Electronic Supplementary Material (ESI) for RSC Advances

2,5-*bis*(Arylethynyl)thienyl systems: Preparation and photophysical properties. Part II. Supplementary Information.

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Experimental Details

Where necessary, reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Dry solvents were obtained dry from an Innovative Technologies Solvent Purification System and deoxygenated (bubbled through with N_2 or freeze–pump–thaw) prior to use (diethyl ether and tetrahydrofuran) and triethylamine was provided by the research group Prof. P.J. Low. Starting materials were obtained from Sigma Aldrich, Acros Organics and Lancaster and used without further purification.

Synthesis Charaterisation Details

GC MS analyses were performed on an Agilent Technologies 6890 N gas chromatograph equipped with a 5973 inert mass selective detector and a 10 m fused silica capillary column (5 % cross-linked phenylmethylsilicone) using the following operating conditions: Injector temperature 250 ^{o}C, detector temperature 300 ^{o}C, the oven temperature was ramped from 70 ^{o}C to 280 ^{o}C at 20 ^{0}C min^{-1}. UHP helium was used as the carrier gas. MALDI mass spectrometry was performed on an Autoflex II ToF/ToF mass spectrometer (Bruker Daltonik GmBH), equipped with a 337 nm nitrogen laser, with analysis performed by a reflectron. trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) was used as the matrix.

Accurate mass analyses were performed on a Xevo QToF mass spectrometer (Waters Ltd., UK) equipped with an Agilent 7890 GC (Agilent Technologies UK Ltd., UK), set up to perform atmospheric pressure of solids analysis probe ionisation (ASAP) of positive ions. MS data was processed using MassLynx 4.1. Exact mass measurements utilised a lock–mass correction to provide < 3 mDa precision. Exact mass measurement used Elemental Composition version 4.0 embedded within MassLynx 4.1 (Waters Ltd., UK).

Routine NMR spectra were collected using either a Varian Unity 300, Mercury 400, Avance 400 MHz Bruker, Varian Inova 500 or Varian 700 MHz instrument, and spectra analysed using Varian NMR software and MestReNova version 5.2.5. Chemical shifts are referenced to the residual protio impurities in the deuterated solvent (1H) or the 13C shift of the solvent (13C). Solvent proton shifts (ppm); $CDCl_3$, 7.27 (s); CD_2Cl_2, 5.34 (t); $(CD_3)_2SO$, 2.50 (s); $C_2D_2Cl_4$, 5.91 (s). Solvent carbon shifts (ppm): $CDCl_3$, 77.2 (t); CD_2Cl_2, 54.0 (quin); $(CD_3)_2SO$, 39.5 (s); $C_2D_2Cl_4$, 73.3 (t).

Elemental analyses were performed by the Analytical Services of the Department of Chemistry University of Durham, using an Exeter Analytical Inc. CE-440 Elemental Analyser (C, H, N). Melting points are reported uncorrected. Raman spectra were recorded using a Horiba Jobin-Yvon LabRAM-HR equipped with a HeNe laser (633 nm).

Photophysical Characterisation Details

All photophysical measurements were made using GPR grade solvents. UV-visible absorption spectra were recorded in quartz cuvettes of path length l = 1 cm with an absorbance, A, < 0.3 at 400 nm and were measured on a Unicam UV2-100 spectrometer operated with the Unicam Vision software. Baseline correction was achieved by reference to pure solvent in the same cuvette.

Excitation and emission photoluminescence spectra were recorded on a Horiba Jobin Yvon SPEX Fluorolog 3-22 spectrofluorometer. Samples were held in quartz fluorescence cuvettes, l = 1 cm x 1 cm and fluorescence was detected at 90^{o} to the excitation beam. Solutions had A = 0.10–0.15 at the excitation wavelength to minimise inner filter effects. PLQYs were measured using the Fluorolog 3-22 and an integrating sphere using a published method.[1] DataMax software was used throughout.

Excited state lifetime measurements were made using the time-correlated photon counting method. Briefly this was achieved as follows: a N_2 laser (337 nm, 10 μJ, 10 Hz) was used as an excitation source with emission detected in a 90° geometry by a Perkin Elmer SPCM-AQR single-photon counting avalanche diode at a wavelength selected by a monochromator (Jobin-Yvon Triax 320) set to a 1 nm bandpass. The signal was digitised by a National Instruments (NI) USB-5133 (8 bit, 100 Ms/s) digitiser and processed and recorded by in-house NI LabVIEW software.

Ab initio Calculation Details

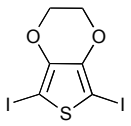
All calculations were carried out using the Gaussian-09 package.[2] Density functional theory (DFT) ground-state optimised structures were calculated using Becke's three parameter Lee-Yang-Parr (B3LYP) exchange-correlation functional with a basis set of 6-31+G. Orbital surfaces generated from the DFT calculations were visualised in GaussView 4.1. Time-dependent (TD)-DFT calculations were performed on the B3LYP/6-31+G optimised ground-state geometries over 10 states (singlets) using the Coulomb-attenuating method - CAM-B3LYP/6-31+G level of theory. The initial geometry input for optimisation was based on the crystallographic coordinates where possible or from a chemically intuitive geometry when experimental data were not available to maximise the probability of locating the global minimum on the potential energy surface.

