Position of substitution: a facile way to tune the spectroscopic properties of dimethylamino-substituted arylene-ethynylenes

Jing-Kun Fang*, Tengxiao Sun, Yu Fang, Zhimin Xu, Hui Zou, Yuan Liu and Fangting Ge

School of Chemical Engineering, Nanjing University of Science and Technology, Xiaolingwei Street No. 200, Nanjing 210094, P.R. China

A series of dimethylamino-substituted arylene-ethynylenes were synthesised by Sonogashira coupling reactions and characterised by the methods of ^{1}H, ^{13}C NMR, UV-Vis, fluorescence, HRMS and theoretical calculations. Effects on spectroscopic properties caused by the different positions of the dimethylamino group in arylene-ethynylenes were studied and discussed. The shortest absorption maximum, the largest Stokes shift and the highest fluorescence efficiency were observed for arylene-ethynylenes with a dimethylamino group present in the *ortho*-position.

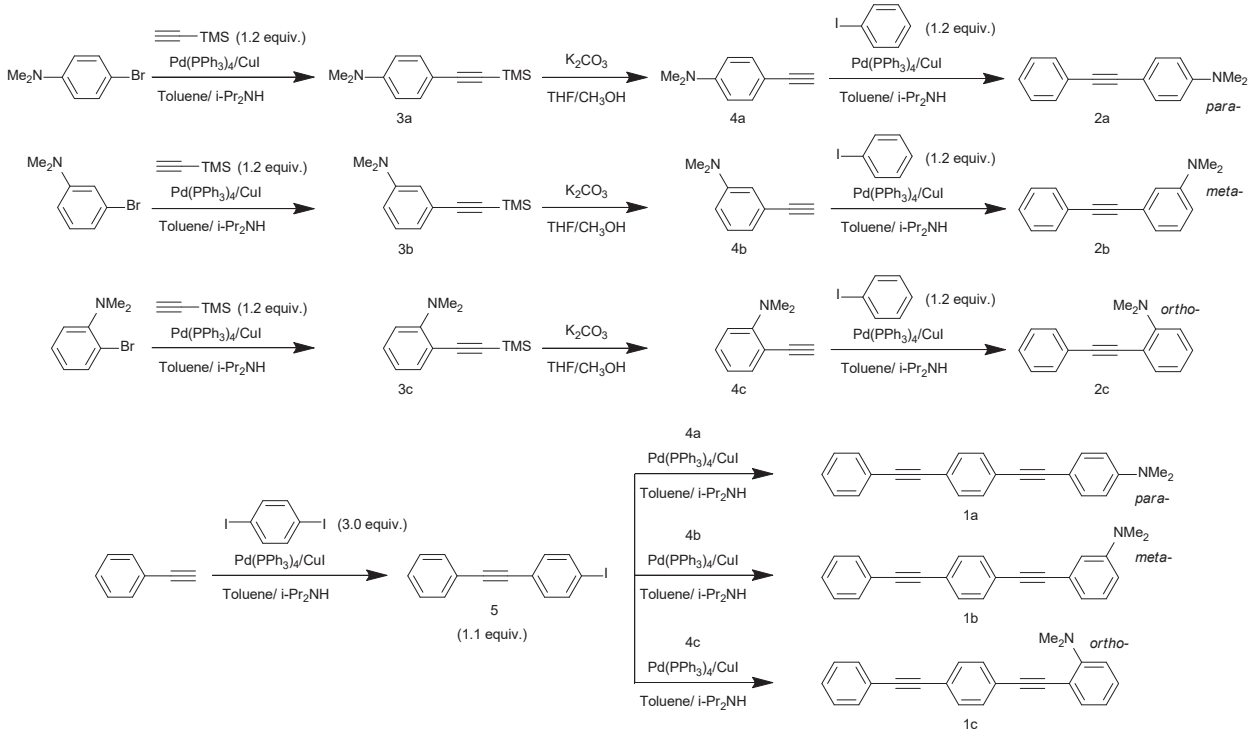
Keywords: arylene-ethynylenes, dimethylamino, organic dyes, spectroscopic properties, Stokes shift, position of substitution

