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Synthesis and thermal cyclopolymerization of heterocycle containing bis-*ortho*-diynyl arenes

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Abstract—A new class of heteroatom terminated bis-*ortho*-diynyl arene (BODA) compounds have been synthesized via efficient in situ palladium catalyzed cross coupling between tetra alkynyl silanes and aryl bromides and iodides. BODA monomers undergo Bergman-type cyclization upon heating, and afford processable intermediates and ultimately network polymers. The new heterocycle terminated oligomers are compared to phenyl terminated derivatives and exhibit bathochromic shifts (25 nm) in their emission spectra.

1. Introduction

The Bergman cyclization[1–13] of enediynes has been used extensively as a viable methodology for developing antitumor drugs.[2] Recent work has shown that the cyclo-rearrangement of enediynes could also be used in preparing linear[3,4] and network polymers.[5–8] Although simple aryldiynes lead to linear polyarylenes which are difficult to process, we focused on the synthesis of bis-*ortho*-diynylarene (BODA) monomers (Scheme 1) which polymerize to highly processable and reactive branched intermediates prior to final cure (Scheme 2).[5]

Phenyl substituted BODA compounds were previously synthesized using a three-step synthetic protocol via selective *ortho* bromination of bisphenols followed by trifluoromethane sulfonato esterfication and subsequent Sonogashira[14] type Pd catalyzed coupling with mono-substituted terminal alkynes to form tetraynes.[5] Thermal polymerization typically above 200°C occurs in melt or in solution, yielding processable intermediates prior to the fully cured network polyarylenes with high thermal stability, low dielectric constant, and possibly electro-optic properties.

In general, many high performance aromatic polymers are currently being pursued as low dielectric insulators in integrated circuits.[15,16] Most, however, do not exhibit adequate thermal and dimensional stability required for current fabrication processes. In our early communication we illustrate that phenyl terminated BODA polymers exhibit about 1%/1 h weight loss at 450°C.[5] BODA derived prepolymers can be easily coated or molded and are excellent precursors for microfabricated glassy carbon micro structures.[8] Recently, BODA derived polymers have been successfully used as precursors to fabricate carbon based photonic crystals.[9] BODA polymers may also be useful in the rapidly expanding area of organic light emitting diodes (OLED).[17] Our current effort has focused on developing a series of heteroaromatic ring terminated BODA monomers (Scheme 1) with hopes of enhancing the optoelectronic as well as the thermal properties of the final network.

2. Results and discussion

Initially we attempted Sonogashira[14] type palladium coupling between aryl triflates and bromides with mono-substituted acetylenes as reported for other BODA monomers previously.[5] However, the instability of the related pyridyl and thienyl acetylene derivatives redirected our approach to in situ direct cross coupling reactions between alkynylsilanes and heteroaromatic bromides and iodides.

The trimethylsilyl group has been extensively used as a protecting group for terminal acetylenes.[18] The C–Si bond of trimethylsilyl acetylene is typically cleaved by fluoride ions, tetrabutyl ammonium fluoride (TBAF), tetrabutyl-ammonium hydroxide (TBAOH) or silver (I) oxide.[19] Tour[20] and others[21] reported a base catalyzed (K_2CO_3) desilylation in situ Pd-catalyzed coupling of an alkyne with an aryl halide to form oligo (1,4-phenylene ethynylene)s. Himaya[22] used F^- to activate the Si–C bond enabling direct coupling of alkynylsilanes with aryl halides and Koseki et al.[23] reported the silver carbonate promoted direct cross

