# To bend or not to bend – are heteroatom interactions within conjugated molecules effective in dictating conformation and planarity?

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Supporting Information

Synthesis
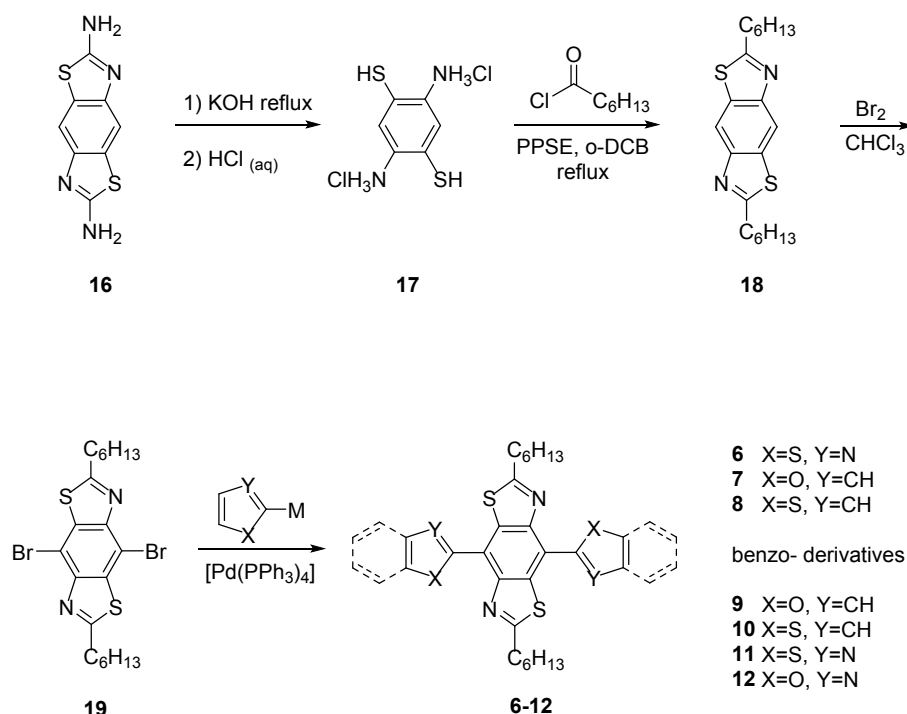
Scheme SI1 Synthesis of target compounds **6-12**.

The synthesis of the target compounds began with the reaction of benzo[1,2-*d*:4,5-*d'*]bis(thiazole)-2,6-diamine[1] (**16**) with KOH. The resulting yellow precipitate was filtered and treated with conc. HCl to give 2,5-diaminobenzene-1,4-dithiol dihydrochloride[2] (**17**) as a white crystalline solid. This compound was then reacted almost immediately with heptanoyl chloride in the presence of trimethylsilyl polyphosphate to give the corresponding 2,6-dihexyl BBT derivative (**18**, 46% yield from **16**). Bromination of compound **18** in dichloromethane solution was achieved in 45% yield by

the addition of bromine at 0°C. Compounds **6-8**, **11**, and **12** were obtained in 50-75% yield by the reaction of the dibromo derivative **19** with the corresponding aryl trialkyltin reagent under Stille coupling conditions. For compounds **9** and **10**, the boronic esters of the corresponding aryl systems were reacted with **19** under Suzuki-Miyaura conditions to give the products in 65 and 43% yield, respectively.

