to that of benzene so the similar CV properties of these two compounds is reasonable. Compounds **10** and **11** both contain three arylamines and both show three reversible oxidation states. Compound **12** has four arylamines and again has three reversible oxidation states. Compound **15**, with an anthracene spacer, shows three reversible oxidation states. This is unusual given that the related compounds **9** and **16**, which have benzene ring and thiophene spacers respectively, only show one reversible oxidation state. This indicates that anthracene, in contrast to benzene and thiophene, extends the delocalisation of the system and promotes conjugation between the two amine centres. Anthracene is itself relatively easily oxidised and

Table 1. Summary of electrochemical analyses. Oxidation potentials, E_{pa}, reduction potentials, E_{pc}, and peak current density ratio's i_{pc}/i_{pa} of triarylamines versus SCE

Compound	1st Redox			2nd Redox			3rd 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}
TPA	1.21	0.91	0.57						
TPD	0.81	0.70	1.0	1.03	0.93	1.0			
8	1.02	0.94	1.0	1.12	1.07	1.0			
9	1.05	0.96	0.97						
10	0.86	0.80	0.95	1.02	0.96	0.97	1.13	1.05	0.91
11	0.82	0.78	0.97	0.94	0.89	0.94	1.07	1.00	0.92
12	0.86	0.79	1.0	0.95	0.84	0.98	1.15	1.08	0.98
15	0.81	0.77	1.0	0.87	0.84	0.97	1.41	1.32	0.96
16	0.96	0.85	1.0						

the reversible redox couple at 1.41 V is the result of this oxidation. The potential gap between the first two oxidation states of 60 mV is however, quite small. The two oxidation states are so close that they are difficult to distinguish and a clearer interpretation was obtained from square wave voltammetry. Square wave voltammetry is a differential technique which takes the difference between the current at the forward step and the current at the reverse step against potential. This has the advantage of amplifying the signal from a reversible redox couple. Square wave voltammetry was also carried out on compound **12** which has two close oxidation states. The square wave voltammagram revealed three redox couples for the four triarylamine moieties. Interestingly the second peak is approximately double the size of the other two suggesting that the second oxidation is a two electron process. Presumably two amines therefore have the same oxidation potential and are oxidised at the same time which explains why four separate oxidation states are not observed (Table 1).

In summary this series of papers has provided synthetic methods and cyclic voltammetry data which is one of the tools for assessing the suitability of aromatic amines as materials for charge transport layers.

4. Experimental

4.1. General

For general details see part 1 in this series.[1]

4.1.1. 1,1′-Dibromo-2-{4-[*N*-(2,4-dimethylphenyl)-*N*-phenyl]benzene}ethene 4. *Method A*. 4-[*N*-(2,4-Dimethylphenyl)-*N*-phenylamino]benzaldehyde **3** (2.0 g, 6.65 mmol) in CH_2Cl_2 (10 mL) was added to a reagent prepared from the interaction of zinc dust (0.86 g, 13.3 mmol), PPh_3 (3.48 g, 13.3 mmol) and CBr_4 (4.40 g, 13.3 mmol) in CH_2Cl_2 (50 mL) for 3 h. After 2 h the reaction mixture was washed with distilled H_2O (×2) and dried over $MgSO_4$. The mixture was then filtered through silica and basic alumina and the solvents removed under reduced pressure to yield the title compound (0.95 g, 31%) as a viscous yellow oil. (Found: C, 58.2; H, 4.3; N, 2.9. $C_{22}H_{19}NBr_2$ requires C, 57.8; H, 4.2; N, 3.1%); λ_{max} (CH_2Cl_2)/nm 298 (log ε 4.71) and 347 (5.35). ν_{max} (KBr)/cm^{-1} 3060m, 3029s, 2960s, 2912s, 2869s, 1602s, 1555m, 1507s, 1489s, 1456m, 1400w, 1377m, 1316s, 1276s, 1232s, 1179s, 1154w, 1123m, 1077w, 1029m, 943m, 920w, 870s, 817s, 779s, 752s, 732m, 695s, 646w and 604m. δ_H(400 MHz; $CDCl_3$) 1.96 (3H, s, Me), 2.30 (3H, s, Me), 6.82–6.84 (2H, d, *J*=9.0 Hz, Ar), 6.93–7.04 (6H, m, Ar), 7.16–7.22 (2H, m, Ar), 7.32 (1H, s, vinyl) and 7.36–7.39 (2H, d, *J*=8.9 Hz, Ar); δ_C (62.9 MHz; $CDCl_3$) 19.4, 22.1, 87.1, 120.3, 123.4, 123.6, 128.1, 129.3, 130.2, 130.4, 130.6, 133.5, 137.4, 143.0, 147.6 and 148.9 (two overlapping peaks). *m*/*z* 457 (M^+, 100%).