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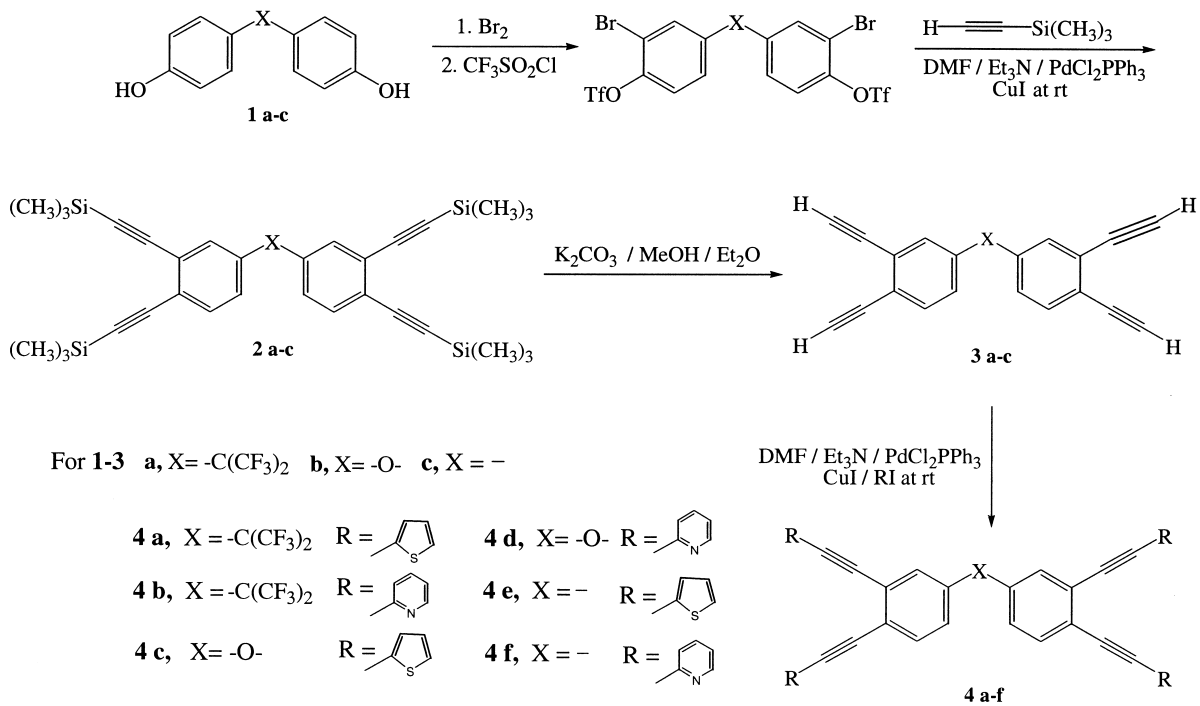
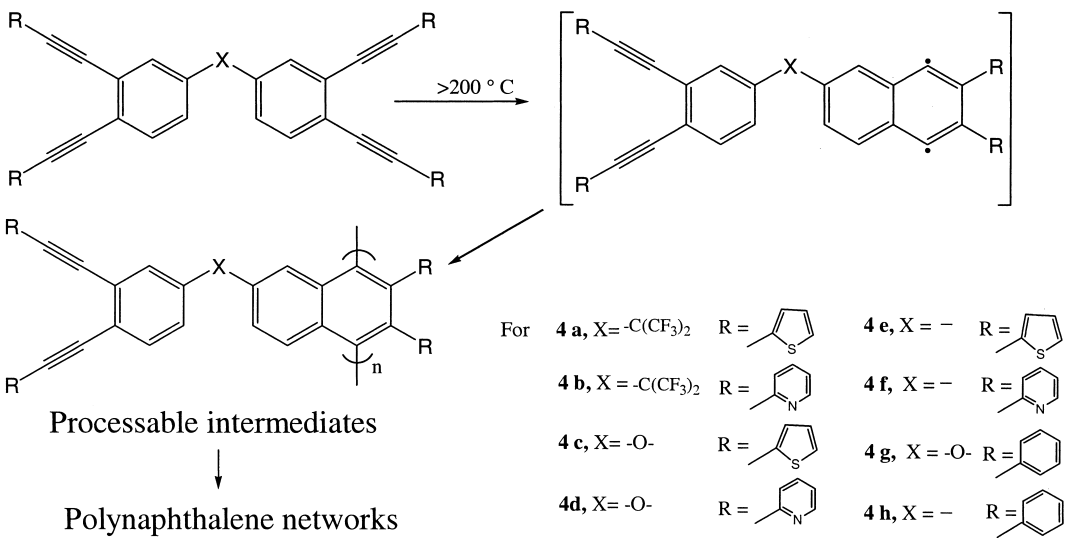


Scheme 1.

coupling reaction between alkynylsilanes and aryl iodides to prevent oxidative homo-coupling[24] as well as increasing the coupling rate. Efficient palladium cross coupling between terminal acetylenes and aryl halides is an established synthetic tool for small molecules as well as macromolecules.[25]

Alkynylsilanes (Scheme 1) were synthesized by Sonogashira type palladium coupling with aryl triflates and bromides with trimethylsilyl acetylenes in high yield (>85%). Subsequent desilylation in situ palladium catalyzed cross coupling afforded the target compounds in good to moderate yields (>60–75%) despite the tendency for oxidative homo-coupling.[24] Typically, when the proton terminated acetylenes were isolated, the colorless solids underwent a rapid color change even under an inert atmosphere.[26] Presumably, the color change is a result of sterically uninhibited monomer polymerization. Isolation of the H-terminated tetraynes followed by coupling with aryl halides resulted in lower yields over the direct in situ coupling route.