Crystallography

Crystallographic data for **2b, 3b, 4b, 5b, 6b** and bis(TMS)-thiophene dioxide are summarized in Table **4**. X-ray diffraction data for all compounds **2b-6b** were collected at 120 K using graphite monochrmated Mo *Kα* (0.71073 Å). Data for bis(TMS)-thiophene dioxide were collected at 215 K since it showed a reversible phase transition at 203 K from orthorhombic to monoclinic; this phase transition was accompanied by non-merohedral twinning. Data were collected on a Bruker SMART 1K CCD (**2b**) diffractometer and a Bruker SMART 6K CCD diffractometer (**3b, 5b, 6b** and bis(TMA)-thiophene dioxide) and processed using SAINT [3], while data for **4b** were collected on an Oxford Diffraction Gemini S Ultra diffractometer and processed using the Oxford Diffraction CrysAlis software.[4] All of the structures were solved by direct methods in SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97.[5] The hydrogen atoms in **2b** and **3b** were located in the Fourier difference map and refined, while all of the hydrogen atoms in the remaining structures were positioned geometrically (aromatic C–H 0.95 Å, ethyl C–H 0.99 Å and methyl C–H 0.98 Å) and refined using a riding model with the isotropic displacement parameters fixed at U_{iso}(H) = 1.2 times U_{eq} of the parent carbon atom for the aromatic and ethyl hydrogens and U_{iso}(H) = 1.5 times U_{eq} of the parent carbon atom for the methyl hydrogens.

Experimental Details

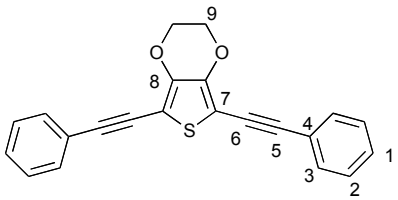
2,5-Diiodo-3,4-ethylenedioxythiophene (2a)



Chemical Formula: $C_6H_4I_2O_2S$
Molecular Weight: 393.97

Under an atmosphere of nitrogen, 3,4-ethylenedioxy thiophene (3.0 g, 21 mmol) and N-iodosuccinimide (8.0 g, 45 mmol) were dissolved in dry DMF (100 mL), and stirred at room temperature for 3 h. The resulting solution was poured into distilled water (200 mL) and extracted with DCM (4 x 30 mL aliquots). The organic fractions were collected and dried over $MgSO_4$ and then reduced in vacuo. The isolated solid was eluted through a silica plug (chloroform eluant) and evaporated to dryness to afford **2a** (4.4 g, 70 %) as an off-white solid. 1H NMR ($CDCl_3$, 400 MHz): δ 4.26 (4 H, s). MS (EI): m/z 394 [M].

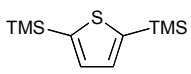
2,5-*bis*(Phenylethynyl)-3,4-ethylenedioxythiophene (2b)



Chemical Formula: $C_{22}H_{14}O_2S$
Molecular Weight: 342.41

2,5-Diiodo-3,4-ethylenedioxythiophene (1.0 g, 2.54 mmol) and phenylacetylene (0.84 mL, 7.61 mmol) were dissolved in dry triethylamine (20 mL). The solution was then degassed by three freeze-pump-thaw cycles. To this was added CuI (0.024 g, 0.127 mmol) and $Pd(PPh_3)_2Cl_2$ (0.036 g, 0.051 mmol) and the mixture was stirred under nitrogen at 25 °C for 16 h. The solvent was then removed and the product chromatographed on silica with DCM/hexane (1:1) to give **2b** (0.54 g, 62 %) which was recrystallised from DCM/Cyclohexane (1:1) to give pale yellow crystals. M.P.: 152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.49 (4H, m, H_3), 7.36-7.30 (6H, m, $H_{1\&2}$), 4.33 (4H, s, H_9). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.2 (C_1), 131.5 (C_8), 128.5 (C_3), 128.3 (C_4), 122.8 (C_2), 99.8 ($C_{6\text{ or }7}$), 96.8 (C_5), 79.7 ($C_{7\text{ or }6}$), 64.9 (C_9). MS (EI): (m/z) 342 [M], HR-MS (ASAP) calc'd for [M+H] m/z = 343.0793, found m/z = 343.0779.

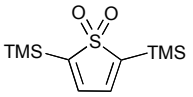
2,5-*bis*(Trimethylsilyl)thiophene



Chemical Formula: $C_{10}H_{20}SSi_2$
Molecular Weight: 228.5

Thiophene (0.8 mL, 10 mmol) was dissolved in dry THF (50 mL) and stirred at -78 °C for 30 minutes. *n*–Butyllithium (*n*–BuLi) (15.6 mL, 1.6M in hexanes, 25 mmol) was added dropwise *via* syringe, and the solution warmed to -20 °C and stirred for a further 30 minutes under N_2. After cooling back to -78 °C, chlorotrimethylsilane (TMSCl) (4 mL, 31 mmol) was added dropwise. After 10 minutes of stirring the solution was allowed to warm to room temperature. Water (3 mL) was added and the organic solvent was removed *in vacuo*. More water (10 mL) was added and the product was extracted with DCM. The organic layer was dried over $MgSO_4$ and the solvent removed *in vacuo* to yield a yellow-brown viscous oil (1.7 g). Preliminary NMR spectroscopic analysis of this material revealed it to be a mixture of both the mono- and bis-trimethylsilylated thiophene compounds. The oil was re-dissolved in THF (40 mL), and reacted with additional *n*-BuLi (6.5 mL, 1.6M in hexanes, 10 mmol) and TMSCl (4 mL, 31 mmol) under the original conditions. The reaction was quenched and the product was isolated as a yellow oil (1.7 g, 75 %) which was used without further purification. ^{1}H NMR ($CDCl_3$, 300 MHz): δ7.30 (2 H, s), 0.34 (18 H, s). MS (EI): (m/z) 228 [M], 213 [M – CH_3].

