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A simple "palladium-free" synthesis of phenyleneethynylene-based molecular materials revisited.

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Experimental details and specific synthetic procedures

General conditions Reactions involving lithium reagents were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Benzoquinone, naphthoquinone and anthraquinone, phenylacetylene (Aldrich), trimethylsilylacetylene (Fluorochem) and *n*-butyl lithium (1.6 M in hexanes, Acros) were purchased and, with the exception of napthoquinone which was purified by chromatography on alumina (dichloromethane) prior to use, were used as received. Solvents were dried and deoxygenated using an Innovative Technologies Inc. Solvent Purification System. The compound 4-nonyloxyphenylacetylene was prepared by modification of the literature methods, as described below.[S1] IR spectra were recorded on an Nicolet Avatar spectrometer from nujol mulls supported between NaCl plates. NMR spectra were recorded from $CDCl_3$ solutions on a Bruker Avance 400 spectrometer, and referenced against solvent resonances. Mass spectra were recorded on Autospec EI and Micromass Quattro II spectrometers.

Preparation of 1,4-bis[(trimethylsilyl)ethynyl]-2,5-cyclohexadiene-1,4-diol (4a).

To trimethylsilylacetylene (7.82 mL, 5.44 g, 54.4 mmol) in THF (50 mL) at –70 ºC, *n*-butyllithium (33 mL, 53 mmol) was added slowly while stirring, and the reaction was then allowed to warm to room temperature. The reaction was then cooled to –70 ºC and a solution of 1,4-benzoquinone (3.00 g, 27.7 mmol) in THF (50 mL) was added dropwise. The solution was then allowed to warm slowly room temperature and stirred overnight. The reaction was treated with a saturated solution of ammonium chloride and extracted with ethyl acetate. The organic solvents were removed under reduced pressure and the product was isolated following column chromatography on silica gel with a CH_2Cl_2/EtOAc gradient (Yield 7.65 g, 25.1 mmol, 95%). ^{1}H NMR: δ 6.02 (s, 4H, C_6H_4); 2.34 (s, 2H, O*H*); 0.15 (s, 18H, CH_3). ^{13}C NMR: δ 129.7(*C*H) 104.5/90.1 -*C*≡*C*-, 61.2 (C(OH)), -0.29 Si(*C*H_3)$_3$ IR: ν(OH) 3314; ν(C≡C) 2184 cm^{-1}. MS (EI): *m/z* (%) 304 (38)[M]$^+$; 286 (3) [M-H_2O]$^+$; 255 (100) [M-CH_3-2H_2O]$^+$.

Preparation of 1,4-bis[(trimethylsilyl)ethynyl]benzene (4b).

Compound **4a** (7.58 g, 24.9 mmol) was dissolved in absolute EtOH (30 mL) and added dropwise to a solution of $SnCl_2.2H_2O$ (11.23 g. 49.8 mmol) in 50% acetic acid (30 mL) at 60 ºC (10 min) and the precipitate formed collected by filtration and washed with water and dried to afford **4b** (3.81 g, 14.1 mol, 57%). ^{1}H NMR: δ = 7.39 (s 4H, C_6H_4); 0.26 (s, 18H CH_3). ^{13}C NMR: δ 132.1, 123.5 (Ar); 104.9, 96.7, (-*C*≡*C*-); 0.3 Si(*C*H_3)$_3$. MS (EI): *m/z* (%) 270 (51)[M]$^+$; 255 (100) [M-CH_3]$^+$.

Preparation of 1,4-dihydro-1,4-bis[(trimethylsilyl)ethynyl]-1,4-naphthalenediol (5a).