Fig. 1 exhibits the X-ray crystal structures of TMS-intermediate **2c** and thiophene monomer **4c**.[29] For monomers **2**, **3** the spacer (X) is, **a**=–C(CF$_3$)$_2$, **b**=–O–, **c**=– and for monomer **4** as illustrated in Scheme 1. It is known that the *trans* alkyne distance between two *ortho*-diynes imparts a dramatic effect on Bergman cyclization activation energy.[10–13,27] Crystallographic data indicated that the steric bulk of the terminal group plays a significant role on influencing the *trans* alkyne distance, thus affecting the overall cyclization kinetics. *trans* Alkyne distances of



Scheme 2.

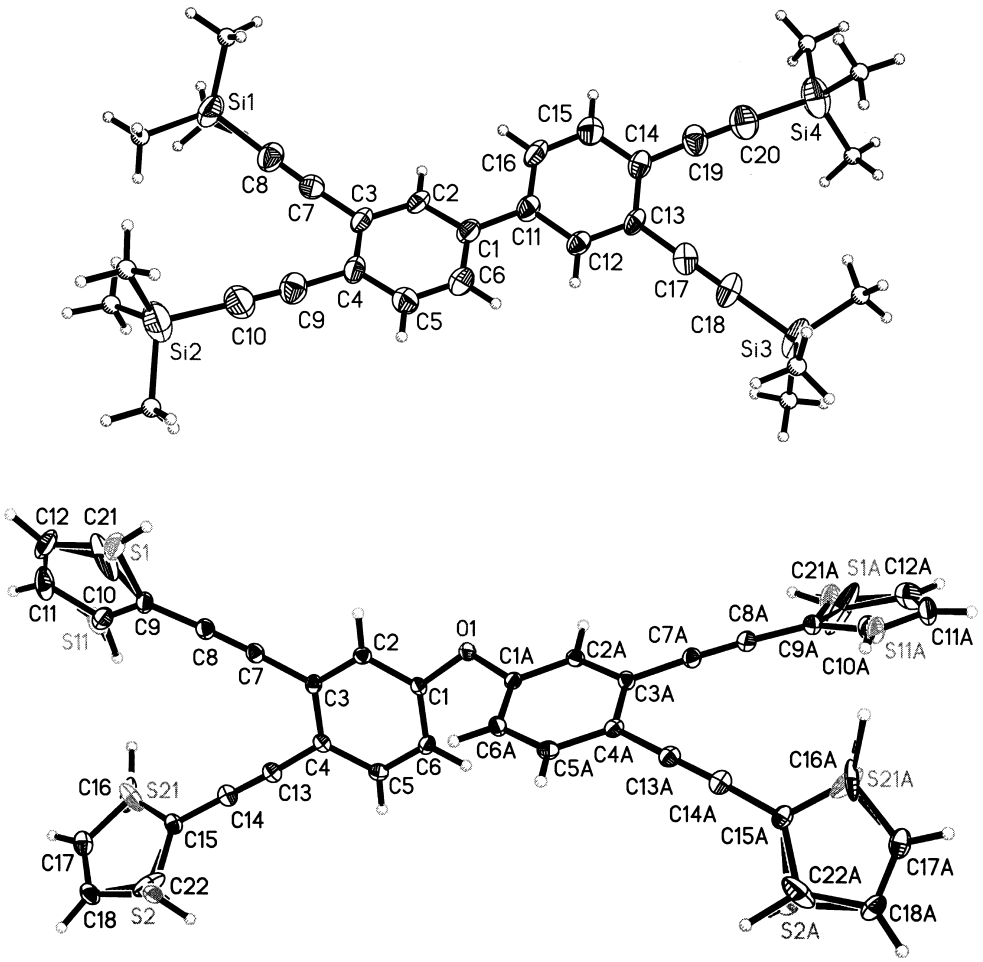


Figure 1. Single Crystal X-ray structures for monomers **2c** (above) and **4c** (below).

different monomers were determined from their X-ray crystal structures and reported elsewhere.[30]