Compound **(16)**[3] was subjected to treatment with base, with the in-situ generated potassium thiolate salt converted to the dihydrochloride intermediate **(17)**.[3] Initial attempts to synthesise **(18)** *via* acid-catalysed ring closure were unsuccessful when conducted under N_2 gas. The yield was increased to 24% when Ar gas was used and intermediate **(17)** dried overnight under vacuum. This was further increased to 46% from **(16)** when intermediate **(17)** was dried under Ar flow for 1 h and used immediately without isolation or exposure to air. It is important to note that these reactions can be scaled up to produce 10g batches of **(18)** without a fall in the isolated yield. Compound **(18)** was then brominated using Br_2 in $CHCl_3$ to yield **(16)** which is suitable for further modification. The seven BBT containing heterocyclic dyads were then synthesised *via* palladium-catalysed cross-coupling reactions using the dibromo parent compound **(16)** and the corresponding heterocyclic stannane or boronate ester to yield compounds **6 – 12** in yields of 43-75% as bright yellow crystalline powders. Crystals of suitable quality for single crystal x-ray diffraction were grown from common organic solvents.

Experimental Section

Anhydrous tetrahydrofuran, toluene and dichloromethane were purified *via* a solvent purification system using alumina as drying agent (SPS 400 from Innovative Technologies) and used immediately. Compounds **(8)**[4]**, (17)**[5], **(18)**[6], and **(19)**[6] were synthesised according to the literature procedures. All other chemicals were purchased from Sigma Aldrich or Alfa Aesar and used without further purification. DSC was conducted using a TA Instruments DSC Q1000 Differential Scanning Calorimeter. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVIII 400 at 400 MHz and 100

MHz and are calibrated to the residual solvent peak. Elemental analyses were obtained on a Perkin-Elmer 2400 analyser. MALDI-TOF spectra were recorded on a Shimadzu Axima-CFR spectrometer (mass range 1-150000 Da). HRMS measurements were recorded using the EPSRC NMSF.

Crystallographic Experimental Detail

For compounds **6** and **12** data were collected using a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) *Saturn724+* detector mounted at the window of an *FR-E+ SuperBright* molybdenum rotating anode generator with VHF *Varimax* optics (70μm focus). For compounds **9** and **10** the data were collected at beamline I19, Diamond Light Source situated on an undulator insertion device with a combination of double crystal monochromator, vertical and horizontal focussing mirrors and a series of beam slits (primary white beam and either side of the focussing mirrors). The experimental hutch (EH1) is equipped with a Crystal Logic 4-circle kappa geometry goniometer with a Rigaku Saturn 724 CCD detector. Both systems are equipped with an Oxford Cryosystems Cryostream plus cryostat and data were collected from a sample cooled and maintained at 100K. Data collection was controlled through *CrystalClear*-SM Expert 3.1 b20 (Rigaku, 2011-2) for all compounds and data processing for **6**, **9** and **12**. Data for compound 10 was processing using *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET). The structures were solved using *SHELXS*, G.M. Sheldrick, Acta Cryst. (2008). A64, 112-122 for **6** and Superflip (Palatinus & Chapuis, 2007;Palatinus & van der Lee, 2008; Palatinus *et al.*, 2012) for **9**, **10** and **12**. Structure refinement were carried out using *SHELXL*, G.M. Sheldrick, Acta Cryst. (2008). A64, 112-122 within OLEX2 (Dolomanov *et al.*, 2009).

In all cases the asymmetric unit contains half a molecule with the other half generated by inversion symmetry.

6 $C_{26}H_{30}N_4S_4$, M_r = 526.78, yellow plate-like crystal 0.11 × 0.04 × 0.01 mm, Triclinic, *P*-1, a = 8.5288 (11) Å, b = 8.7463 (11) Å, c = 9.9866 (14) Å, α = 105.144 (7)°, β = 93.192 (7)°, γ = 117.597 (8)°, V = 623.53 (14) Å^3, Z = 1, D_x = 1.403 Mg m^{-3}, μ = 0.41 mm^{-1}, Mo $K\alpha$ radiation, λ = 0.71075 Å, T = 100

K, $\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$, 5158 measured reflections, 2823 independent reflections, $R_{int} = 0.041$, $R[F^2 > 2\sigma(F^2)] = 0.045$ (2175 reflections with $I > 2\sigma(I)$), $wR(F^2) = 0.113$, $\Delta\rho_{max} = 0.47$ e Å^{-3}, $\Delta\rho_{min} = -0.42$ e Å^{-3}. CCDC 1440981 contains the supplementary crystallographic data for this paper. These data are supplied free of charge by The Cambridge Crystallographic Data Centre.