Trimethylsilylacetylene (6.8 mL, 4.70 g, 4.78×10^{-2} mol) in THF (50 mL) was treated with *n*-butyllithium (30 mL, 48 mmol) at –70 ºC and allowed to warm to room temperature. The reaction mixture was cooled to –70 ºC, 1,4-naphthoquinone (3.60 g, 22.8 mmol) in THF (50 mL) was added dropwise, and the reaction was allowed to warm to room temperature and stirred overnight. The reaction was then quenched at 0 ºC with aqueous ammonium chloride, extracted with EtOAc and washed with concentrated brine. The organic phase was evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel and eluted with a $\mathrm{CH_2Cl_2}$/EtOAc gradient (Yield 7.62 g, 21.5 mmol, 90%). ^{1}H NMR: δ 7.83 [dd, ^{3}J(H,H) = 5.9 Hz, ^{4}J(H,H) = 3.2 Hz, 2H, Ar*H*]; 7.43 [dd, ^{3}J(H,H) = 5.9 Hz, ^{4}J(H,H) = 3.2 Hz, 2H, Ar*H*]; 6.19 (s, 2H, $\mathrm{H_4C_{10}}H_2\mathrm{(OH)_2}$); 2.49 (s, 2H, C-O*H*); 0.16 (s, 18H, Si(CH_3)$_3$). ^{13}C NMR: δ 136.7, 130.5, 129.5, 128.2 (Ar); 106.9, 90.5 (-*C*≡*C*-); 64.4 (C(OH)$_2$); 0.1 (Si(*C*H$_3$)$_3$. IR: ν (OH) 3513, 3428; ν (C≡C) 2164 cm^{-1}. MS (EI): *m/z* (%) 354 (7.45) [M]$^{+}$; 337 (7.00) [M-(OH)]$^{+}$; 321, (8.38) [M-2(HO)]$^{+}$; 305, (10.65) [M-$\mathrm{H_2O}$-OH-$\mathrm{CH_3}$]$^{+}$.

Preparation of 1,4-bis[(trimethylsilyl)ethynyl]naphthalene (5b).

Compound **5a** (1.40 g, 3.95 mmol) was dissolved in EtOH (20 mL) and treated with excess $\mathrm{SnCl_2.2H_2O}$ (1.78 g, 7.9 mmol) in 50% acetic acid (20 mL) at 60 ºC. The crude product precipitated from solution, was collected by filtration, washed with water and methanol, and purified by chromatography on silica gel using hexane as eluent (Yield 0.87 g, 2.71 mmol, 69%). ^{1}H NMR: δ 8.37 [dd, ^{3}J(H,H) = 6.7Hz, ^{4}J(H,H) = 3.2 Hz, 2H, Ar*H*]; 7.65 (s, 2H, C*H*); 7.63 [dd, ^{3}J(H,H) = 6.7 Hz, ^{4}J(H,H) = 3.2 Hz, 2H, Ar*H*]; 0.35 (s, 18H, $\mathrm{Si}(\mathrm{C}H_3)_3$). ^{13}C NMR: δ 133.5, 130.3, 127.6, 126.9, 121.9 (Ar); 103.2, 101.7 (-*C*≡*C*-); 0.4 ($\mathrm{Si}(C\mathrm{H}_3)_3$. MS (EI): *m/z* (%) 320 (100) $[\mathrm{M}]^+$; 305 (94) $[\mathrm{M}\text{-}(\mathrm{CH}_3)]^+$. Anal. Calcd (%) for $\mathrm{C}_{20}\mathrm{H}_{24}\mathrm{Si}_2$ (320.58) C 74.93, H 7.55; found C 74.90, H 7.61.

Preparation of 9,10-dihydro-9,10-bis[(trimethylsilyl)ethynyl]-9,10-anthracenediol (6a).

Trimethylsilylacetylene (6.0 mL, 4.16 g, 42.4 mmol) in THF (50 mL) was treated with *n*-butyllithium (26 mL, 41.6 mmol) at –70 ºC and allowed to warm to 0 ºC. The reaction mixture was cooled to –70 ºC and 9,10-anthraquinone (4.00 g, 19.2 mmol) in THF (50 mL) was added dropwise, and the reaction was allowed to warm to room temperature before being allowed to stir overnight. The reaction mixture was then quenched with aqueous ammonium chloride, extracted into EtOAc, and washed twice with brine. The crude product was then obtained by removal of the solvent, and used in the reduction without further purification (Yield 7.6 g, 18.8 mmol, 98 %). ^{1}H NMR: δ = 8.05 [dd, $^3J(\mathrm{H,H}) = 5.8$ Hz, $^4J(\mathrm{H,H}) = 3.2$ Hz, 4H, Ar*H*]; 7.45 [dd, $^3J(\mathrm{H,H}) = 5.8$ Hz, $^4J(\mathrm{H,H}) = 3.2$ Hz, 4H, Ar*H*]; 3.31 (m, 2H, $\mathrm{C}(\mathrm{O}H)_2$); 0.17 (s, 18H, $\mathrm{C}H_3$). ^{13}C NMR: δ = 138.3, 129.3, 126.8 (Ar); 107.7, 92.6 (-*C*≡*C*-); 68.7 (*C*-OH); -0.06 ($\mathrm{Si}(C\mathrm{H}_3)_3$. IR: ν(OH) 3506, 3410; ν(C≡C) 2171, 2157 cm^{-1}. MS (EI): *m/z* (%) 404 (2) $[\mathrm{M})]^+$; 387 (36) $[\mathrm{M}\text{-}(\mathrm{OH})]^+$; 370 (22) $[\mathrm{M}\text{-}2(\mathrm{OH})]^+$**.**