Method B. To a solution of CBr_4 (4.40 g, 13.30 mmol) in dry CH_2Cl_2 (100 mL), under nitrogen, was added, at −20°C (CH_2Cl_2/nitrogen slush bath), a solution of PPh_3 (3.48 g, 13.30 mmol). An intense yellow colour developed which darkened after 15 min. A solution of 4-[*N*-(2,4-dimethylphenyl)-*N*-phenylamino]benzaldehyde **3** (2.0 g, 6.64 mmol) and NEt_3 (0.67 g, 6.64 mmol) in dry CH_2Cl_2 (30 mL) was added at −60°C ($CHCl_3$/dry CO_2). After warming the mixture was stirred for 1 h and then poured into H_2O, extracted with CH_2Cl_2, and dried over $MgSO_4$. Solvents were removed under reduced pressure. Column chromatography, eluting with dichloromethane/light petroleum (15:85), yielded the title compound (1.26 g, 42%) as a viscous yellow oil. Spectroscopic properties identical to those obtained for Method A.

4.1.2. *N*-(2,4-Dimethyl)phenyl-*N*-phenyl-4-(ethynyl)phenylamine 1. In a dry, nitrogen purged flask 1,1′-dibromo-2-{4-[*N*-(2,4-dimethylphenyl)-*N*-phenylamino]benzene}ethene **4** (1.37 g, 2.99 mmol) was dissolved in dry THF (30 mL). The solution was cooled to −78°C. Under nitrogen with stirring *n*-BuLi (4.0 mL, 6.28 mmol, 1.57 M in hexane) was added dropwise forming a yellow then dark red solution. After 30 min the reaction mixture was allowed to warm to room temperature and allowed to stir for a further hour then poured into H_2O and extracted with CH_2Cl_2, dried over $MgSO_4$ and solvents removed under reduced pressure to leave a dark orange/red oil. Column chromatography, eluting with dichloromethane/light petroleum (15:85) yielded the title compound (0.51 g, 57%) as a viscous light yellow oil. (Found: C, 88.2; H, 6.0; N, 4.9. $C_{22}H_{19}N$ requires C, 88.45; H, 6.4; N, 4.7%); λ_{max} (CH_2Cl_2)/nm 323 (log ε 5.63); ν_{max} (KBr)/cm^{-1} 3313m, 3289s, 3036m, 2956s, 2922s, 2867m, 2103m, 1543s, 1558w, 1499s, 1456m, 1377w, 1315s, 1293s, 1231m, 1172m, 1029w, 818w, 829m, 751m, 732w, 695m and 584w; δ_H (400 MHz; $CDCl_3$) 1.96 (3H, s, Me), 2.31 (3H, s, Me), 2.96 (1H, s, ethynyl), 6.78–6.81 (2H, d, *J*=9.1 Hz, Ar), 6.91–7.03 (6H, m, Ar), 7.17–7.22 (2H, m, Ar) and 7.25–7.27 (2H, d, *J*=9.1 Hz, Ar); δ_C (100.5 MHz; $CDCl_3$) 19.3, 22.0, 76.7, 85.2, 114.3, 120.4, 123.5, 123.7, 129.3, 130.2, 130.5, 133.5, 134.0, 137.4, 143.0, 147.6 and 149.1 (one overlapping peak); *m*/*z* 297 (M^+, 100%).