9 $C_{36}H_{36}N_2O_2S_2$ $M_r = 592.79$, Platelet, yellow 0.05 × 0.03 × 0.01 mm, Monoclinic, $P2_1/c$, $a = 14.575$ (19) Å, $b = 7.664$ (9) Å, $c = 14.393$ (19) Å, $c = 14.393$ (19) Å, $\beta = 111.280$ (14)°, $V = 1498$ (3) Å^3, $Z = 2$, $D_x = 1.314$ Mg m^{-3}, $\mu = 0.20$ mm^{-1}, synchrotron radiation $\lambda = 0.6889$ Å, $T = 100$ K, $\theta_{max} = 26.6°$, $\theta_{min} = 2.8°$, 13997 measured reflections, 3408 independent reflections, $R_{int} = 0.146$, $R[F^2 > 2\sigma(F^2)] = 0.108$ (2286 reflections with $I > 2\sigma(I)$), $wR(F^2) = 0.306$, $\Delta\rho_{max} = 0.92$ e Å^{-3}, $\Delta\rho_{min} = -0.57$ e Å^{-3}.

CCDC 1440982 contains the supplementary crystallographic data for this paper. These data are supplied free of charge by The Cambridge Crystallographic Data Centre.

10 $C_{36}H_{36}N_2S_4$, $M_r = 624.91$, Lath, yellow 0.14 × 0.05 × 0.01 mm, Monoclinic, $C2/c$, $a = 15.2375$ (10) Å, $b = 7.3024$ (6) Å, $c = 28.201$ (3) Å, $\beta = 99.461$ (7)°, $V = 3095.2$ (4) Å^3, $Z = 4$, $D_x = 1.341$ Mg m^{-3}, $\mu = 0.31$ mm^{-1}, synchrotron radiation, $\lambda = 0.6889$ Å, $T = 100$ K, $\theta_{max} = 24.2°$, $\theta_{min} = 2.8°$, 14285 measured reflections, 2719 independent reflections, $R_{int} = 0.067$, $R[F^2 > 2\sigma(F^2)] = 0.088$ (2259 reflections with $I > 2\sigma(I)$), $wR(F^2) = 0.255$, $\Delta\rho_{max} = 1.05$ e Å^{-3}, $\Delta\rho_{min} = -0.56$ e Å^{-3}.

CCDC 1440983 contains the supplementary crystallographic data for this paper. These data are supplied free of charge by The Cambridge Crystallographic Data Centre.

In compound **10** the disorder is such that the major component 72% (S1 and C7) is with the S atoms adjacent to one another and the minor one (S1a and C7a) with the C and S adjacent to one another.

12 $C_{34}H_{34}N_4O_2S_2$, M_r = 594.77, Block, yellow 0.09 × 0.05 × 0.03 mm, Monoclinic, $P2_1/c$, a = 14.526 (2) Å, b = 5.1215 (7) Å, c = 20.577 (3) Å, β = 109.041 (8)°, V = 1447.0 (4) Å^3, Z = 2, D_x = 1.365 Mg m^{-3}, μ = 0.22 mm^{-1}, Mo $K\alpha$ radiation, λ = 0.71075 Å, T = 100 K, θ_{max} = 25.1°, θ_{min} = 3.0°, 16020 measured reflections, 2550 independent reflections, R_{int} = 0.148, $R[F^2 > 2\sigma(F^2)]$ = 0.145 (938 reflections with $I > 2\sigma(I)$), $wR(F^2)$ = 0.436, $\Delta\rho_{max}$ = 0.75 e Å^{-3}, $\Delta\rho_{min}$ = -0.36 e Å^{-3}.