Preparation of 9,10-bis[(trimethylsilyl)ethynyl]anthracene (6b).

Compound **6a** (5.0 g, 12.3 mmol) was dissolved in EtOH (20 mL) and treated with $\mathrm{SnCl_2.2H_2O}$ (13.34 g, 59.1 mmol) in 50% acetic acid (20 mL) at 60º C. The precipitate formed was collected by filtration and washed with water and methanol before being recrystallised from toluene (Yield 1.80 g, 4.83 mmol, 39%). ^{1}H NMR: δ = 8.58 [dd, ^3J(H,H) = 6.8 Hz, ^4J(H,H) = 3.4 Hz, 4H, ArH]; 7.60 [dd, ^3J(H,H) = 6.8 Hz, ^4J(H,H) = 3.6 Hz, 4H, ArH]; 0.43 (s, 18H, CH_3). ^{13}C NMR: δ = 132.6, 127.6, 127.2, 118.8 (Ar); 108.5, 101.9 (-C≡C-); 0.56 (Si(CH$_3$)$_3$. MS (EI): *m/z* (%) = 370 (100) [M)]$^+$; 355 (40) [M-(CH$_3$)]$^+$. Anal. Calcd. (%) for $C_{24}H_{26}Si_2$: C 77.77, H 7.07; found: C 77.65.19, H.7.10.

Preparation of 1,4-bis(phenylethynyl)-2,5-cyclohexadiene-1,4-diol (7a).

Phenylacetylene (5.56 g, 54.4 mmol) in THF (50 mL) was treated with *n*-butyllithium (33 mL 52.8 mmol) at –70 ºC and the reaction mixture was allowed to warm to room temperature. This solution was cooled (-70 ºC) and a solution of benzoquinone (3.00 g, 27.7 mmol) in THF (50 mL) was added dropwise as the solution was allowed to warm to room temperature overnight. The reaction was quenched with aqueous ammonium chloride and extracted into EtOAc and washed with water (50 mL × 2) and brine (20 mL). The crude product was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc gradient) (Yield: 6.1 g, 19.5 mmol, 74%). ^{1}H NMR: δ 7.39 (m, 4H, ArH); 7.24 (m, 6H, ArH); 6.13/6.07 (s, 4H, $C_6(OH)_2H_2$); 6.07 (s, 2H, $C(OH)_2H_2$); 3.58 (s, 2H, $C_6H_4(OH)_2$). ^{13}C NMR: δ 132.2, 132.2, 130.2, 129.7, 129.2, 129.1, 128.6, 128.5 (Ar); 88.9, 85.5 (-C≡C-); 70.8/61.8 (COH). IR: ν(OH) 3266; ν (C≡C) 2217 cm^{-1}. MS (EI): *m/z* (%) 312 (20) [M]$^+$; 294 (66) [M-(H$_2$O)]$^+$; 278 (57) [M-2(OH)$_2$]$^+$.

Preparation of 1,4-bis(phenylethynyl)benzene (7b).