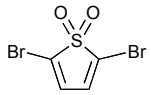
2,5-*bis*(Trimethylsilyl)thiophene-1,1-dioxide



Chemical Formula: $C_{10}H_{20}O_2SSi_2$
Molecular Weight: 260.5

2,5-*bis*-(Trimethylsilyl)thiophene (500 mg, 2.27 mmol) was dissolved in DCM (20 mL) and, separately, *m*-CPBA (1.2 g, 7 mmol) was dissolved in DCM (20 mL). The two solutions were combined by dropwise addition of the *m*-CPBA solution and the resulting solution was stirred at room temperature. After 3 h the solution turned an opaque creamy colour. After stirring overnight, saturated aqueous K_2CO_3 solution was added to quench the reaction and neutralise the solution. The organic layer was separated and washed with more aqueous K_2CO_3, extracted with DCM and dried over anhydrous $MgSO_4$. The solvent was reduced *in vacuo* to yield a light brown solid (420 mg), which was purified using column chromatography on silica gel, eluting with hexane and DCM (1:1) to yield 2,5-*bis*(trimethylsilyl)thiophene-1,1-dioxide (330 mg, 56 %) as a cream/brown solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.74 (2 H, s), 0.34 (18 H, s). MS (EI): (m/z) 260 [M], 245 [M – CH_3].

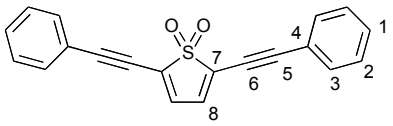
2,5-dibromothiophene-1,1-dioxide (3a)



Chemical Formula: $C_4H_2Br_2O_2S$
Molecular Weight: 273.93

A solution of bromine in DCM (0.4M solution, 0.76 mmol, 1.9 mL) was added carefully to 2,5-bis(trimethylsilyl)thiophene-1,1-dioxide (100mg, 0.38 mmol) and $AgBF_4$ (220 mg, 1.14 mmol) dissolved in DCM (20 mL), in a aluminium foil–covered vessel. Fumes were evolved during this step, necessitating slow addition. After complete addition of the bromine solution, the reactants were stirred at 0 °C for 1 h after which DCM (10 mL) was added, and the solution was filtered through a silica plug, eluting with DCM. The resulting solution was reduced *in vacuo* to afford 2,5- dibromothiophene-1,1-dioxide (**3a**) as a light beige solid (66 mg, 60 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.90 (s). ^{13}C{^{1}H}NMR ($CDCl_3$, 75 MHz): δ 128.5, 119.5. MS (EI): (m/z) 272-274-276.

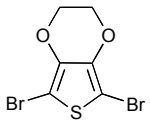
2,5-*bis*(Phenylethynyl)thiophene-1,1-dioxide (3b)



Chemical Formula: $C_{20}H_{12}O_2S$
Molecular Weight: 316.37
Elemental Analysis: C, 75.93; H, 3.82; O, 10.11; S, 10.14

2,5-Dibromothiophene-1,1-dioxide (550 mg, 2 mmol) and phenylacetylene (2.5 equivalents, 0.6 mL, 5 mmol) were dissolved in dry THF (15 mL), and the solution degassed through four freeze-pump-thaw cycles. Under a flow of N_2, dry Et_3N (0.7 mL, 5 mmol), CuI (50 mg, 13 mol%) and $PdCl_2(PPh_3)_2$ (180 mg, 13 mol%) were added, and the dark red mixture stirred at room temperature for 30 minutes. The solvent of the resulting suspension was removed under reduced pressure and the solid product purified by column chromatography, eluting with hexane/DCM (1:1) on silica gel. The product was recrystallised from warmed ether/ cold hexane to yield 2,5-*bis*(phenylethynyl)thiophene-1,1-dioxide (**3b**) as orange needles (365 mg, 58 %). M.P.: 178 – 179 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.61 (4 H, d, ^{3}J 7.5 Hz, H_3), 7.16 (6 H, m, H_{1+2}), 6.69 (2 H, s, H_8). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 132.3 (C_3), 130.1 (C_1), 128.5 (C_2), 128.1 (C_8), 126.8 (C_6), 121.05 (C_4), 104.1 (C_5), 77.4 (C_7). Acc. MS (ES+): (m/z) calcd. for [M + H]+ 317.06308, for [M + Na]+ 339.04502; found for [M + H]+, 317.06310, for [M + Na]+ 339.04501. Elemental analysis: expected ($C_{20}H_{12}O_2S$): C, 75.93 %; H, 3.82 %; found: C, 75.78 %, H, 3.76 %.

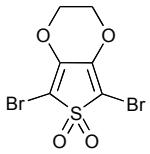
2,5-Dibromo-3,4-ethylenedioxythiophene



Chemical Formula: $C_6H_4Br_2O_2S$
Molecular Weight: 299.97

3,4-Ethylenedioxy thiophene (3.0 g, 21 mmol) and N-bromosuccinimide (8.0 g, 45 mmol) were dissolved in chloroform and glacial acetic acid (1:1 v/v, 100 mL), and stirred at room temperature for 3 h. The resulting solution was poured into distilled water (200 mL) and neutralised by addition of $NaHCO_3$. The solution was extracted into DCM (4 x 30 mL aliquots), the organic fractions collected, combined and dried over $MgSO_4$, and then reduced *in vacuo*. The isolated solid was eluted through a silica plug with chloroform and evaporated to dryness to afford 2,5-dibromo-3,4-ethylenedioxy thiophene (4.4 g, 70 %) as a cream solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.27 (4 H, s). MS (EI): (m/z) 298-300-302 [M]

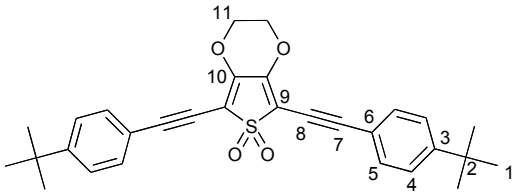
2,5-Dibromo-3,4-ethylenedioxythiophene-1,1-dioxide (4a)



Chemical Formula: $C_6H_4Br_2O_4S$
Molecular Weight: 331.97

2,5-Dibromo-3,4-ethylenedioxy thiophene (1.6 g, 5.3 mmol) and *m*-CPBA (2.3 g, 13.5 mmol) were dissolved in CH_2Cl_2 (40 mL) and stirred at room temperature over night. The reaction mixture was filtered and the filtrate washed with aqueous sodium bicarbonate (2 x 50 mL) and then water (2 x 50 mL). The organic layer was dried over $MgSO_4$, filtered, and reduced *in vacuo* to leave an orange residue. Analysis by TLC revealed multiple spots so the isolated solid was chromatographed on silica, eluting with DCM/Petroleum ether (4:1 v/v). **4a** was collected as a yellow solid (420 mg, 40 %). The compound was found to decompose over a period of hours at room temperature and hence was stored under nitrogen at - 20 ^{o}C, where it was stable for extended periods. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.49 (4 H, s). MS (EI): (m/z) 330-332-334 [M].