4.1.3. *N*,*N*-Di(4-tolyl)-4′-iodophenylamine 5. *N*,*N*-Di-(tolyl)phenylamine (5.0 g, 18.3 mmol) was dissolved in boiling EtOH (80 mL) to which red mercuric oxide (7.39 g, 34.2 mmol) was added and slurried with vigorous stirring. Iodine (11.72 g, 46.2 mmol) was gradually added and the mixture left to reflux at 78°C for 2.5 h. The EtOH was removed under reduced pressure and the residues dissolved in CH_2Cl_2, washed with aqueous $Na_2S_2O_3$ solution then distilled H_2O and filtered through silica. The solvents were removed under reduced pressure. Column chromatography, eluting with dichloromethane/light petroleum (15:85), gave a viscous yellow oil which recrystallised on standing to yield the title compound (4.50 g, 62%) as a yellow crystalline solid, mp 93–94°C (from hexane) (lit. 88–89°C).[7] (Found: C, 59.4; H, 4.25; N, 3.0. $C_{20}H_{18}NI$ requires C, 60.1; H, 4.5; N, 3.5%); λ_{max} (CH_2Cl_2)/nm 302 (log ε 5.68); ν_{max} (KBr)/cm^{-1}: 3024m, 2914m, 2856m, 1604m, 1578s, 1535w, 1507s, 1482s, 1320s, 1269s, 1176m, 1109m, 1060w, 999m, 916w, 854s, 709m, 563m, 512s, 488m and 445w; δ_H (250 MHz; $CDCl_3$) 2.30 (6H, s, Me), 6.74–6.77 (2H, d, *J*=8.2 Hz, Ar), 6.94–6.98 (4H, d, *J*=8.3 Hz, Ar), 7.04–7.07 (4H, d, *J*=8.4 Hz, Ar) and 7.42–7.46 (2H, d, *J*=8.2 Hz, Ar); δ_C (100.5 MHz; $CDCl_3$) 21.9, 84.4, 125.1, 125.8, 131.0, 134.1, 138.8, 145.8 and 149.2; *m*/*z* 399 (M^+, 100%).

4.1.4. *N,N*-Di(4-tolyl)-4′-(ethynyl)phenylamine 2. *N,N*-Di(4-tolyl)-4′-iodophenylamine **5** (4.0 g, 10.0 mmol) was dissolved in dry, degassed NEt_3 (20 mL) under nitrogen. To this was added trimethylsilylacetylene (1.70 mL, 12.0 mmol), bis(triphenylphosphine)palladium(II) chloride (35 mg) and copper iodide (5 mg). The mixture was refluxed at 66°C under nitrogen with stirring for 2 h. The mixture was cooled and poured into distilled H_2O (100 mL), extracted with CH_2Cl_2, dried over $MgSO_4$ and solvents were removed under reduced pressure. The residues were dissolved in dichloromethane/light petroleum and filtered through silica and the solvent removed. The resultant yellow oil was then dissolved in dry MeOH to which K_2CO_3 (1.38 g, 10.0 mmol) was added and the mixture left to stir under nitrogen for 18 h. The MeOH was removed under reduced pressure and the residues were dissolved in CH_2Cl_2, washed with distilled H_2O (×2), dried over $MgSO_4$ and the CH_2Cl_2, removed under reduced pressure. Column chromatography, eluting with dichloromethane/light petroleum (15:85) yielded an orange oil which recrystallised on standing to give the title compound (1.73 g, 62%) as an orange crystalline solid, mp 95–96°C. λ_{max} (CH_2Cl_2)/nm 326 (log ε 5.73); ν_{max} (KBr)/cm^{-1} 3310w, 3283s, 3026m, 2922m, 2854m, 2101m, 1597s, 1499s, 1381w, 1320s, 1292s, 1268s, 1213m, 1175m, 1109m, 1015w, 816s, 714w, 655m, 608m and 551m; δ_H (250 MHz; $CDCl_3$) 2.31 (6H, s, Me), 2.99 (1H, s, ethynyl), 6.87–6.91 (2H, d, J=9.2 Hz, Ar), 6.97–7.01 (4H, d, J=8.4 Hz, Ar) and 7.06–7.09 (4H, d, J=8.3 Hz, Ar), 7.26–7.30 (2H, d, J=9.1 Hz); δ_C (62.9 MHz; $CDCl_3$) 20.9, 75.8, 84.2, 113.7, 120.8, 125.3, 130.1, 133.0, 133.4, 144.6 and 148.8; *m/z* 297 (M^+, 100%).