Compound **7a** (6.1 g, 19.5 mmol) was dissolved in ethanol (20 mL) and treated with $SnCl_2.2H_2O$ (8.78 g, 39.0 mmol) in 50% acetic acid (20 mL) at 60 ºC, giving a precipitate, which was collected by filtration, washed with water and methanol and dried (Yield 3.4 g, 12.2 mmol, 63%). ^{1}H NMR: δ 7.55 (m, 4H, Ar*H*); 7.52 (m, 4H, Ar*H*); 7.36 (m, 6H, Ar*H*). ^{13}C-NMR: δ 132.0, 131.9, 128.8, 128.8, 123.5, 123.4 (Ar); 91.6, 89.5 (-*C*≡*C*-). MS (EI): *m/z* (%) 278 (100) [M]$^{+}$. Anal. Calcd. (%) for $C_{22}H_{14}$ C 94.93**,** H 5.07; found: C 95.01, H 5.04.

Preparation of 1,4-dihydro-1,4-bis(phenylethynyl)-1,4-naphthalenediol (8a).

Phenylacetylene (4.91 g, 48.1 mmol) in THF (50 mL) was treated with *n*-butyllithium (28 mL, 44.8 mmol) at -70 ºC. The reaction was allowed to warm to 0 ºC and was cooled again to -70 ºC and a solution of 1,4-naphthoquinone (3.69 g, 23.3 mmol) in THF (50 mL) was added. The reaction was then allowed to warm to room temperature while stirring overnight. The reaction was quenched with aqueous ammonium chloride and extracted into EtOAc and washed with water (2 × 50 mL) and brine (20 mL) at 0 °C. The crude product was purified by passing through a short column of silica gel, eluting with CH_2Cl_2/EtOAc gradient (Yield 5.67 g, 15.6 mmol, 67%). ^{1}H NMR: δ 7.98 [dd, ^{3}J(H,H) = 6.2 Hz, ^{4}J(H,H) = 3.6 Hz, 2H, Ar*H*]; 7.45 (m, 6H, Ar*H*); 7.32 (m, 6H, Ar*H*); 6.33 (s, 2H, $C_6(OH)_2H_2$); 3.05 (s, 2H, C-(O*H*); ^{13}C-NMR: δ 136.8, 132.1, 130.3, 129.5, 128.9, 128.5, 128.3, 122.4 (Ar); 91.1, 85.6 (-*C*≡*C*-); 64.5 (*C*-OH). IR: ν(OH) 3250; ν(C≡C) 2224 cm^{-1}. MS (EI): *m/z* (%) 362 (1) [M]$^{+}$; 344 [M-(OH_2)]$^{+}$; 328 [M-$(OH)_2$]$^{+}$.

Preparation of 1,4-bis(phenylethynyl)naphthalene (8b).

Compound **8a** (4.5 g, 12.4 mmol) was dissolved in ethanol (20 mL) and treated with $SnCl_2.2H_2O$ (2.79 g, 12.4 mmol) in 50% acetic acid (20 mL) at 60 ºC, giving a precipitate which was collected by filtration, washed with water and methanol and dried (Yield 3.1 g, 9.44 mmol, 76%). ^{1}H NMR: δ = 8.50 [dd, ^3J(H,H) = 6.2 Hz, ^4J(H,H) = 3.6Hz, 2H, Ar*H*]; 7.75 (s, 2H, Ar*H*); 7.67 (m, 6H, Ar*H*); 7.41 (m, 6H, Ar*H*). ^{13}C-NMR: δ 133.5, 132.1, 130.1, 128.9, 128.8, 127.6, 127.0, 123.6, 121.9 (Ar); 96.3, 87.9 (-*C*≡*C*-). MS(EI): *m/z* (%) 328 (93) $[M]^+$. Anal. Calcd. (%) for $C_{26}H_{16}$ C 95.09, H 4.91; found: C 95.01, H 4.96.

Preparation of 9,10-dihydro-9,10-bis(phenylethynyl)-9,10-anthracenediol (9a).