Organic dyes have been widely applied in solar energy conversion,[1] fluorescent probes,[2] biological chemistry,[3] light-harvesting/emitting materials[4] and nanoscience.[5] An ideal dye has an adjustable absorption/emission spectra, high molar extinction coefficient and fluorescence efficiency, a large Stokes shift and good stability. However, there are few dye molecules with outstanding performance in all aspects. The undesirable properties of organic dyes will restrict their potential applications. For example, the small Stokes shift of boron dipyrromethane (BODIPY) will result in a self-quenching, which is detrimental for fluorescence response.[6] Thus, it is important to find the crucial factors that affect these key properties of dyes.

Arylene-ethynylenes are a common architecture for dyes and have attracted extensive attention in fluorescent materials, optoelectrical materials, liquid crystal materials and dye-sensitised solar cells.[7-10] We have reported a series of diphenylamino-substituted phenylene-(poly)ethynylenes. A large bathochromic shift and thus a large Stokes shift were observed by alternating the locations of the ethynylene moiety.[11,12] Amino groups are widely adopted in functional molecules in many fields, but amino groups were only located at the *para*-position in most cases.[13-15] It is important to investigate the changes in spectroscopic properties influenced by the different positions of the amino substituents, with the aim of scrutinising the properties of the amino-substituted molecules. In this paper, arylene-ethynylenes with a dimethylamino group substituted at the *para*, *meta*- and *ortho*- positions were synthesised, numbered **1a–c** and **2a–c** (Scheme 1). Their spectroscopic properties were studied and theoretical calculations on these molecules have been performed.

Results and discussion

Absorption spectra: The absorption spectra of arylene-ethynylenes **1a–c** and **2a–c** in dilute CH_2Cl_2 solution (2.0×10^{-4} M) are shown in Figs 1 and 2, respectively. The data are listed in Table 1.



Scheme 1 Synthesis of **1a–c** and **2a–c**.

* Correspondent. E-mail: fjk_003@163.com

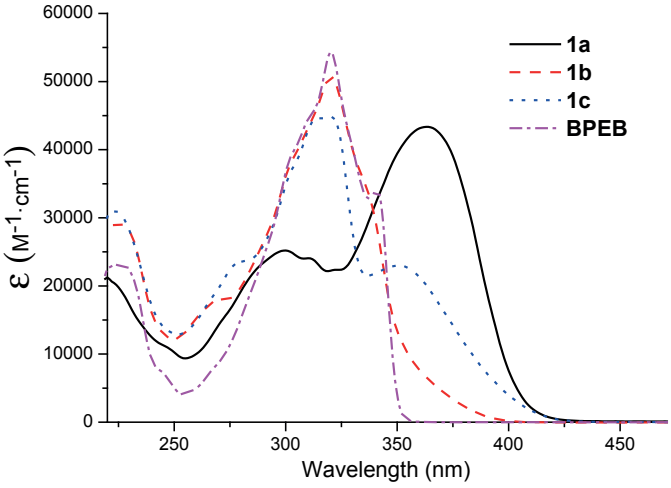


Fig. 1 Absorption spectra of **1a–c** and 1,4-bis(phenylethynyl)benzene (BPEB).

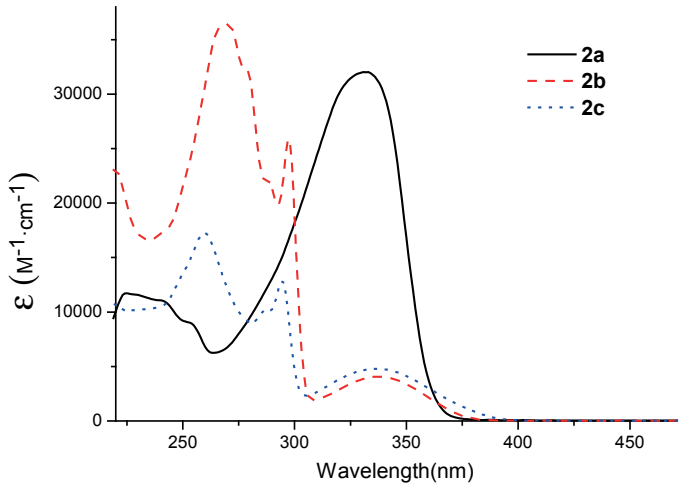


Fig. 2 Absorption spectra of **2a–c**.