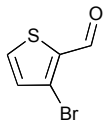
2,5-*bis*(4'-*tert*butylphenylethynyl)-3,4-ethylenedioxythiophene-1,1-dioxide (4b)



Chemical Formula: $C_{30}H_{30}O_4S$
Molecular Weight: 486.62
Elemental Analysis: C, 74.05; H, 6.21; O, 13.15; S, 6.59

In an oven-dried Schlenk flask 2,5-dibromo-3,4-ethylenedioxythiophene-1,1-dioxide (250 mg, 0.75 mmol) and 4-*t*-butylphenylacetylene (240 mg, 0.28 mL, 1.5 mmol) were dissolved in Et_3N (15 mL) and THF (10 mL) and degassed through 4 freeze-pump-thaw cycles. The reaction vessel was back-filled with nitrogen, and the solution heated to 50 ^{o}C. Under a blanket of N_2 CuI (3 mg, 2 mol%) and $Pd(PPh_3)_4$ (18 mg, 2 mol%) were added and the reaction mixture heated to 70 ^{o}C and allowed to stir for 24 h. The deep red suspension was evaporated to dryness and the residue remaining was eluted through a silica plug with ether. The orange solid isolated was absorbed onto silica and chromatographed on silica gel, eluting initially with 1:1 hexane/ether and finally with 3:2 ether/hexane. 2,5-*bis*(4-*t*-butylphenylethynyl)-3,4-ethylenedioxythiophene-1,1-dioxide (**4b**) was isolated as a yellow powder (40 mg, 11 %). M.P.: 234-236 ^{o}C ^{1}H NMR (CD_2Cl_2, 700 MHz): δ 7.46 (4 H, d, ^{3}J 7 Hz, H_5), 7.39 (4 H, d, ^{3}J 7 Hz, H_4), 4.51 (4 H, s, H_{11}), 1.30 (18 H, s, H_1). ^{13}C NMR (CD_2Cl_2, 176 MHz): δ 153.6 (C_3), 149.2 (C_{10}), 131.8 (C_5), 125.9 (C_4), 118.7 (C_6), 103.8 ($C_{7,8\text{ or }9}$), 103.7 ($C_{7,8\text{ or }9}$), 73.5 ($C_{8\text{ or }9}$), 66.7 (C_{11}), 35.1 (C_2), 31.0 (C_1). Acc. MS (AP+): (m/z) Calcd. for [M + H]+ 487.1945; Found for [M + H]+ 487.1943.

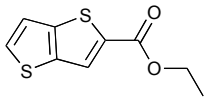
3-Bromothiophene-2-carbaldehyde.



Chemical Formula: C_5H_3BrOS
Molecular Weight: 191.05

Under a nitrogen atmosphere diisopropylamine (6.33 g, 8.75 mL, 62.5 mmol) was dissolved in dry THF (100 mL) and cooled to -78 ^oC. To this stirred solution was added *n*-BuLi (25 mL, 2.5 M in hexane, 62.5 mmol) and the resulting solution stirred for 30 mins. The solution was then warmed up to 0 ^oC with ice cooling and 3-bromothiophene (10.2 g, 5.9 mL, 62.5 mmol) was added dropwise and stirring continued for a further 30 mins. N-Formylpiperidine (7.10 g, 6.9 mL, 62.5 mmol) was added and the solution allowed to stir at room temperature for 3 h, during which time a precipitate formed. Aqueous ammonium chloride (20 %, 50 mL) was added and the volatile solvent was removed under reduced pressure. The product was extracted with diethyl ether, dried over $MgSO_4$, and evaporated to dryness to yield the crude product as a brown oil. Fractional distillation was performed to purify the material (Kugelrohr apparatus, 80 ^oC, 2 x 10^{-4} bar) and afforded 3-bromothiophene-2-carbaldehyde (9.2 g, 76 %) as a dark yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.96 (1 H, s), 7.70 (1 H, d, ^3J 4.8 Hz) 7.13 (1 H, d, ^3J 5.2 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 183.2, 135.1, 132.2, 68.1, 25.8. MS (EI): (m/z) 191 [M].

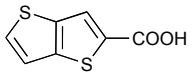
Ethyl thieno[3,2-*b*]thiophene-5-carboxylate



Chemical Formula: $C_9H_8O_2S_2$
Molecular Weight: 212.29

Ethyl thioglycolate (3 mL, 27 mmol) and potassium carbonate (5 g) were dissolved in DMF (50 mL) and 3-bromothiophene-2-carbaldehyde (5.2 g, 26.8 mmol) was added dropwise over 5 minutes. The mixture was allowed to stir at room temperature for 24 h, after which it was poured into water (100 mL) and the product extracted with DCM, dried over $MgSO_4$ and concentrated *in vacuo*. The crude oil was purified by fractional distillation (Kugelrohr apparatus, 160 – 180 ^oC, 2 x 10^{-4} bar) to a light orange oil, ethyl thieno[3,2-*b*]thiophene-5-carboxylate (4.5 g, 85 %). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.99 (1 H, s), 7.58 (1 H, d, ^3J 5.2 Hz), 7.28 (1 H, d, ^3J 5.2Hz), 4.38 (2 H, q, ^3J 7.2 Hz), 1.4 (3 H, t, ^3J 7.2 Hz). MS (AP+): (m/z) 213 [M + H]+.