Phenylacetylene (4.69 g, 46.0 mmol) in THF (50 mL) was treated with *n*-butyllithium (27.5 mL, 44.0 mmol) at -70 ºC. The reaction was then allowed to warm to room temperature, was cooled again to -70 ºC, and a solution of 9,10-anthraquinone (4.60 g, 22.0 mmol) in THF (50 mL) was added and the mixture was allowed to warm to room temperature while stirring overnight. The reaction was cooled (0 °C), quenched with aqueous ammonium chloride, extracted into EtOAc and washed with water (2 × 50 mL) and brine (20 mL) before being dried over $MgSO_4$. After removal of the organic solvent under reduced pressure, the crude product was recrystallised from CH_2Cl_2 and hexane (Yield: 4.3 g, 10.4 mmol, 47%). ^{1}H NMR: δ 8.08 [dd, ^3J(H,H) = 5.9 Hz, ^4J(H,H) = 3.2Hz, 4H, Ar*H*]; 7.41 [dd, ^3J(H,H) = 5.9Hz, ^4J(H,H) = 3.2Hz, 4H, Ar*H*]; 7.35 (m, 4H, Ar*H*); 7.22 (m, 6H, (Ar*H*), 3.10 (s, 2H, $C(OH)_2$). ^{13}C NMR: δ 138.2, 132.1, 129.6, 129.1, 128.6, 127.4, 122.4 (Ar); 91.8, 87.3 (-*C*≡*C*-); 68.7 (*C*-OH). IR: ν(OH) 3271; ν(C≡C)

2254 cm^{-1}. MS (EI): *m/z* (%) 412 (2) $[M)]^+$; 394 (24) $[M\text{-}(H_2O)]^+$; 378 (37) $[M\text{-}(OH)_2]^+$; 294 (100) $[M\text{-}C_6H_5C_2(OH)]^+$.

Preparation of 9,10-bis(phenylethynyl)anthracene (9b).

Compound **9a** (3.5 g, 8.49 mmol) was dissolved in EtOH (20 mL) and treated with $SnCl_2.2H_2O$ (3.86 g, 17.1 mmol) in 50% acetic acid at 60 ºC. The precipitate formed was collected by filtration, washed with water and methanol and recrystallised from toluene to afford **9b** (Yield 2.1 g, 5.55 mmol, 65%). ^{1}H NMR: δ 8.70 [dd, ^3J(H,H) = 6.7 Hz, ^4J(H,H) = 3.4Hz, 4H, Ar*H*]; 7.80 (m, 4H, Ar*H*); 7.65 [dd, ^3J(H,H) = 6.7 Hz, ^4J(H,H) = 3.4 Hz, 4H, Ar*H*]; 7.45 (m, 6H, Ar*H*). ^{13}C NMR: δ 132.5, 132.1, 129.1, 128.9, 127.6, 127.2, 123.8, 118.9 (Ar); 102.8, 86.9 (-*C*≡*C*-). MS (EI): *m/z* (%) 378 (2) $[M)]^+$; 394 (24) $[M\text{-}(H_2O)]^+$; 378 (37) $[M\text{-}(OH)_2]^+$; 294 (100) $[M\text{-}C_6H_5C_2(OH)]^+$. Anal. Calcd. (%) for $C_{30}H_{18}$ C 95.21, H 4.79 found: C 95.42, H 4.75.

Preparatin of 1-(phenylethynyl)-4-[(trimethylsilyl)ethynyl]-2,5-cyclohexadiene-1,4-diol (10a).

A solution of phenylacetylene (3.00 g, 29.4 mmol) in THF (50 mL) was treated with *n*-butyllithium (17 mL, 27.2 mmol) at -70 ºC and allowed to warm to room temperature. The reaction mixture was cooled to -70 ºC and 1,4-benzoquinone (3.00 g, 27.7 mmol) in THF (50 mL) was added dropwise and the reaction allowed to warm to 0 ºC with stirring. The reaction mixture was then cooled once more to -70 ºC whereupon lithium trimethylsilylacetylide (27.2 mmol) in THF (50 mL) was added and the reaction mixture was allowed to stir, while warming slowly to room temperature overnight. The reaction was quenched with aqueous ammonium chloride at 0º C and extracted into EtOAc, washed twice with brine. The crude product was purified by passage through a short column of silica, eluting with a CH_2Cl_2/EtOAc gradient (Yield 6.9 g, 22.4 mmol 82%). ^{1}H NMR: δ 7.43 (m, 2H, Ar*H*); 7.30 (m, 3H, Ar*H*); 6.10 (m, 4H, *C*-$(OH)_2$); 2.35, 2.27 (s, 2H, C-(O*H*)); 0.14 (s, 9H, $Si(CH_3)_3$). ^{13}C-NMR: δ 132.2, 130.2, 130.1, 129.2, 128.6, 128.7, 128.6, 122.3 (Ar); 104.9, 90.6, 88.9, 85.5 (-*C*≡*C*-); 61.74, 61.57 (C(OH)); 0.1 ($Si(CH_3)_3$). IR: ν(OH) 3314; ν(C≡C) 2219, 2162 cm^{-1}, MS (EI): m/z (%) 308 (10) $[M]^+$; 290 (4) $[M-(H_2O)]^+$; 275 (13) $[M-(OH)_2]^+$; 294 (100) $[M-C_6H_5C_2(OH)]^+$.