Upon heating, the monomers exhibited an endothermic melting transition, followed by exothermic cyclopolymerization (by differential scanning calorimetry (DSC)). Monomer **4c** shows two distinct melting points as a result of melting two polymorphs, which is quite common for BODA monomers in general.[7] In order to illustrate the terminal group steric influence on the cyclization, three representative BODA monomers with the same spacer group (X=–O–, Scheme 1) and different terminal groups are highlighted here. The DSC data for the three monomers **4g**, **4d** and **4c** clearly illustrate the steric effects on cyclization. For monomers with terminal group R=Ph (**4g**), pyridine (**4d**), thiophene (**4c**) and spacer (X=–O–), the onset cyclopolymerization temperatures are 231, 230 and 205°C, respectively. Larger terminal groups thus increase the interalkyne distance and impart higher activation barriers. Three position substituted pyridine terminated arenediynes have been synthesized and the cyclization temperatures have also been reported (264°C).[28] However, the cylization temperature was calculated as the peak maximum of the dynamic DSC profile and is completely in accordance with our observed value (265°C) for 2-substituted pyridine terminated derivatives. Polymerization kinetics of BODA monomers with different spacer (X=–$C(CF_3)_2$, –O–, and –, Scheme 1) and same terminal group (R=Ph) have been investigated and no significant difference in reactivity is observed.[7]

Upon heating neat above 200°C for 2 h, BODA monomers **2**–**4** (Scheme 1) formed branched oligomers with M_w approaching 8000–9000 and broad polydispersities ($M_w/M_n>10$) which could be dissolved in THF and studied by UV–visible absorption and emission spectroscopy. Phenyl terminated BODA derived pre-networks and thermoset structures have been shown to exhibit photoluminescent properties.[6,31] The absorption spectra of phenyl and thiophene derivatives exhibited a λ_{max} values of 295 and 320 nm, respectively, as shown in Fig. 2. Pyridine terminated oligomers exhibit a 15 nm bathochromic (310 nm) shift over phenyl terminated derivative. The electron rich thiophene moiety imparts a much higher bathochromic shift than does pyridine over the phenyl derivative. In general, polymers prepared from **2**–**4** exhibit emission in the visible regions where thiophene and phenyl termination gave λ_{max} values of 445 nm and 410 nm, respectively, as shown in Fig. 2. Thiophene and pyridine terminated oligomers exhibit a 25 and 15 nm bathochromic shift, respectively, over phenyl terminated oligomers, and are qualitatively much more intense than those previously prepared. The reason for the bathochromic shift for thiophene and pyridine terminated derivatives is not yet clearly understood. Quantitative absorption, emission behavior and thermal properties for the fully cured networks