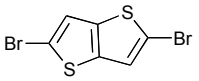
Thieno[3,2-*b*]thiophene-5-carboxylic acid



Chemical Formula: $C_7H_4O_2S_2$
Molecular Weight: 184.24

Ethyl thieno[3,2-*b*]thiophene-5-carboxylate (4.0 g, 19 mmol) was stirred in THF (40 mL) with aqueous lithium hydroxide (40 mL, 1 M) added slowly. The mixture was stirred at reflux for 12 h. The solution was concentrated *in vacuo* and 5M HCl acid was added, which precipitated a white solid. The precipitate was isolated by filtration, washed with water and ether, and dried under vacuum to give thieno[3,2-*b*]thiophene-5-carboxylic acid (3.1 g, 90 %). ^1H NMR (DMSO, 400 MHz): δ 13.2 (1 H, broad s), 8.1 (1 H, s), 7.91 (1 H, d, ^3J 5.6 Hz), 7.49 (1 H, d, ^3J 5.6 Hz). MS (AP+): (m/z) 185 [M + H]+.

2,5-Dibromothieno[3,2-*b*]thiophene (5a).

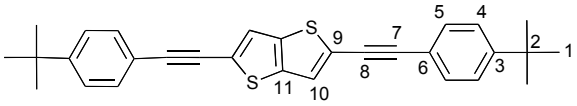


Chemical Formula: $C_6H_2Br_2S_2$
Molecular Weight: 298.02

A solution of NBS (2.3 g, 13 mmol) in water (15 mL) was added added portionwise to thieno[3,2-*b*]thiophene-5-carboxylic acid (1.0 g, 5.6 mmol) dissolved in nMP (100 mL) over 1h. The mixture was allowed to stir for 18 h and then water (100 mL) was added, where upon a solid precipitated. The precipitate was isolated by filtration and dried under vacuum as the white solid 2,5-dibromothieno[3,2-*b*]thiophene

(**5a**) (1.4 g, 83 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.17 (s). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 138.3, 121.8, 113.6. MS (EI): (m/z) 296-298-300 [M].

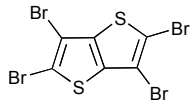
2,5-*bis*(4-*t*-Butylphenylethynyl)thieno[3,2-*b*]thiophene (5b).



Chemical Formula: $C_{30}H_{28}S_2$
Molecular Weight: 452.67
Elemental Analysis: C, 79.60; H, 6.23; S, 14.17

Under a nitrogen atmosphere using Schlenk-line apparatus, 2,5-dibromothieno[3,2-*b*]thiophene (540 mg, 1.8 mmol) was dissolved in Et_3N (20 mL) and THF (15 mL). The mixture was degassed *via* five freeze-pump-thaw cycles. Under a flow of N_2 4-*t*-butylphenylacetylene (0.81 mL, 4.5 mmol) was added, followed by $Pd(PPh_3)_4$ (100 mg, 5 mol%) and CuI (10 mg, 3 mol%). The mixture was stirred at 65 ^{o}C for 24 h after which it was reduced *in vacuo* and filtered through a silica plug, eluting with ether. The ether fraction was reduced *in vacuo*. Column chromatography on silica gel was performed, eluting with hexane, and then ether. 2,5-*bis*(4-*t*-Butylphenylethynyl) thieno[3,2-*b*]thiophene (**5b**) was isolated as a fluffy yellow powder (490 mg, 60 %). M.P. = 303 – 305 ^{o}C. ^{1}H NMR ($CDCl_3$, 700 MHz): δ $ 7.47 (4 H, d, ^{3}J 6.8 Hz, H_5), 7.39 (4 H, d, ^{3}J 6.8 Hz, H_4), 7.35 (2 H, s, H_{10}), 1.33 (18 H, s, H_1). ^{13}C NMR ($CDCl_3$, 176 MHz): δ 152.3 (C_3), 139.2 (C_{11}), 131.4 (C_5), 126.9 (C_9), 125.7 (C_4), 123.9 (C_{10}), 119.7 (C_6), 95.9 (C_7), 82.7 (C_8), 35.1 (C_2), 31.4 (C_1). Acc. MS (AP+): (m/z) calcd. for [M + H]+ 453.1711; found 453.1703. Elemental analysis: expected ($C_{30}H_{28}S_2$): C, 79.60 %; H, 6.23 %: found: C, 79.49 %; H, 6.15 %.

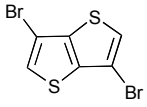
2,3,5,6-Tetrabromothieno[3,2-*b*]thiophene.



Chemical Formula: $C_6Br_4S_2$
Molecular Weight: 455.81

2,5-Dibromo thieno[3,2-*b*]thiophene (4 g, 22 mmol) was dissolved in acetic acid (300 mL) with stirring, and bromine (1.13 mL, 22 mmol) added slowly. After stirring for 1 h at room temperature, water (80 mL) was added, causing precipitation. The mixture was then heated at reflux and another portion of bromine added (1.13 mL, 22 mmol). After 4 h excess bromine (4.5 mL, 80 mmol) was added, and the solution stirred for a further 12 h at 65 °C. The white precipitate formed was filtered, washed with water and isolated as a pink solid. 2,3,5,6-Tetrabromo thieno[3,2-*b*]thiophene was recrystallised from THF as white needle-shaped crystals (7.5 g, 75 %). MS(EI): (m/z) 455 [M]. Elemental analysis: expected ($C_6Br_4S_2$): C, 15.81 %; found: C, 15.83 %.

3,6-Dibromothieno[3,2-*b*]thiophene (6a).