Preparation of 1-(phenylethynyl)-4-[(trimethylsilyl)ethynyl]benzene (10b).

Compound **10a** (6.20 g, 20.1 mmol) was dissolved in EtOH (20 mL) and treated with $SnCl_2.2H_2O$ (5.52 g, 24.5 mmol) in 50% acetic acid (20 mL) at 60 ºC. The precipitate formed was collected by filtration, washed with water and methanol and the product was recrystallised from toluene (Yield 4.1 g, 14.9 mmol, 74%). ^{1}H NMR: δ 7.54 (m, 3H, Ar*H*); 7.45 (m, 3H, Ar*H*); 7.35 (m, 3H, Ar*H*); 0.27 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR: δ 132.3, 131.9, 131.8, 128.8, 128.7, 123.7, 123.4, 123.3 (Ar); 105.0, 96.6, 91.7, 89.3 (-*C*≡*C*-); 0.28 ($Si(CH_3)_3$). MS (EI): *m/z* (%) 274 (61) $[M]^+$; 259 (91) $[M-CH_3]^+$. Anal. Calcd. (%) for $C_{19}H_{18}Si$ C 83.15, H 6.61; found: C 83.14, H 6.48.

Preparation of 1-([4-nonyloxyphenyl)ethynyl]-4-(phenylethynyl)-2,5-cyclohexadiene-1,4-diol (11a).

Phenylacetylene (0.90 mL, 0.834 g, 8.17 mmol) in THF (50 mL) at –78 °C was treated with *n*-butyllithium (5.1 mL, 8.16 mmol) and allowed to warm slowly to 0 °C. The lithium phenylacetylide suspension was then cooled again to –78 °C and a solution of 1,4-benzoquinone (0.88 g, 8.14 mmol) in THF (50 mL) was added dropwise forming a deep blue colour. The reaction was allowed to stir for 1h at –78 °C and then warmed to 0 °C to ensure complete reaction and then re-cooled to –78 ºC. In a separate flask, a solution of 4-(nonyloxy)phenylethyne (2.00 g, 8.18 mmol) in THF (40 mL) at –78 °C was treated with *n*-butyllithium (5.1 mL, 8.16×10^{-3} mol) and allowed to stir for 1h while warming to 0 °C. This solution was added to the cold solution contained in the first flask, and allowed to warm to 0 ºC before being quenched with aqueous ammonium chloride. The reaction mixture was then extracted with EtOAc and the solvent removed from the extracts to give the crude product which was purified by column chromatography using CH_2Cl_2 as the eluent (Yield 1.30 g, 2.86 mmol, 35%). ^{1}H NMR: δ 7.42 (m, 2H, Ar*H*); 7.34 (m, 2H, Ar*H*); 7.28 (m, 2H, Ar*H*); 6.78 (m, 2H, Ar*H*); 6.11 (m, 4H, $C_6H_4(OH)_2$); 3.91 [t, ^3J(H,H) = 6.8 Hz, 2H, OCH_2R]; 3.55 (s, br 2H, $C_6H_4(OH)_2$); 1.75, 1.47, 1.22 (m, 14H, aliphatic); 0.89 (t, ^3J(H,H) = 6.8 Hz, 3H CH_3). ^{13}C-NMR: δ 159.9, 133.7, 133.3, 132.8, 132.2, 132.1, 129.5, 129.0, 128.6, 122.5, 114.8 (Ar); 89.1, 87.6, 85.8, 85.5 (-*C*≡*C*-); 68.4 (O*C*H); 61.7, (*C*-OH); 31.9, 29.5, 26.4, 26.0, 22.9, 18.7 (aliphatic); 14.4 (CH_3)IR: ν (OH) 3309; ν (C≡C) 2223 cm^{-1}. MS (EI): *m/z* (%) 454 (2) $[M)]^+$; 436 (72) $[M-(H_2O)]^+$; 420 (33) $[M-2(OH)]^+$.