4.1.5. *N,N*′-Diphenyl-*N,N*′-bis(2,4-dimethylphenyl)-4-(diethynyl)diphenyldiamine 8. In a dry flask *N*-(2,4-dimethyl)phenyl-*N*-phenyl-4-(ethynyl)phenylamine **1** (0.20 g, 67.3 was dissolved in dry THF (25 mL) and Et_3N (5 mL). To this was added bis(triphenylphosphine)palladium(II) chloride (10 mg) and copper iodide (3 mg). The reaction mixture was refluxed at 65°C under nitrogen with stirring for 1 h. Once cooled the reaction mixture was washed in distilled H_2O (×2), extracted with CH_2Cl_2, dried over $MgSO_4$ and the solvents removed under reduced pressure. Column chromatography, eluting with dichloromethane/light petroleum (15:85) yielded a viscous yellow/orange oil which solidified on complete removal of solvent (50 mg, 25%) as an orange solid, mp 79–80°C. λ_{max} (CH_2Cl_2)/nm 297 (log ε 5.45) and 371 (6.71); ν_{max} (KBr)/cm^{-1} 3035w, 2953w, 2917w, 2855w, 2144w, 1601w, 1590s, 1497s, 1383w, 1315s, 1291m, 1231m, 1171m, 1124w, 1028w, 826m, 752w, 694m and 622w; δ_H (250 MHz; $CDCl_3$): 2.08 (6H, s, Me), 2.43 (6H, s, Me), 6.74–6.87 (4H, d, J=9.1 Hz, Ar), 6.97–7.13 (10H, m, Ar), 7.18–7.28 (6H, m, Ar) and 7.29–7.33 (4H, d, J=9.1 Hz, Ar); δ_C (100.5 MHz; $CDCl_3$) 18.3, 21.1, 73.2, 82.1, 112.9, 119.1, 122.8, 123.0, 128.3, 129.2, 129.5, 132.5, 133.4, 136.3, 136.5, 141.8, 146.3 and 148.2; *m/z* 592 (M^+, 100%). Accurate mass: calculated 593.2957, found 593.2918.

4.1.6. 1,4-Bis[*N*-(2,4-dimethyl)-*N*-phenyl-4-(ethynyl)-phenylamine]benzene 9. *N*-(2,4-Dimethyl)-*N*-phenyl-4-(ethynyl)phenylamine **1** (0.40 g, 1.37 mmol) and diiodobenzene (0.22 g, 0.667 mmol) were dissolved in dry, degassed Et_3N (25 mL) to which catalytic amounts of copper iodide and bis(triphenylphosphine)palladium(II) chloride were added. With stirring in a strictly nitrogen atmosphere the mixture was refluxed at 89°C for 1 h. After cooling the reaction mixture was washed with distilled H_2O (×2) and dried over $MgSO_4$. Solvents were removed under reduced pressure. Column chromatography, eluting with dichloromethane/light petroleum (25:75) yielded two products. The more polar fraction was recrystallised from dichloromethane/light petroleum to give the title compound (0.22 g, 49%) as a yellow crystalline solid, mp 244–245°C. (Found: C, 90.1; H, 6.2; N, 3.9. $C_{50}H_{40}N_2$ requires C, 89.8; H, 6.0; N, 4.2%); λ_{max} (CH_2Cl_2)/nm 295 (log ε 4.98) and 382 (5.47); ν_{max} (KBr)/cm^{-1} 3045m, 2917m, 2211m, 1589s, 1515s, 1490s, 1402w, 1382w, 1316s, 1289s, 1231m, 1177m, 1147m, 1122w, 1028w, 881w, 836s, 749m, 720w, 693m and 625w; δ_H (250 MHz; $CDCl_3$) 2.01 (6H, s, Me), 2.34 (6H, s, Me), 6.84–6.88 (4H, d, J=8.9 Hz, Ar), 6.94–7.07 (9H, m, Ar), 7.20–7.30 (7H, m, Ar), 7.30–7.34 (4H, d, J=9.0 Hz, Ar) and 7.44 (4H, s, Ar); δ_C (100.5 MHz; $CDCl_3$): 19.4, 22.1, 89.2, 92.7, 115.4, 120.6, 123.4, 123.7, 124.1, 129.3, 130.2, 130.5, 132.3, 133.5, 133.6, 137.3, 143.1, 147.7 and 148.8 (one overlapping peak); *m/z* 668 (M^+, 100%). Additionally 4-[*N*-(2,4-dimethyl)-*N*-phenyl-4-(ethynyl)phenylamine]iodobenzene was isolated and recrystallised from dichloromethane/light petroleum (0.11 g, 32%), mp 89–90°C.