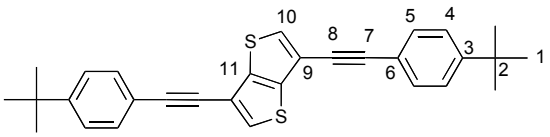


Chemical Formula: $C_6H_2Br_2S_2$
Molecular Weight: 298.02

2,3,5,6-Tetrabromothieno[3,2-*b*]thiophene (640 mg, 1.4 mmol) was dissolved in acetic acid (100 mL) with stirring at reflux. Zinc dust (96 mg, 1.5 mmol) was added and stirring continued for 30 mins. A second portion of zinc dust (96 mg, 1.5 mmol) was added, and heating at reflux was continued for a further 30 mins. At this time the solution was cooled to ambient temperature, water added, and the precipitate isolated by filtration and vacuum dried. NMR spectroscopy revealed the isolated solid to be a combination of the dibrominated and tribrominated species. Consequently, the solid was redissolved in acetic acid (100 mL) and stirred at reflux whilst excess zinc dust (~ 300 mg) was added. The mixture was allowed to stir for 1.5 h, after which time it was quenched and worked up as previously described, enabling isolation of pure 3,6-

dibromothieno[3,2-*b*]thiophene (**6a**) (250 mg, 60 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34 (s). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 139.8, 125.1, 103.0. MS (EI): (m/z) 296-298-300 [M].

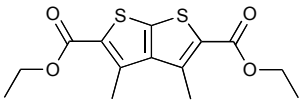
3,6-*bis*(4-*tert*-Butylphenylethynyl)-thieno[3,2-*b*]thiophene (6b).



Chemical Formula: $C_{30}H_{28}S_2$
Molecular Weight: 452.67
Elemental Analysis: C, 79.60; H, 6.23; S, 14.17

3,6-Dibromothieno[3,2-*b*]thiophene (160 mg, 0.53 mmol) was dissolved in dry Et_3N (20 mL) using Schlenk-line apparatus under N_2, and five freeze-pump-thaw cycles were performed. Under a flow of N_2 4-*t*-butylphenylacetylene (1.6 mL, 3.7 mmol) was added, followed by $Pd(PPh_3)_4$ (15 mg, 2 mol%) and CuI (2 mg, 2 mol%). The mixture was stirred at reflux for 40 h, after which it was reduced in volume *in vacuo* and filtered through a silica plug, eluting with ether. The crude residue isolated here was dissolved in DCM, and any insoluble solid removed. The DCM was removed under reduced pressure and the residue taken into hot ether. From this a light brown solid precipitated. This was washed in cold ether, affording 3,6-*bis*(4-*t*-butylphenylethynyl)thieno[3,2-*b*]thiophene (**6b**) as a lustrous, light brown solid (96 mg, 40 %). This was further recrystallised from DCM/cyclohexane to afford colourless plate-like crystals. M.P. = 278 – 280 °C. ^{1}H NMR ($CDCl_3$, 700 MHz): δ 7.58 (2 H, s, H_{11}), 7.49 (4 H, d, ^{3}J 7 Hz, H_5), 7.38 (4 H, d, ^{3}J 7 Hz, H_4), 1.33 (18 H, s, H_1). ^{13}C NMR ($CDCl_3$, 176 MHz): δ 152.0 (C_3), 140.0 ($C_{9\ or\ 10}$), 131.4 (C_5), 130.5 (C_{11}), 125.4 (C_4), 119.6 (C_6), 115.8 ($C_{10\ or\ 9}$), 91.9 (C_7), 81.4 (C_8), 34.8 (C_2), 31.1 (C). Acc. MS (AP+): (m/z) calcd. for [M + H]+ 453.1711; found 453.1711. Elemental analysis: expected ($C_{30}H_{28}S_2$): C, 79.6 %; H, 6.23 %; found: C, 78.14 %, H, 6.10 % – indicative of 8(**6b**):1(DCM).

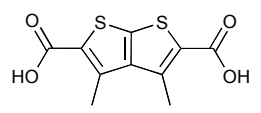
3,4-Dimethylthieno[2,3-*b*]thiophene-2,5-dicarboxylate.



Chemical Formula: $C_{14}H_{16}O_4S_2$
Molecular Weight: 312.4

A solution of pentane-2,4-dione (10.2 mL, 0.1 mol) and CS_2 (9 mL, 0.15 mol) in DMF (15 mL) was added dropwise to a solution of potassium carbonate (41.5 g, 0.3 mol) in DMF (60 mL), with vigorous stirring. After 30 mins the mixture was cooled to 0 °C and ethyl bromoacetate (22 mL, 0.2 mol) in DMF (5 mL) was added dropwise over 30 mins. The reaction mixture was then allowed to stir at room temperature for 12 h, after which it was poured into cold water (200 mL). The precipitate was collected by filtration, washed with cold water (3 x 100 mL aliquots) and allowed to dry to give a white solid of 3,4-dimethylthieno[2,3-*b*]thiophene-2,5-dicarboxylate (30 g, 93 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.36 (4 H, q, ^{3}J 7.2 Hz), 2.88 (6 H, s), 1.39 (6 H, t, ^{3}J 6.8 Hz). MS (EI): (m/z) 312 [M].

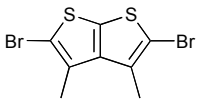
3,4-Dimethylthieno[2,3-*b*]thiophene-2,5-dicarboxylic acid.



Chemical Formula: $C_{10}H_8O_4S_2$
Molecular Weight: 256.3

3,4-Dimethylthieno[2,3-*b*]thiophene-2,5-dicarboxylate (12.5 g, 40 mmol) was heated at reflux with an excess of potassium hydroxide (11.2 g, 200 mmol) in ethanol (50 mL) and water (10 mL) for 24 h. The solvent was removed *in vacuo* and the residue acidified with 5 M HCl. The crude acid precipitated out and was isolated by filtration to afford 3,4-dimethylthieno[2,3-*b*]thiophene-2,5-dicarboxylic acid (**7a**) as a tacky white solid (8.7 g, 85 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.4 (v. broad s), 2.8 (6 H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.3, 147.8, 144.3, 140.5, 131.3, 14.5. MS (AP+): (m/z) 257 [M + H]+.