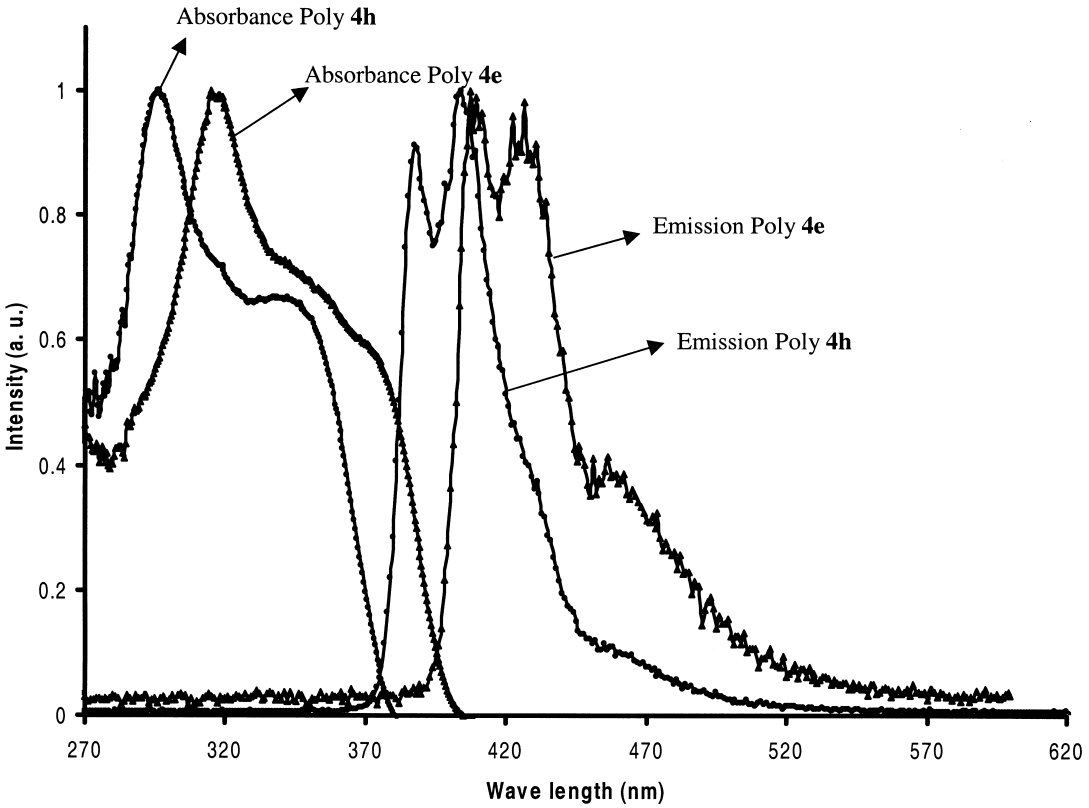


Figure 2. Solution (THF) absorption and emission spectra for oligomers derived from monomer **4e** and monomer **4h**.

in the solid state is currently underway and will be reported elsewhere.

3. Conclusion

New bis-*ortho*-diynylarene compounds containing terminal heterocyclic rings have been synthesized from bisphenols via desilylation in situ palladium coupling. Emission spectra of thiophene terminated oligomers in solution indicated a bathochromic shift (25 nm) over phenyl terminated BODA monomers. BODA monomer cyclopolymerization kinetics changes dramatically with the steric changes of the terminal group where thiophene and pyridine terminated derivatives exhibited a significantly lower cyclization temperatures.

4. Experimental

4.1. General

All chemicals were purchased from Aldrich Chemicals and were used as supplied without further purification unless otherwise stated. House nitrogen filtered through a Drierite filter/dryer was used for all synthetic operations. ^{1}H NMR 500 MHz, proton decoupled ^{13}C NMR 125 MHz, ^{1}H NMR 300 MHz, proton decoupled ^{13}C NMR 75 MHz, and ^{19}F NMR 188 MHz spectra were obtained with JOEL Eclipse+500, Bruker AF-300 and Bruker AF-200 spectrometer systems, respectively. Chloroform-*d* was used as the solvent and chemical shifts reported were internally referenced to tetramethylsilane (0 ppm), $CDCl_3$ (77 ppm), and $CFCl_3$ (0 ppm) for ^{1}H, ^{13}C, and ^{19}F nuclei, respectively. Coupling constants (*J*) were reported in Hz. Yields refer to isolated yields of compounds estimated to be up to 95% pure as determined by ^{1}H NMR and up to 98% pure as determined by HPLC.

Infrared (IR) analyses were performed on neat KBr disks using a Nicolet Magna spectrometer 550. High-resolution masses were obtained from FAB micromass 70-SE-4FE and micromass 70VSE (chemical ionization) instruments at University of Illinois. HPLC data were recorded on Waters 2690 separations module with Waters 996 Photodiode array detector. DSC and TGA data were obtained from a Mettler-Toledo 820 System. The cure onset temperatures of all monomers were measured as the point of intersection of the extrapolated baseline and the initial steep portion of the curve. UV–Vis absorption spectra were measured on a computer controlled Shimadzu UV-2101 PC spectrophotometer. Emission spectra were recorded on a Spex Fluorolog-2 photon-counting emission spectrometer equipped with a 450 W xenon lamp, a Spex 340S dual-grating and dual-exit monochromator, and two detectors. For all absorption and emission measurements, 0.001 mol/L sample concentration in Tetrahydrofuran has been used.

4.2. General procedure for the bromination of the bisphenols

To a 250 mL 4-neck flask equipped with gas vent attached to an acid gas scrubber, N_2 purging tube, thermocouple, and condenser, 10.00 g (0.0297 mol) of 2,2-Bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (**1a**) and 0.35 g (0.00595 mol) of iron powder was added to 100 mL of CCl_4 and 16.64 mL of glacial acetic acid (HOAc). The

solution was maintained at room temperature and 19.5 g (0.122 mole) bromine was added dropwise over 150 min. The reaction mixture was stirred for 3 h and the organic layer was washed once with sat. aq. $NaHCO_3$, twice with water, dried over $MgSO_4$, filtered and evaporated providing 13.14 g (0.026 mol) of dibromo (**1a**) as yellow powder in 90% yield.