ν_{max} (KBr)/cm^{-1} 3033m, 2916m, 2856w, 2208m, 1591s, 1505s, 1492s, 1388w, 1313s, 1289s, 1268s, 1231m, 1174m, 1135m, 1056w, 1004m, 880w, 816s, 755s, 731m, 694s, 597w, 572m and 516m; δ_H (250 MHz; $CDCl_3$) 2.00 (6H, s, Me), 2.34 (3H, s, Me), 6.83–6.87 (2H, d, J=9.0 Hz, Ar), 6.94–7.07 (5H, m, Ar), 7.19–7.33 (7H, m, Ar) and 7.63–7.67 (2H, d, J=9.1 Hz Ar); δ_C (100.5 MHz; $CDCl_3$) 19.4, 22.1, 88.4, 92.5, 94.4, 115.1, 120.5, 123.5, 123.7, 124.4, 129.3, 130.2, 130.5, 133.5, 133.6, 134.0, 137.3, 137.3, 138.5, 143.0, 147.6 and 148.9; *m/z* 499 (M^+, 100%).

4.1.7. 4,4′-Bis[*N*-(2,4-dimethyl)-*N*-phenyl-4-(ethynyl)-phenylamine]-*N,N*-diphenyltolylamine 10. General procedure as for **9**. *N*-(2,4-Dimethyl)-*N*-phenyl-4-(ethynyl)-phenylamine **1** (0.25 g, 0.862 mmol), *N,N*-di(4-iodophenyl)-tolylamine **6** (0.15 g, 0.431 mmol), Et_3N (20 mL), copper iodide and bis(triphenylphosphine)palladium(II) chloride in catalytic quantities were refluxed for 1 h. Yield 24%; yellow crystalline solid, mp 117–118°C (from light petroleum). λ_{max} (CH_2Cl_2)/nm 280 (log ε 5.25) and 388 (6.20); ν_{max} (KBr)/cm^{-1} 3036m, 2954m, 2916m, 2863m, 1597s, 1508s, 1490s, 1377w, 1318s, 1289s, 1231m, 1175m, 1108w, 1030w, 918w, 876w, 829s, 735m, 721m, 694s, 572s, 521m and 456w; δ_H (250 MHz; $CDCl_3$) 1.99 (6H, s, Me), 2.34 (9H, s, Me), 6.84–6.87 (4H, d, J=8.2 Hz, Ar), 6.92–7.11 (20H, m, Ar), 7.18–7.22 (4H, d, J=8.1 Hz, Ar) and 7.28–7.35 (8H, m, Ar); δ_C (100.5 MHz; $CDCl_3$) 19.4, 21.9, 22.1, 89.3, 90.3, 116.0, 118.3, 120.8, 123.2, 123.5, 123.9, 126.8, 129.3, 130.2, 130.5, 131.2, 133.3, 133.4, 133.5, 135. 0, 137.2, 137.3, 143.2, 145.2, 147.8, 148.1 and 148.4; *m/z* 849 (M^+, 100%). Accurate mass: calculated 849.4943, found 849.4955.