Table 1 Absorption and fluorescence data of **1a–c** and **2a–c**

Compound	λ_{abs}/nm(log ε)	λ_{em}/nm[a]	Stokes shift/nm	Φ_F
1a	363(4.64)	468	105	0.78
1b	320(4.70)	470	150	0.32
1c	320(4.65)	468	148	0.87
2a	331(4.51)	392	61	0.04
2b	270(4.56)	409	139	0.21
2c	260(4.24)	411	151	0.76

[a] Excited at the longest absorption maxima.

It is clear that the absorption maximum (λ_{abs}) of **1a** (363 nm) appears at a longer wavelength than those of **1b** and **1c** (320 nm and 320 nm). The dimethylamino group is an auxochrome with nonbonded electrons and[16] if this group is in direct conjugation with the π-system of the chromophore, it may increase the wavelength at which the light is absorbed. By attaching a dimethylamino group to 1,4-bis(phenylethynyl)benzene (λ_{abs} = 320nm in CH_2Cl_2, Fig. 1) to the *para*-position (**1a**), a bathochromic shift of 43 nm was observed. That is to say, it modifies the ability of 1,4-bis(phenylethynyl)benzene to absorb light. If an auxochrome is present in the *meta*- position to the chromophore, it does not affect the colour. That is the reason why the absorption spectrum of **1b** shows no bathochromic shift compared to that of 1,4-bis(phenylethynyl)benzene. Due to the steric effects of the dimethylamino group with the phenylethynyl moiety, **1c** cannot achieve coplanarity, which limits the extent of conjugation. Finally, a bathochromic shift is also not observed for **1c**. This will be further discussed in the theoretical calculations.

Similarly, the absorption maximum (λ_{abs}) of **2a** (331 nm) also appears at a longer wavelength than those of **2b** and **2c** (270 nm and 260 nm). The steric effects of the dimethylamino group with the phenylethynyl moiety is more remarkable in a limited conjugation range. So, **2c** exhibits the shortest λ_{abs} and the weakest intensity of the absorption among these three compounds. In the absorption spectra of **2b** and **2c**, both the E_2 and the B band can be observed. But in the absorption spectrum of **2a**, in which the dimethylamino group was introduced in the *para*-position as an auxochrome, the E_2 band shows a greater bathochromic shift than the B band. As a result, the B band and the E_2 band overlap and only one absorption can be observed.

Emission spectra: The emission spectra of arylene-ethynylenes **1a–c** and **2a–c** in dilute CH_2Cl_2 solution (1.0×10^{-6} M) are shown in Figs 3 and 4, respectively. The data are listed in Table 1. It is clear that the positon of the dimethylamino group shows no influence on the emission peak wavelength (λ_{em}) for **1a–c**, and that the λ_{em} of **2a** with a dimethylamino group present in the *para*-position shows a hypsochromic shift of less than 20 nm compared to λ_{em} of **2b** and **2c** with a dimethylamino group present in the *meta*- and *ortho*- position, respectively.

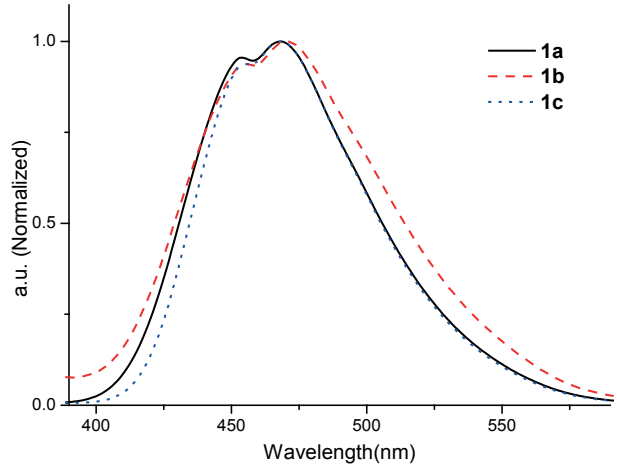


Fig. 3 Emission spectra of **1a–c**.