4.3. General procedure for the synthesis of bis-bromo-bis-triflates

To a 250 mL three neck flask equipped with N_2 inlet and thermocouple was added 34 mL CH_2Cl_2, 5 mL Et_3N, and 6.0 g (0.012 moles) dibromo (**1a**) at 25°C. The solution was cooled to 10°C and 3.56 g (0.0256 mol) CF_3SO_2Cl was added and the mixture was stirred for 3 h, then quenched with 200 mL of water and washed with sat. aq. $NaHCO_3$, dried over $MgSO_4$, filtered and evaporated to provide 8.38 g of bis-bromo-bis-triflate (**1a**) as white crystals in 91% yield.

4.4. General procedure for the preparation of trimethylsilyl BODA compounds (2a–c)

To a 250 mL four neck flask equipped with thermocouple, N_2 purging tube, dropping funnel and magnetic stirrer was added 10.00 g (0.01323 mol) of the bis-bromo-bis-triflate, 50 mL DMF, and 50 mL of Et_3N. The solution was deoxygenated for 20 min by sparging with dry N_2 and 0.687 g, (9.79×10^{-4} mol) $[P(Ph)_3]_2PdCl_2$, and 0.11 g (9.79×10^{-4} mol) CuI were added and the solution was heated to 90°C. Deoxygenated trimethylsilyl acetylene, 5.8 g (0.059 mol), was added dropwise over 15 min and the mixture was heated at 90°C for ca. 12 h. The resulting dark brown solution was diluted with CH_2Cl_2 (100 mL), washed with 10% HCl, water twice, dried over $MgSO_4$ and evaporated to give 8.9 g of **2** dark brown oil. The crude product was further purified by column chromatography as indicated below.

4.5. Desilylation in situ coupling, (3a–c and 4a–f)

To a three neck flask was added 5 g of trimethylsilyl intermediate (**2a–c**), potassium carbonate (4 equiv. per alkyne) and 30 mL diethyl ether/methanol (1:2). The flask was capped and the mixture was stirred for ca. 12 h at 25°C. Aryl halide (5 equiv. based on tetrayne), bis(triphenylphosphine) palladium (II) dichloride, and copper (I) iodide (0.011 equiv. per alkyne) were then added followed by addition of 20 mL of dimethyl formamide (DMF) and 20 mL of triethyl amine (Et_3N) at room temperature under nitrogen and stirred for ca. 8–12 h. Observed yields for each halide was indicated below.

4.5.1. 2,2-Bis(3,4-di(trimethylsilylethynyl)-1,1,1,3,3,3-hexafluoropropane (2a). The crude product was purified by column chromatography (silica gel, hexane) and gave 7.37 g of yellow solid in 81% yield, mp 148°C (by DSC). FTIR (KBr disk): (cm^{-1}) 721, 760, 844, 867, 1488, 2160, 2900, 2961. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.24 (s, 36H), 7.21 (d, J=8.4 Hz, 2H), 7.35 (d, J=8.3 Hz, 2H), 7.38 (s, 2H). ^{13}C NMR δ: 0.29, 64.00 (m), 99.96, 100.88, 102.03, 102.16, 126.13, 126.93, 129.47, 132.22, 132.65, 133.60. HRMS for $C_{35}H_{42}F_6Si_4$ calcd (found): 688.2267 (688.2269).

4.5.2. 3,3′,4,4′-Tetra(trimethylsiylethynyl)phenyl ether (2b). The crude product was purified by column chromatography (silica gel, hexane) and gave 7.48 g of yellow/red solid in 84% yield, mp 145°C (by DSC). ^1H NMR (300 MHz, $CDCl_3$) δ: 0.26 (s, 36H), 6.87 (m, 2H), 7.01 (m, 2H), 7.44 (d, J=8.6 Hz, 2H). ^{13}C NMR δ: 0.09, 98.02, 98.04, 99.53, 102.30, 102.60, 119.35, 121.41, 122.17, 127.55, 134.03, 156.05. HRMS for $C_{32}H_{42}Si_4O$ calcd (found): 554.2312 (554.2323).

4.5.3. 3,3′,4,4′-Tetra(trimethylsilyl ethynyl)biphenyl (2c). The crude product was purified by column chromatography (silica gel, hexane) and gave 6.3 g of an orange/yellow solid in 89% yield, mp 147°C (by DSC). FTIR (KBr disk): (cm^{-1}) 644.5, 758.3, 839.3, 1248, 1470, 1632, 2852, 2921, 2958, 3357. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.11 (s, 36H), 7.32–7.45 (m, 6H). ^{13}C NMR δ: 0.33, 98.73, 99.46, 102.89, 102.9, 125.08, 126.26, 126.38, 128.22, 132.65. 133.60. HRMS for $C_{32}H_{42}Si_4$ calcd (found): 538.2363 (538.2363).