4.1.8. 4,4′-Bis[*N,N*-di(tolyl)-4′-(ethynyl)phenylamine]-*N,N*-diphenyltolylamine 11. General procedure as for **9**. *N,N*-Di(4-tolyl)-4′-(ethynyl)phenylamine **2** (0.50 g, 1.68 mmol) and *N,N*-di(4-iodophenyl)tolylamine **6** (0.29 g, 0.840 mmol), Et_3N (20 mL) and copper iodide and bis(triphenylphosphine)palladium(II) chloride in catalytic quantities were refluxed for 1 h. Yield 41%; yellow crystalline solid, mp 136–137°C (from light petroleum). (Found: C, 88.6; H, 6.0; N, 4.6. $C_{63}H_{51}N_3$ requires C, 89.0; H, 6.05; N, 4.9%); λ_{max} (CH_2Cl_2)/nm 304 (log ε 5.34) and 390 (5.89); ν_{max} (KBr)/cm^{-1} 3030m, 2962m, 2925m, 1602s, 1505s, 1410w, 1321s, 1288s, 1276s, 1175m, 1106w, 1017w, 814m, 719w, 628w, 574m, 536w and 495w; δ_H (250 MHz; $CDCl_3$) 2.32 (15H, s, Me), 6.91–7.09 (28H, m, Ar) and 7.29–7.36 (8H, m, Ar); δ_C (100.5 MHz; $CDCl_3$) 20.9, 88.5, 89.3, 115.5, 117.2, 121.3, 123.0, 125.2, 125.8, 130.0, 130.2, 132.3, 132.4, 133.2, 134.0, 144.2, 144.8, 147.1 and 148.1 (one overlapping peak at δ 20.9); *m*/*z* 849 (M^+, 25%).

4.1.9. 4,4′,4″-Tris[*N*,*N*-di(tolyl)-4′-(ethynyl)phenylamine]triphenylamine 12. General procedure as for **9**. *N*,*N*-Di(4-tolyl)-4′-(ethynyl)phenylamine **2** (0.30 g, 1.01 mmol) and 4,4′,4″-triodotriphenylamine **7** (0.29 g, 0.840 mmol), Et_3N (25 mL) and copper iodide and bis(triphenylphosphine)palladium(II) chloride in catalytic quantities were refluxed for 1 h. Yield 31%; yellow crystalline solid, mp 142–143°C (from dichloromethane/light petroleum). λ_{max} (CH_2Cl_2)/nm 301 (log ε 5.72) and 390 (6.35); ν_{max} (KBr)/cm^{-1} 3033m, 2951m, 2920m, 2860m, 1601s, 1507s, 1383w, 1321s, 1286s, 1269s, 1175m, 1107m, 1016w, 917w, 814m, 719m, 641w, 576m, 500m and 405w; δ_H (250 MHz; $CDCl_3$) 2.31 (18H, s, Me), 6.90–7.09 (38H, m, Ar) and 7.28–7.39 (10H, m, Ar); δ_C (62.9 MHz; $CDCl_3$) 20.9, 88.2, 89.7, 115.2, 118.3, 121.2, 124.0, 125.2, 130.0, 132.3, 132.6, 133.3, 144.7, 146.4 and 148.2; *m*/*z* 1131(M^+, 100%). Accurate mass: calculated 1131.5366, found 1131.5325.

4.1.10. 9,10-Diiodoanthracene 13. 9,10-Dibromoanthracene (2.0 g, 5.95 mmol) was placed in a dry flask and slurried in anhydrous diethyl ether (20 mL) under nitrogen. To this was added *n*-BuLi (11.30 mL, 15.6 mol) dropwise while cooled to −78°C. The reaction mixture was then allowed to warm to room temperature and left to stir for 1 h. Iodine (5.0 g, 39.4 mmol) was then added and the mixture stirred until a dark brown colouration predominated. The mixture was then washed in an aqueous $Na_2S_2O_3$ solution (×2) and then with distilled H_2O. After filtering under vacuum the solids were dried in a vacuum oven at 80°C and subsequently recrystallised from hot CCl_4 to give the title compound (1.14 g, 45%) as a yellow crystalline solid, mp 257–258°C. (lit. 254–255°C).[8] δ_H (250 MHz; $CDCl_3$) 7.56–7.60 (4H, dd, *J*=3, 4 Hz, Ar) and 8.51–8.56 (4H, dd, *J*=3, 4 Hz, Ar); *m*/*z* 429 (M^+, 10%).