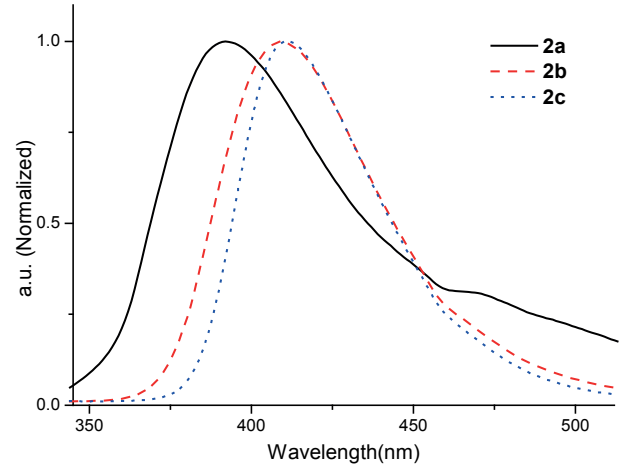


Fig. 4 Emission spectra of **2a–c**.

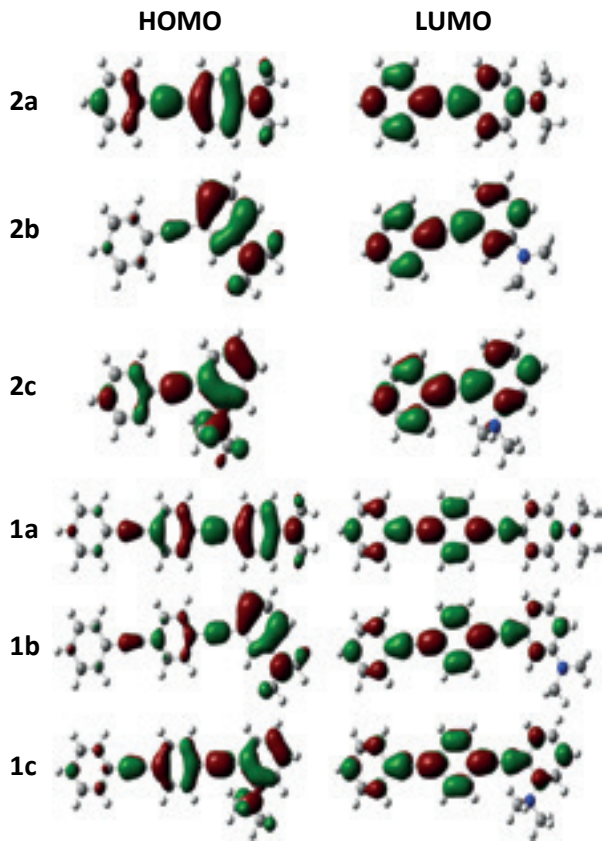


Fig. 5 HOMOs and LUMOs of **1a–c** and **2a–c**.

The results above indicate that arylene-ethynylenes with a dimethylamino group present in the *meta-* and *ortho-* position show shorter λ_{abs} than those with the group in the *para-*position, while the value of their λ_{em} is similar. As a result, remarkable Stokes shifts (139–151 nm) are observed within arylene-ethynylenes with a dimethylamino group present in the *meta-* and *ortho-* position (**1b**, **1c**, **2b** and **2c**). It is noteworthy that a particularly large Stokes shifts (151 nm) in **2c** was observed with such a limited conjugation extent of two benzene rings.

These interesting results prompted us to carry out further investigations. The fluorescence efficiency (Φ_F) of **1a–c** and **2a–c** in CH_2Cl_2 were measured. As is shown in Table 1, **1c** and **2c** with a dimethylamino group present in the *ortho-* position each show the highest fluorescence efficiency in the corresponding series, 0.87 and 0.76, respectively. Based on the above results, arylene-ethynylenes with a dimethylamino group present in the *ortho-* position would show the shortest absorption maxima, the largest Stokes shift and the highest fluorescence efficiency.