4.5.4. 3,3′,4,4′-Tetra(2-ethynyl)1,1,1,3,3,3-hexafluoropropane (3a). The crude product was purified by column chromatography (silica gel, 5:1 hexane/ethyl acetate) and gave 2.6 g of white solid in 90% yield with rapid color change in the presence of the air or N_2 resulting red oil. ^1H NMR (300 MHz, $CDCl_3$) δ: 3.37 (s, 2H), 3.43 (s, 2H), 7.27–7.30 (m, 2H), 7.52–7.55 (m, 4H). ^{13}C NMR δ: 64.00 (m), 80.69, 80.94, 82.41, 83.19, 122.00, 125.55, 126.34, 130.05, 132.65, 133.07, 133.99. HRMS for $C_{23}H_{10}F_6$ calcd (found): 400.0682 (400.0686).

4.5.5. 3,3′,4,4′-Tetra(2-ethynyl)phenyl ether (3b). The crude product was purified by column chromatography (silica gel, 8:1 hexane/ethyl acetate) and gave 2.18 g of white solid in 91% yield with rapid color change in the presence of the air and N_2 yielding red oil. ^1H NMR (300 MHz, $CDCl_3$) δ: 3.27 (s, 2H), 3.32 (s, 2H), 6.89 (m, 2H), 7.1 (m, 2H), 7.47 (d, J=8.5 Hz, 2H). ^{13}C NMR δ: 80.91, 81.00, 81.16, 82.09, 119.56, 120.71, 122.62, 126.88, 134.37, 156.11. HRMS for $C_{23}H_{10}F_6$ calcd (found): 266.0731 (266.0732).

4.5.6. 3,3′,4,4′-Tetra(2-ethynyl)biphenyl (3c). The crude product was purified by column chromatography (silica gel, 10:1 hexane/ethyl acetate) and gave 2.01 g of white/yellow solid in 89% yield with rapid color change in the presence of the air and N_2 yielding red oil. ^1H NMR (300 MHz, $CDCl_3$) δ: 3.36 (s, 2H), 3.45 (s, 2H), 7.49 (dd, J=8.16, 1.9 Hz, 2H), 7.57 (s, 2H), 7.72 (m, 2H). ^{13}C NMR δ: 80.16, 81.56, 82.61, 82.75, 124.60, 125.76, 127.00, 131.04, 133.25, 139.49. HRMS for $C_{20}H_{10}$ calcd (found) 250.0782 (250.0783).

4.5.7. 3,3′,4,4′-Tetra(2-ethynylthienyl)1,1,1,3,3,3-hexafluoropropane (4a). The crude product was purified by column chromatography (silica gel, 8:1 hexane/ethyl acetate) and gave 2.9 g of white/orange solid in 60% yield, mp 210–211°C. FTIR (KBr disk): (cm^{-1}) 721, 760, 844, 867, 1488, 2160, 2900, 2961. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.01–7.05 (m, 4H), 7.32–7.39 (m, 10H), 7.5–7.57 (m, 4H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 64.00 (m),

88.06, 88.89, 90.89, 91.06, 122.74, 122.78, 125.64, 126.44, 127.25, 127.29, 128.09, 128.22, 129.44, 131.24, 132.51, 132.66, 132.72. HRMS for $C_{39}H_{18}F_6S$ calcd (found): 728.0195 (728.0193).

4.5.8. 2,2-Bis(3,4-di(2-2-ethynylpyridyl)-1,1,1,3,3,3-hexafluoropropane (4b). The crude product was purified by column chromatography (silica gel, 1:1 hexane/ethyl acetate) and gave 3.45 g of an orange solid in 75% yield, mp 215–216°C. FTIR (KBr disk): (cm^{-1}) 713, 736, 785, 831, 881, 968, 987, 1044, 1079, 1110, 1151, 1185, 1204, 1254, 1372, 1422, 1456, 1486, 1570, 1582, 1723, 2214, 2919. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.26–7.28 (m, 3H), 7.38–7.41 (m, 2H), 7.68–7.74 (m, 13H), 8.62–8.66 (m, 4H). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 64.00 (m), 87.18, 87.37, 93.51, 94.07, 123.39, 123.48, 125.86, 126.55, 128.02, 128.23, 130.34, 132.40, 133.46, 133.80, 136.60, 136.85, 142.59, 142.74, 149.72, 149.93. HRMS $C_{43}H_{22}N_4F_6$ calcd (found): 708.1748 (708.1752).