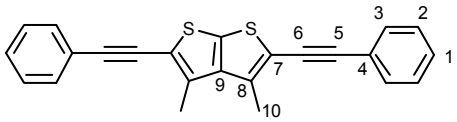
2,5-Dibromo-3,4-dimethylthieno[2,3-*b*]thiophene (7a).



Chemical Formula: $C_8H_6Br_2S_2$
Molecular Weight: 326.07

NBS (1.96 g, 11 mmol) in water (20 mL) was added portionwise over 30 minutes to 3,4-dimethylthieno[2,3-*b*}]thiophene-2,5-dicarboxylic acid (1.2 g, 4.7 mmol) dissolved in NMP (100 mL). The mixture was then allowed to stir for 18 h. Water (100 mL) was added and the white solid that precipitated was isolated and dried under vacuum to afford 2,5-dibromo-3,4-dimethyl thieno[2,3-*b*]thiophene} (1.4 g, 90 %) as a cream/white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.4 (s). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 143.2, 133.4, 130.6, 110.5, 14.4. MS (EI): (m/z) 324-326-328 [M *including splitting characteristic of isotopic abundances of dibrominated species* $C_8H_6Br_2S_2$].

2,5-*bis*(Phenylethynyl)-3,4-dimethylthieno[2,3-*b*]thiophene (7b).



Chemical Formula: $C_{24}H_{16}S_2$
Molecular Weight: 368.51
Elemental Analysis: C, 78.22; H, 4.38; S, 17.40

Under a nitrogen atmosphere using Schlenk line apparatus, 2,5-dibromo-3,4-dimethyl thieno[2,3-*b*]thiophene (1.28 g, 3.9 mmol) was dissolved in dry Et_3N (75 mL) and five freeze-pump-thaw cycles were performed. Under a flow of N_2 phenylacetylene (0.9 mL, 8.2 mmol) was added, followed by $Pd(PPh_3)_4$ (900 mg, 20 mol%) and CuI (70 mg, 10 mol%). The mixture was stirred under reflux conditions for 12 h after which it was reduced *in vacuo* and filtered through a silica plug, eluting with ether. The crude product isolated was purified further on silica gel eluting with toluene, affording the product 2,5-*bis*(phenylethynyl)-3,4-dimethyl thieno[2,3-*b*]thiophene (**7b**) as a yellow solid upon concentration *in vacuo* (500 mg, 35 %). Recrystallisation from hot toluene afforded plate–like yellow crystals. M.P. = 200 – 201 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.54 (4 H, d, ^{3}J 6.5 Hz, H_3), 7.37 (6 H, m, $H_{1\&2}$), 2.62 (6 H, s, H_{10}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.8 ($C_{7,\ 8\ or\ 9}$), 137.6 ($C_{1\ or\ 4}$), 135.9 ($C_{7,\ 8\ or\ 9}$), 131.6 (C_3), 128.7 (C_2), 123.1 ($C_{1\ or\ 4}$), 121.4 ($C_{7,\ 8\ or\ 9}$), 96.6 (C_5), 82.8 (C_6), 14.7 (C_{10}). Acc. MS. (AP+): (m/z) calcd. for [M + H]+ 369.0772; found 369.0779. Elemental analysis: expected ($C_{24}H_{16}S_2$): C, 78.20 %; H, 4.38 %. found: C, 78.48 %; H, 4.45 %.