The overall data quality for compound **12** was poor. A dataset was also collected at Diamond Light Source but gave no improvement in data quality or model and the original dataset and refinement is reported.

CCDC 1440984 contains the supplementary crystallographic data for this paper. These data are supplied free of charge by The Cambridge Crystallographic Data Centre.

Computational studies

The HOMO and LUMO wave functions of the BBT derivatives (the side-chains were replaced by methyl groups) were calculated at the M06-2X/6-311G(d,p) level of theory using the Gaussian 09 package. The geometries were optimised starting from the experimental (X-Ray) geometries when available. For other compounds, the experimental geometry available for the closest analogue was used as the starting geometry. E.g., for the bis(furan) **7** the experimental geometry of the bis-(benzofuran) **9** was available and was applied, removing the benzene ring to generate the starting geometry for compound **7**.

2,5-Diaminobenzene-1,4-dithiol dihydrochloride **(17)**
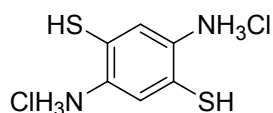
Benzo[1,2-d:4,5-d']bis(thiazole)-2,6-diamine (12.0 g, 54.0 mmol) **(16)** was added to a 250 ml round bottomed flask and the flask degassed several times. Potassium hydroxide (48.5 g, 864 mmol) was dissolved in another round bottom flask in degassed water (60 ml) then transferred *via* syringe to the reaction flask. The mixture was stirred for 5 h under reflux then cooled overnight with stirring. The resulting mixture was filtered under Ar. The yellow precipitate was then dissolved in deaerated water (60 ml) and filtered directly into a flask containing deaerated water (120 ml) and concentrated hydrochloric acid (120 ml). The resulting white crystals were filtered, washed with degassed methanol and dried under Ar for 1 h before being used immediately in the next step without purification or exposure to air.
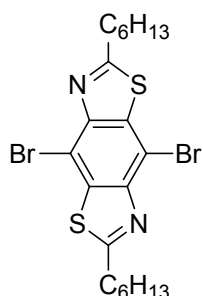
2,6-Dihexylbenzo[1,2-d:4,5-d']bis(thiazole) **(18)**
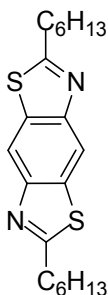
To an evacuated 250 ml 2-neck flask containing freshly synthesised **(17)** under Ar was added 1,2-dichlorobenzene (100 ml), heptanoyl chloride (18.94 ml, 122 mmol) and trimethylsilyl polyphosphate (33.7 ml, 294 mmol) and the flask heated to reflux for 48 h under Ar. Upon cooling the solution was quenched with sat. $NaHCO_3$ solution and then extracted with dichloromethane (3 × 100 ml). The solution was then washed with sat $NaHCO_3$ (3 × 200 ml) and brine (200 ml). The combined organics were then dried ($MgSO_4$) and the dichloromethane removed by rotary evaporation. The dichlorobenzene was distilled via Kughelrohr distillation and the resulting dark brown residue purified by silica gel column chromatography eluting with dichloromethane. The off-white solid was reprecipitated from dichloromethane/methanol and dried under vacuum to yield the title compound as a white