Theoretical calculations: To investigate the geometrical and photophysical properties, molecular orbital calculations of arylene-ethynylenes **1a–c** and **2a–c** were carried out using DFT calculations with the Gaussian 09 program.[17] Full geometrical optimisations were performed and all of the calculations were performed with the B3LYP exchange correlation functional under the 6-31G (d) basis set.

The HOMOs and LUMOs of arylene-ethynylenes **1a–c** and **2a–c** are shown in Fig. 5, the isodensity surface values are fixed at 0.03. It can be seen that from HOMO to LUMO, all of these arylene-ethynylenes exhibit a tendency for the electron density geometry distributions to move from the dimethylamino group to the phenylene acetylene units. Obviously, the electron distribution of the HOMOs of **1b** and **2b** indicate that dimethylamino groups are not well conjugated with the whole

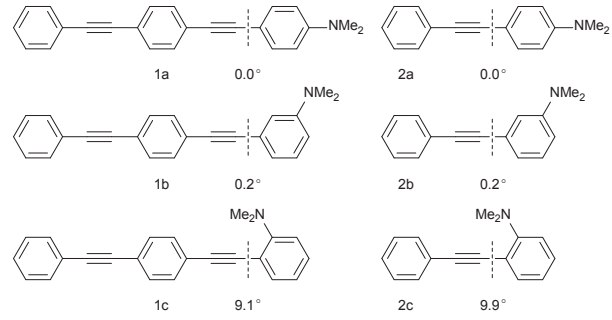


Fig. 6 Calculated dihedral angles between the neighbouring benzene rings in the optimised geometries of **1a–c** and **2a–c**.

π-system of the chromophore in these two molecules. This is why shorter wavelength absorption maxima are observed for **1b** and **2b**.

Figure 6 shows the optimised ground-state geometries of arylene-ethynylenes **1a–c** and **2a–c** with the dihedral angles between two neighbouring benzene rings indicated. The dimethylamino-substituted benzene rings are coplanar with the phenylene acetylene units in **1a**, **1b**, **2a** and **2b**, but for **1c** and **2c** there is a twist between the dimethylamino substituted benzene rings and the phenylene acetylene units (9.1° for **1c**, 9.9° for **2c**), which restricts the conjugation within these two molecules resulting in shorter wavelength absorption maxima.

Experimental

Melting points were measured on an XRC-1 apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on JEOL Lambda 500 instruments with tetramethylsilane as an internal reference. Mass spectra were recorded on a Waters Q-TOF Micro™ spectrometer. Elemental analysis was performed with a Yanagimoto MT3CHN instrument. UV-Vis absorption spectra and emission spectra were recorded by HITACHI U-3310 and JASCO FP-6600 at room temperature, respectively. Absolute quantum yields of photoluminescence were recorded by an integration sphere system (Hamamatsu photonics C9920-02). All reactions were carried out under an atmosphere of nitrogen with freshly distilled solvents and all reagents were obtained from commercial sources and used without further purification, unless otherwise noted. Toluene and diisopropylamine were distilled from CaH_2. Compounds **5** and **2a–c** were prepared according to the corresponding literature methods.[11,18-20]

Synthesis of N,N-*dimethyl-[(trimethylsilyl)ethynyl]anilines* (**3a–c**)*; general procedure*

Bromo-*N,N*-dimethylaniline (400 mg, 2.0 mmol), (trimethylsilyl) acetylene (236 mg, 2.4 mmol), $Pd(PPh_3)_4$ (116 mg, 0.1 mmol), CuI (19 mg, 0.1 mmol), diisopropylamine (5 mL) and toluene (15 mL) were added to a flask and the mixture was stirred at 80 °C overnight. Then the reaction mixture was poured into saturated NH_4Cl (50 mL) and extracted with CH_2Cl_2 (3 x 20 mL), the organic layer was washed with saturated brine (1 x 50 mL) and dried over $MgSO_4$. After filtration, solvents were removed by rotary evaporation (40–45 °C). The crude product was subjected to column chromatography (SiO_2; eluent, hexane/ CH_2Cl_2, 3:1) to give the corresponding compounds.