Raman Spectra

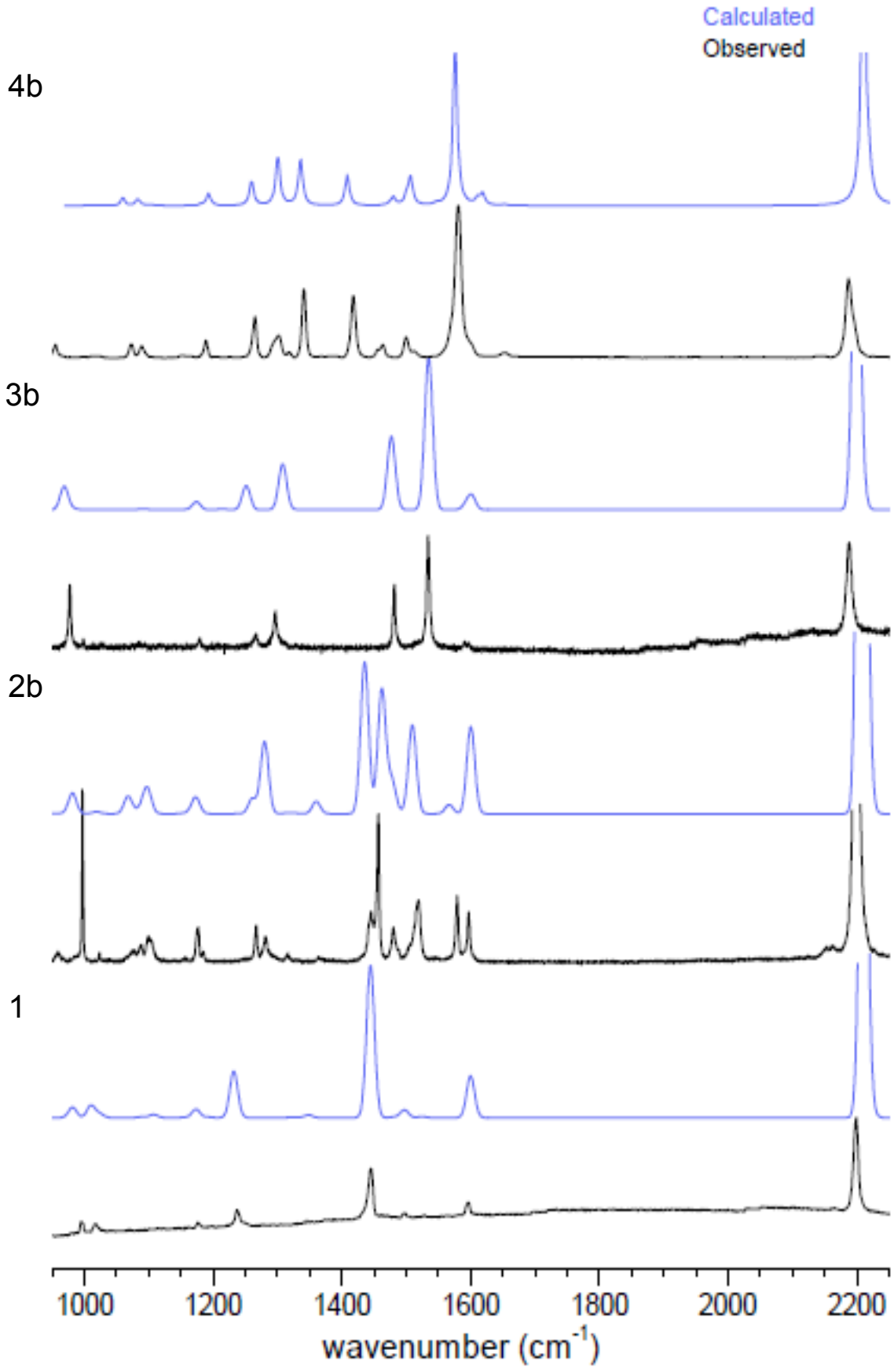


Figure 1. Predicted and observed Raman spectra for compounds **1-4b**. Computed using DFT methods (B3LYP, 6-31G(d))

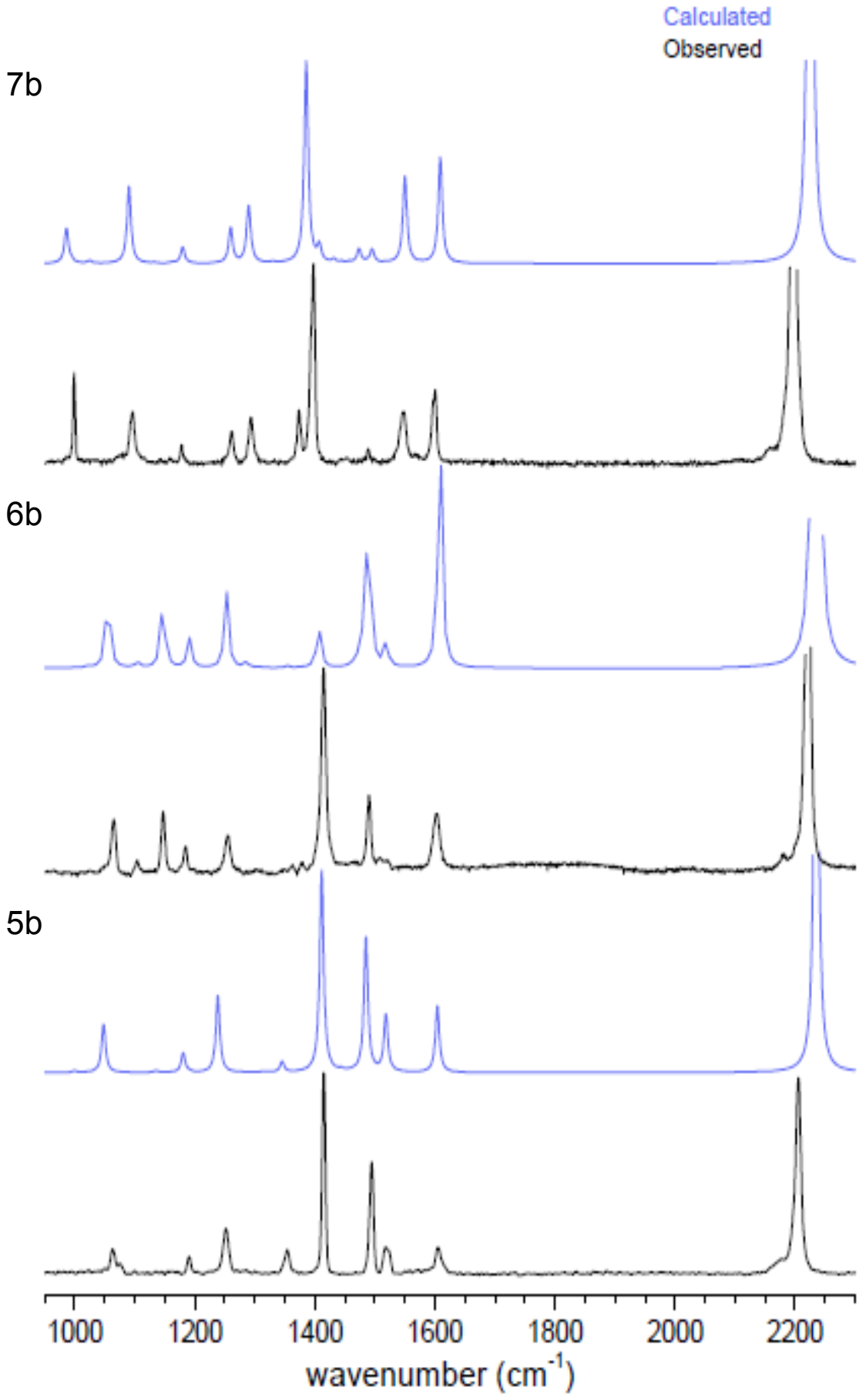


Figure 2. Predicted and observed Raman spectra for compounds **5b-7b**. Computed using DFT methods (B3LYP, 6-31G(d))

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