4.5.9. 3,3′,4,4′-Tetra(2-ethynylthienyl)phenyl ether (4c). The crude product was purified by column chromatography (silica gel, 10:1 hexane/ethyl acetate) and gave 3.40 g of an orange solid 70% yield, mp 210–211°C. FTIR (KBr disk): (cm^{-1}) 592, 689, 837, 964, 1040, 1198, 1351, 1417, 1468, 1524, 1590, 2195, 2938, 3086. ^1H NMR (300 MHz, $CDCl_3$) δ: 6.97–7.03 (m, 6H), 7.14–7.15 (m, 2H), 7.29–7.34 (m, 8H), 7.50–7.53 (d, J=8.5 Hz, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 86.70, 87.95, 91.26, 91.37, 119.38, 120.00, 121.42, 123.00, 123.50, 127.28, 127.31, 127.65, 128.12, 132.14, 132.65, 133.27, 156.19. HRMS for $C_{36}H_{18}O_1S_4$ calcd (found): 594.0240 (594.0231).

4.5.10. 3,3′,4,4′-Tetra(2-ethynylpyridyl)phenyl ether (4d). The crude product was purified by column chromatography (silica gel, 9:1 hexane/ethyl acetate) and gave 3.01 g of an orange solid in 64% yield, mp 210–211°C. FTIR (KBr disk): (cm^{-1}) 660, 732, 767, 815, 886, 982, 1031, 1088, 1141, 1211, 1246, 1304, 1422, 1453, 1475, 1550, 1581, 2215, 2954. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.06–7.10 (m, 2H), 7.23–7.31 (m, 6H), 7.64–7.69 (m, 10H), 8.62–8.63 (m, 4H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 86.76, 87.13, 92.67, 93.57, 119.85, 121.04, 122.19, 122.78, 123.03, 127.25, 127.59, 127.69, 134.02, 136.06, 143.07, 143.42, 150.10, 150.04, 156.36. FAB HRMS for $C_{40}H_{23}O_1N_4$ calcd (found): 575.1873 (575.1871), (M^++H).

4.5.11. 3,3′,4,4′-Tetra(2-ethynylthienyl)biphenyl (4e). The crude product was purified by column chromatography (silica gel, 10:1 hexane/ethyl acetate) and gave 2.52 g of an orange/yellow solid in 60% yield, mp 212–213°C. FTIR (KBr disk): (cm^{-1}) 685, 824, 846, 888, 1027, 1208, 1257, 1373, 1452, 1561, 1648, 1731, 2190, 2908. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.02–7.05 (m, 4H), 7.32–7.36 (m, 8H), 7.53–7.62 (m, 4H), 7.79 (m, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 87.68, 88.80, 91.97, 91.99, 123.28, 123.30, 124.69, 126.00, 126.47, 127.22, 127.83, 129.72, 131.96, 132.36, 132.38, 139.10. HRMS for $C_{36}H_{18}S_4$ calcd (found): 578.0291 (578.0283).

4.5.12. 3,3′,4,4′-Tetra(2-ethynylpyridyl)biphenyl (4f). The crude product was purified by column chromatography (silica gel, 9:1 hexane/ethyl acetate) and gave 2.75 g of an orange solid in 68% yield, mp 152–157°C. FTIR (KBr disk): (cm^{-1}) 683, 741, 780, 820, 835, 911, 1020, 1100, 1211, 1250, 1300, 1400, 1460, 1470, 1581, 2215, 2954. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.24–7.29 (m, 4H), 7.61–7.75 (m, 12H), 7.94 (m, 2H), 8.65–8.67 (m, 4H). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 87.45, 87.55, 93.32, 94.10, 123.06, 123.11, 124.94, 126.23, 127.24, 127.78, 127.90, 130.79, 132.99, 136.23, 139.65, 143.39, 143.45, 150.17, 150.21. HRMS for $C_{40}H_{22}N_4$ calcd (found): 558.1844 (558.1848).

Acknowledgements

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29. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 179393 and CCDC 178820 for monomers *2c* and *4c*, respectively. The structure solutions and refinements are performed with Bruker SHELXTL, v. 6.1 program suite. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit @ccdc.cam.ac.uk).
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