N,N-*Dimethyl-4-[(trimethylsilyl)ethynyl]aniline* (**3a**): Pale yellow powder; yield 74%, m.p. 86–88 °C (lit.[21] 88–89 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.23(s, 9H), 2.97(s, 6H), 6.59(d, *J* = 9.0 Hz, 2H), 7.34(d, *J* = 9.0 Hz, 2H).

N,N-*Dimethyl-3-[(trimethylsilyl)ethynyl]aniline* (**3b**): Pale yellow oil; yield 84%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.25(s, 9H), 2.94(s, 6H), 6.69(d, *J* = 7.0 Hz, 1H), 6.81–6.84(m, 2H), 7.15(t, *J* = 8.0 Hz, 1H). (lit.[22] ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.25(s, 9H), 2.93 (s, 6H), 6.66–6.71 (m, 1H), 6.79-6.85 (m, 2H), 7.10–7.17 (m, 1H).

N,N-*Dimethyl-2-[(trimethylsilyl)ethynyl]aniline* (**3c**): Pale yellow oil; yield 81%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.26(s, 9H), 2.95(s, 6H), 6.81–6.87(m, 2H), 7.22(t, *J* = 7.5 Hz, 1H), 7.42(d, *J* = 7.5 Hz, 1H). (lit.[23] ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.26 (s, 9H), 2.95 (s, 6H), 6.83 (td, *J* = 7.6, 0.8 Hz, 1H), 6.86(d, *J* = 8.4 Hz, 1H), 7.20–7.24 (m, 1H), 7.42 (dd, *J* = 7.6, 1.6 Hz, 1H).

Synthesis of ethynyl-N,N-*dimethylanilines (***4a–c***); general procedure*

Compound **3** (326 mg, 1.5 mmol), K_2CO_3 (2.073 g, 15.0 mmol), THF (5 mL) and MeOH (5 mL) were added to a flask, and the mixture was stirred at room temperature for 2 h. Then the reaction mixture was poured into water (50 mL) and extracted with CH_2Cl_2 (3 x 20 mL), the organic layer was washed with saturated brine (1 x 50 mL) and dried over $MgSO_4$. After filtration, the solvent was removed in a rotary evaporator (40–45 °C) were evaporated. The crude product was subjected to column chromatography (SiO_2; eluent, hexane/ CH_2Cl_2, 3:1) to give the corresponding compounds.

4-Ethynyl-N,N-*dimethylaniline* (**4a**): Pale yellow powder; yield 98.2%, m.p. 50–51°C (lit.[24] 51–52°C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.96(s, 6H), 2.97(s, 1H), 6.62(d, *J* = 9.0 Hz, 2H), 7.36(d, *J* = 9.0 Hz, 2H).

3-Ethynyl-N,N-*dimethylaniline* (**4b**): Pale yellow oil; yield 94.6%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.95(s, 6H), 3.01(s, 1H), 6.72(d, *J* = 9.0 Hz, 1H), 6.85–6.86(m, 2H), 7.17(t, *J* = 8.0 Hz, 1H). (lit.[24] ^{1}H NMR ($CDCl_3$): δ 2.94 (s, 6H), 3.01 (s, 1H), 6.71 (d, J = 8.1 Hz, 1H), 6.82–6.90 (m, 2H), 7.17 (td, J = 8.1, 0.8 Hz, 1H).

2-Ethynyl-N,N-dimethylaniline (**4c**): Pale yellow oil; yield 91.1%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.93(s, 6H), 3.43(s, 1H), 6.89(t, *J* = 7.5 Hz, 1H), 6.94(d, *J* = 8.5 Hz, 1H), 7.28(t, *J* = 8.5 Hz, 1H), 7.46(d, *J* = 7.5 Hz, 1H). (lit.[23] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.93 (s, 6H), 3.42 (s, 1H), 6.88 (td, *J* = 7.6, 1.2 Hz, 1H), 6.93 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.25–7.29 (m, 1H), 7.46 (dd, *J* = 7.6, 1.6 Hz, 1H).