solid (8.9g, 46% over two steps). ^{1}H NMR; δ_H (400 MHz CDCl$_3$): 8.38 (2H, s, Ar-H), 3.13 (4H, t, J 7.8 Hz, CH$_2$), 1.90 (4H, quin, J 7.7 Hz CH$_2$), 1.50-1.26 (12H, m, CH$_2$), 0.90 (6H, t, J 7.0 Hz, CH$_3$); ^{13}C NMR; δ_C (125 MHz, CDCl$_3$): 173.7, 151.3, 134.4, 114.9, 35.0, 31.8, 29.9, 29.2, 22.8, 14.3; m/z (MALDI-TOF): 361; HRMS calculated for C$_{20}$H$_{28}$N$_2$S$_2$: 361.1761. Found 361.1767.
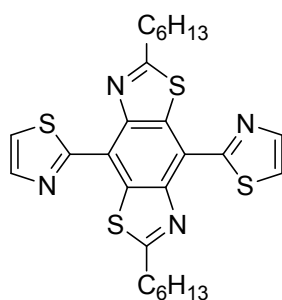
4,8-Dibromo-2,6-dihexylbenzo[1,2-d:4,5-d']bis(thiazole) **(19)**

2,6-Dihexylbenzo[1,2-d:4,5-d']bis(thiazole) (8.0 g, 22.19 mmol) **(18)** was added to a 250 ml two neck flask under Ar. Dichloromethane (80 ml) was then added and the flask cooled to 0 °C. Bromine (2.86 ml, 55.5 mmol) in dichloromethane (80 ml) was then added dropwise while at 0 °C. The reaction was then stirred at 0 °C for 6 hours and then allowed to stir at room temperature overnight. The reaction was then diluted with dichloromethane (250 ml), quenched with sat. sodium sulphite (50 ml) and washed with water (2 × 100 ml) before being dried (MgSO$_4$) and concentrated to dryness. Purification by silica gel column chromatography eluting with 3:2 hexane:dichloromethane yielded the title compound as a white solid which was recrystallised with hexane:methanol to yield a crystalline solid (5.12 g, 45% yield). ^{1}H NMR; δ_H (400 MHz CDCl$_3$): 3.17 (4H, t, J 7.8 Hz, CH$_2$), 1.90 (4H, quin, J 7.7 Hz CH$_2$), 1.50-1.26 (12H, m, CH$_2$), 0.92 (6H, t, J 7.0 Hz, CH$_3$); ^{13}C NMR; δ_C (125 MHz, CDCl$_3$): 174.8, 148.1, 137.4, 106.2, 35.3, 31.8, 30.1, 29.2, 22.8, 14.4; m/z (MALDI-TOF):

519; Anal. Calculated for $C_{20}H_{26}Br_2N_2S_2$: C, 46.34; H, 5.06; N, 5.40. Found C, 46.46; H, 5.01; N, 5.28.
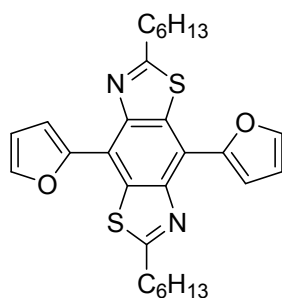
2,6-Dihexyl-4,8-di(thiazol-2-yl)benzo[1,2-d:4,5-d']bis(thiazole) **(6)**

4,8-Dibromo-2,6-dihexylbenzo[1,2-d:4,5-d']bis(thiazole) **(16)** (100 mg, 0.193 mmol), and tetrakis(triphenylphosphine) palladium(0) (44.6 mg, 0.039 mmol) were added to a 50 ml round bottom flask under Ar. 2-(Tributylstannyl)thiazole **(17)**[5] (180 mg, 0.482 mmol) was added and the flask purged further with Ar. Dry toluene (20 ml) was then added and reaction was heated to 100 °C for 24 h then cooled. The solution was diluted with dichloromethane (100 ml) and washed with water (100 ml) and brine (100 ml) before being dried (MgSO₄) and concentrated to dryness. The crude residue was purified by silica gel column chromatography eluting with 1:1 dichloromethane:hexane to yield a yellow powder which was recrystallised from ethanol to yield fine yellow needles (76 mg, 75% yield; MPt 126°C by DSC). ¹H NMR; δ_H (400 MHz CDCl₃): 8.14 (2H, d, *J* 3.3 Hz, Ar-H), 7.58 (2H, d, *J* 3.3 Hz, Ar-H), 3.27 (4H, t, *J* 7.6 Hz, CH₂) 2.07 (4H, quin, *J* 7.5 Hz CH₂), 1.60-1.50 (4H, m, CH₂), 1.47-1.30 (8H, m,