Preparation of 1-[(4-nonyloxyphenyl)ethynyl]-4-(phenylethynyl)benzene (11b)

Compound **11a** (1.30 g, 2.86 mmol) in EtOH (10 mL) was added to $SnCl_2.2H_2O$ (0.77 g, 3.4 mmol) in 50 % aqueous acetic acid (10 mL) and heated to 60 °C. The crude product which precipitated was collected by filtration and allowed to dry in air. The product was purified by column chromatography on silica gel, eluting with hexane (Yield 0.40 g, 0.95 mmol, 33 %). ^{1}H NMR: δ 7.55 (m, 8H, Ar*H*); 7.35 (m, 3H, Ar*H*); 6.87 (m, 2H, Ar*H*); 3.97 [t, ^3J(H,H) = 6.8 Hz, 2H, OC*H*$_2$R]; 1.77, 1.48 (m, 14H, -CH$_2$-aliphatic); 0.89 [t, ^3J(H,H) = 6.8Hz, 3H, aliphatic]. ^{13}C NMR: δ 159.8, 133.5, 131.98, 131.9, 131.7, 128.7, 123.9, 123.5, 123.0, 115.2, 114.9 (Ar); 91.9, 91.4, 89.6, 88.2 (-*C*≡*C*-); 68.5 (OC*H*$_2$-aliphatic); 31.9, 29.5, 26.1, 22.95, (aliphatic), 14.4 (CH$_3$). MS (EI): *m/z* (%) 420 (97) [M]$^+$; 294 (100) [M-(C$_6$H$_{12}$)]$^+$. Anal. Calcd. (%) for $C_{31}H_{32}O$ C 88.53, H 7.67; found: C 88.72, H 7.67.

Preparation of 1-iodo-4-nonyloxybenzene.

Potassium carbonate (20.00 g 1.45 × 10^{-1} mol) and 1-bromononane (10.36 g, 5.00 × 10^{-2} mol) were added to 4-iodophenol (10.00 g, 4.55 × 10^{-2} mol) dissolved in acetone (150 mL) and the reaction mixture was then heated under reflux (48 hours). The excess potassium carbonate was then filtered off and solvent was then removed from the filtrate to give the crude product. The crude product then purified by silica gel chromatography, eluting with hexane to yield the product as a white solid. Yield 11.1 g, 3.20 × 10^{-2} mol. ^{1}H NMR δ 7.55 (m, 2H, Ar*H*); 6.67 (m, 2H, Ar*H*); 3.91 [t, ^3J(H,H) = 6.4 Hz, 2H, OC*H*$_2$R]; 1.75 (m 2H, -CH$_2$-aliphatic); 1.33 (m, 12H, -CH$_2$-aliphatic); 0.89 [t ^3J(HH) = 6.8 Hz 3H, -CH$_3$]. ^{13}C NMR: δ 159.4, 138.1, 117.3, 82.7 (Ar); 68.5 (O*C*H$_2$-R), 32.2, 29.9, 29.7, 29.6, 29.5, 26.4, 23.0, (aliphatic) 14.4 (-*C*H$_3$). EI-MS 346.0 (68) [M]$^+$, 219.9 [M-I]$^+$, 202.9(25.6) [M-C$_9$H$_{19}$O]$^+$.

Preparation of 4-nonyloxyphenylacetylene.