*Synthesis of 1-iodo-4-(phenylethynyl)benzene (***5***)*

1,4-Diiodobenzene (990 mg, 3.0 mmol), phenylacetylene (102 mg, 1.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), CuI (10 mg, 0.05 mmol), diisopropylamine (5 mL) and toluene (15 mL) were added to a flask and the mixture was stirred at room temperature overnight. Then the reaction mixture was poured into saturated NH_4Cl and extracted with CH_2Cl_2 (3 x 20 mL), the organic layer was washed with saturated brine (1 x 50 mL) and dried over $MgSO_4$. After filtration, solvent was removed in a rotary evaporator (40–45 °C). The crude product was subjected to column chromatography (SiO_2; eluent, hexane) to give **5** as a white powder; yield 78%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26(d, *J* = 8.5 Hz, 2H), 7.34–7.37(m, 3H), 7.51–7.54(m, 2H), 7.69(d, *J* = 8.5 Hz, 2H). (lit.[25] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.33–7.35 (m, 3H), 7.50–7.52 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 2H).

Synthesis of N,N-*dimethyl-(phenylethynyl)anilines (***2a–c***) and* N,N-*dimethyl-{[(4-(phenylethynyl)phenyl]ethynyl}anilines (***1a–c***); general procedure*

Compound **4** (145 mg, 1.0 mmol), iodobenzene (245 mg, 1.2 mmol) or **5** (335 mg, 1.1 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), CuI (10 mg, 0.05 mmol), diisopropylamine (3 mL) and toluene (10 mL) were added to the flask and the mixture was stirred at room temperature overnight. Then the reaction mixture was poured into saturated NH_4Cl and extracted with CH_2Cl_2 (3 x 20 mL), the organic layer was washed with saturated brine and dried over $MgSO_4$. After filtration, the solvent was removed in a rotary evaporator (40–45 °C). The crude product was subjected to column chromatography (SiO_2; eluent, hexane/ CH_2Cl_2, 3:1) to give the corresponding compounds.

N,N-*dimethyl-4-(phenylethynyl)aniline* (**2a**): Pale yellow powder; yield 88; m.p. 107–109°C (lit.[26] 109–110°C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.97(s, 6H), 6.65(d, *J* = 9.0 Hz, 2H), 7.25-7.32(m, 3H), 7.40(d, *J* = 9.0 Hz, 2H), 7.49(d, *J* = 9.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.2, 87.3, 90.6, 110.1, 111.9, 124.2, 127.4, 128.2, 131.3, 132.7, 150.1. Anal. calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33; found: C, 86.56; H, 6.85; N, 6.27%.

N,N-*Dimethyl-3-(phenylethynyl)aniline* (**2b**): Pale yellow powder; yield 92%; m.p. 70–71°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.95(s, 6H), 6.71(dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 6.89–6.91(m, 2H), 7.20(t, *J* = 8.0 Hz, 1H), 7.29–7.35(m, 3H), 7.54(dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.5, 88.2, 90.3, 112.8, 115.2, 119.9, 123.4, 123.5, 128.0, 128.3, 129.0, 131. 6, 150.3. Anal. calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33; found: C, 86.61; H, 6.86; N, 6.28%. (lit.[19] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.97 (s, 6H), 6.71–6.74(m, 1H), 6.92 (d, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.32–7.35(m, 3H), 7.54–7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.4, 88.2, 90.3, 112.8, 115.2, 119.9, 123.4, 123.5, 128.0, 128.2, 129.0, 131.5,150.3).