4.1.11. 9,10-Bis[*N*,*N*-di(tolyl)-4′-(ethynyl)phenylamine]anthracene 15. General procedure as for **9**. *N*,*N*-Di(4-tolyl)-4′-(ethynyl)phenylamine **2** (0.28 g, 0.932 mmol) and 9,10-diiodoanthracene **13** (0.20 g, 0.466 mmol), Et_3N (20 mL) and copper iodide and bis(triphenylphosphine)-palladium(II) chloride in catalytic quantities were refluxed for 1 h. Yield 66%; orange crystalline solid, mp 269–270°C (from dichloromethane/hexane). (Found: C, 90.2; H, 5.8; N, 3.2. $C_{58}H_{44}N_2$ requires C, 90.6; H, 5.8; N, 3.6%); λ_{max} (CH_2Cl_2)/nm 288 (log ε 5.12), 339 (4.95) and 504 (5.18); ν_{max} (KBr)/cm^{-1} 3024m, 2955w, 2917m, 2860w, 2210m, 1598s, 1504s, 1384w, 1320s, 1294s, 1276s, 1178m, 1107m, 1024m, 813m, 762m, 638m, 570w and 511m; δ_H (250 MHz; $CDCl_3$) 2.33 (12H, s, Me), 7.01–7.13 (20H, m, Ar), 7.53–7.61 (8H. m, Ar) and 8.63–8.68 (4H, q, *J*=3.2, 3.5 Hz, Ar); δ_C (62.9 MHz; $CDCl_3$) 20.9, 85.8, 103.1, 115.2, 118.5, 121.1, 125.3, 126.6, 127.4, 130.1, 132.0, 132.6, 133.5, 144.6 and 148.7; *m*/*z*768 (M^+, 100%).

4.1.12. 2,5-Bis[*N*,*N*-di(tolyl)-4′-(ethynyl)phenylamine]thiophene 16. General procedure as for **9**. *N*,*N*-Di(4-tolyl)-4′-(ethynyl)phenylamine **2** (0.30 g, 1.01 mmol) and 2,5-diiodothiophene **14** (0.17 g, 0.505 mmol), Et_3N and copper iodide and bis(triphenylphosphine)palladium(II) chloride in catalytic quantities were refluxed for 1 h. Yield 32%; yellow crystalline solid, mp 231–232°C (from dichloromethane/light petroleum). (Found: C, 85.7; H, 5.8; N, 3.9. $C_{48}H_{38}N_2S$ requires C, 85.4; H, 5.7; N, 4.15%); λ_{max} (CH_2Cl_2)/nm 299 (log ε 5.60) and 401 (6.12); ν_{max} (KBr)/cm^{-1} 3022m, 2956w, 2917m, 2855w, 2196m, 1597s, 1528s, 1507s, 1495s, 1384, 1320s, 1294s, 1268s, 1210m, 1178m, 1106m, 1018m, 815s and 718m; δ_H (250 MHz; $CDCl_3$) 2.31 (12H, s, Me), 6.89–6.93 (4H, d, *J*=8.8 Hz, Ar), 6.98–7.01 (8H, d, *J*=8.5 Hz, Ar), 7.06–7.09 (8H, d, *J*=8.5 Hz, Ar), 7.24 (2H, s, Ar) and 7.27–7.31 (4H, d, *J*=8.5 Hz, Ar); δ_C (62.9 MHz; $CDCl_3$) 20.9, 81.4, 94.6, 114.1, 120.8, 124.7, 125.4, 130.1, 131.2, 132.3, 133.5, 144.6 and 148.6; *m*/*z* 674 (M^+, 100%).

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