To 1-iodo-nonyloxybenzene (10.30 g, 2.97×10^{-2} mol) in triethylamine (100 mL), Bis(triphenylphosphine)palladium (II) dichloride (0.209 g, 2.98×10^{-4} mol), copper (I) iodide (0.112 g, 5.88×10^{-4} mol) and trimethylsilylacetylene (3.21 g, 3.27×10^{-2} mol) were added and stirred overnight. The solvent was then removed under vacuum, and the crude product was dissolved in methanol (100 mL) to which potassium carbonate (0.124 g, 9.00×10^{-3} mol) was added and stirred 6 hours. The reaction mixture was diluted with water (200 mL) and extracted with diethyl ether (2 × 75 mL). The crude product was purified by column chromatography on silica gel, eluted with hexane. Yield 4.86g, 1.99×10^{-2} mol, 67%. ^{1}H NMR δ 7.44 (m, 2H, Ar*H*); 6.85 (m, 2H, Ar*H*); 3.95 [t, ^3J(H,H) = 6.8 Hz, 2H, OC*H*$_2$R]; 2.99 (s 1H, C≡C-H); 1.78 (m 2H, -CH$_2$-aliphatic); 1.45 (m, 2H, -CH$_2$-aliphatic); 1.30 (m, 10H, -CH$_2$-aliphatic); 0.91 [t ^3J(HH) = 6.8 Hz 3H, -CH$_3$]. ^{13}C NMR: δ 159.9, 133.9, 114.8, 114.3 (Ar); 84.1, 75.9 (-*C*≡*C*-); 68.4 (O*C*H$_2$-R), 32.5, 29.9, 29.7, 29.6, 29.4, 29.3, 29.2, 26.1, 22.7 (aliphatic); 14.1(-*C*H$_3$). IR: ν(C≡C-H) 3318, 3300; ν(C≡C) 2108 cm^{-1}. EI-MS 244.1 (61) [M]$^+$, 117.9 (100) [M-C$_9$H$_{18}$]$^+$, 101 (48) [M-C$_9$H$_{19}$O]$^+$.

Supplementary Material (ESI) for New Journal of Chemistry
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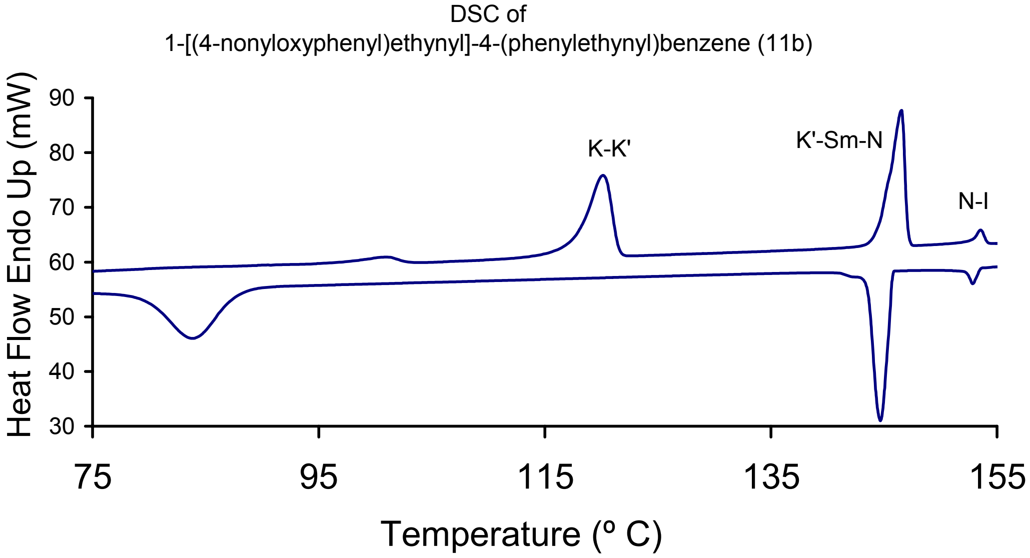

Fig S1. Thermal Analysis of 1-[(4-nonyloxyphenyl)ethynyl]-4-(phenylethynyl)benzene (11b)

S1. (a) Y.G. Yang, G. Tang, Z. Gong and J.X. Wen, *Mol. Cryst. Liq Cryst.*, 2000, **348**, 153; (b) C. Pugh and V. Percec, *Chem. Mater.*, 1991, **3**, 107; (c) D.W. Bruce, D. Dunmur, E. Lalinde, P.M. Maitlis and P. Styring, *Liq. Cryst.*, 1998, **3**, 385, 395.