N,N-*Dimethyl-2-(phenylethynyl)aniline* (**2c**): Pale yellow oil; yield 52%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.99(s, 6H), 6.89(t, *J* = 8.0 Hz, 1H), 6.92(d, *J* = 8.0 Hz, 1H), 7.24(t, *J* = 8.0 Hz, 1H), 7.28–7.35(m, 3H), 7.49(dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.54(dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 43.4, 88.8, 94.7, 115.0, 116.9, 120.4, 123.8, 128.0, 128.3, 129.2, 131.2, 134.2, 154.7. Anal. calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33; found: C, 86.57; H, 6.77; N, 6.28%. (lit.[20] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.01 (s, 6H), 6.88–6.94 (m, 2H), 7.25 (t, *J* = 6.3 Hz, 1H), 7.31–7.37 (m, 3H), 7.49 (d, *J* = 5.7 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.8, 89.1, 95.0, 115.3, 117.2, 120.7, 124.1, 128.2, 128.5, 129.5, 131.5, 134.6, 155.0).

N,N-Dimethyl-4-{[4-(phenylethynyl)phenyl]ethynyl}aniline (**1a**): Pale yellow powder; yield 81%, m.p. 207–209°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.98(s, 6H), 6.65(d, *J* = 9.0 Hz, 2H), 7.32–7.36(m, 3H), 7.41(d, *J* = 9.0 Hz, 2H), 7.44–7.50(m, 4H), 7.52–7.54(m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.2, 87.3, 89.4, 90.8, 92.8, 109.7, 111.8, 122.1, 123.2, 124.1, 128.3, 128.3, 131.1, 131.4, 131.6, 132.8, 150.2. HRMS (ESI$^+$) *m/z*: calcd for $(M+H)^+$ $C_{24}H_{20}N$: 322.1591, found: 322.1588. Anal. calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36; found: C, 89.52; H, 5.90; N, 4.32%.

N,N-*Dimethyl-3-{[4-(phenylethynyl)phenyl]ethynyl}aniline* (**1b**): Pale yellow powder; yield 92%, m.p. 186–188°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.97(s, 6H), 6.65(dd, *J* = 8.0 Hz, *J* = 2.5 Hz, 1H), 6.89–6.91(m, 2H), 7.21(t, *J* = 8.0 Hz, 1H), 7.34–7.37(m, 3H), 7.49–7.54(m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.5, 88.0, 89.2, 91.1, 92.3, 113.1, 115.3, 112.0, 122.9, 123.1, 123.4, 123.4, 128.4, 128.4, 129.1, 131.5, 131.5, 131.6, 150.4. HRMS (ESI$^+$) *m/z*: calcd for $(M+H)^+$ $C_{24}H_{20}N$: 322.1591, found: 322.1590. Anal. calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36; found: C, 89.51; H, 5.88; N, 4.26%.

N,N-*Dimethyl-2-{[4-(phenylethynyl)phenyl]ethynyl}aniline* (**1c**): Pale yellow powder; yield 63%, m.p. 65–66°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.99(s, 6H), 6.89(t, *J* = 7.5 Hz, 1H), 6.92(d, *J* = 8.5 Hz, 1H), 7.25(d, *J* = 8.5 Hz, 1H), 7.32–7.35(m, 3H), 7.48–7.54(m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 43.5, 89.2, 90.8, 91.1, 94.4, 114.7, 116.9, 120.4, 122.7, 123.0, 123.6, 128.3, 128.4, 129.4, 131.1, 131.5, 131.6, 134.3, 154.7. HRMS (ESI$^+$) *m/z*: calcd for $(M+H)^+$ $C_{24}H_{20}N$: 322.1591, found: 322.1601. Anal. calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36; found: C, 89.44; H, 5.87; N, 4.29%.

Conclusions

Dimethylamino-substituted arylene-ethynylenes **1a–c** and **2a–c** were synthesised by Sonogashira coupling reactions. Spectroscopic studies and theoretical calculations were performed. The spectroscopic properties of arylene-ethynylenes depend on the position of dimethylamino group. Arylene-ethynylenes with a dimethylamino group present in the *ortho*-position show the shortest wavelength absorption maxima, the largest Stokes shift and the highest fluorescence efficiency. Notably, a particularly large Stokes shift (151 nm) of **2c** was observed with a limited conjugation extent of two benzene rings.

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