CH$_2$), 0.92 (6H, t, J 7.0 Hz, CH$_3$); ^{13}C NMR; δ_C (125 MHz, CDCl$_3$): 177.1, 161.9, 147.1, 141.7, 131.0, 122.0, 120.5, 33.74, 31.09, 28.64, 28.41, 22.06, 13.62; m/z (MALDI-TOF): 527; HRMS calculated for C$_{26}$H$_{30}$N$_4$S$_4$: 527.1426. Found: 527.1418.
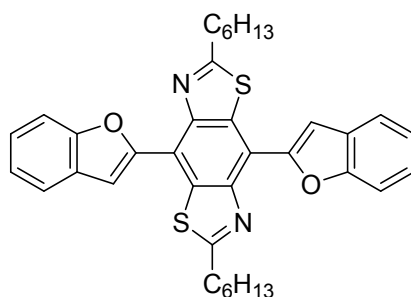
4,8-Di(furan-2-yl)-2,6-dihexylbenzo[1,2-d:4,5-d']bis(thiazole) **(7)**

To a 50 ml round bottom flask under Ar was added tributyl(furan-2-yl)stannane (0.228 ml, 0.723 mmol), 4,8-dibromo-2,6-dihexylbenzo[1,2-d:4,5-d']bis(thiazole) **(16)** (150 mg, 0.289 mmol) and tetrakis(triphenylphosphine) palladium(0) (66.9 mg, 0.058 mmol) and the flask evacuated again with Ar. Dry toluene (15 ml) was then added via syringe and the flask heated to reflux for 24 h before being cooled and poured into water. The solution was then extracted with dichloromethane (3 × 50 ml). The combined organic layers were then washed with water (2 × 50 ml), dried (MgSO$_4$) and concentrated to dryness. Silica gel column chromatography eluting with 1:2 dichloromethane:hexane yielded the product as an off-white solid which was further purified by recrystallisation from hexane to yield the product as fine off-white needles (95 mg, 67% yield; MPt 125°C by DSC). ^{1}H NMR; δ_H (400 MHz CDCl$_3$): 7.90 (2H, d, J 3.4

Hz, Ar-H), 7.72 (2H, d, *J* 1.4 Hz, Ar-H), 6.68 (2H, dd, *J* 1.7 Hz, Ar-H), 3.23 (4H, t, *J* 7.6 Hz, CH$_2$) 2.00 (4H, quin, *J* 7.5 Hz CH$_2$), 1.57-1.48 (4H, m, CH$_2$), 1.45-1.30 (8H, m, CH$_2$), 0.92 (6H, t, *J* 7.0 Hz, CH$_3$); ^{13}C NMR; δ_C (125 MHz, CDCl$_3$): 174.5, 150.6, 146.8, 142.4, 130.6, 117.1, 113.6, 112.9, 34.8, 31.9, 29.7, 29.3, 22.9, 14.4; *m/z* (MALDI-TOF): 492; Anal. Calculated for C$_{28}$H$_{32}$N$_2$O$_2$S$_2$: C, 68.26; H, 6.55; N, 5.69. Found C, 68.11; H, 6.49; N, 5.72.
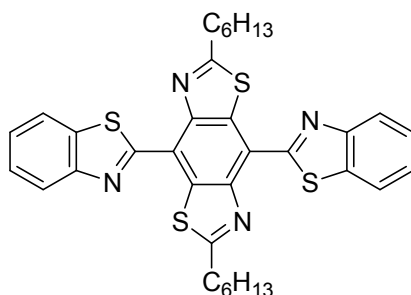
4,8-Di(benzofuran-2-yl)-2,6-dihexylbenzo[1,2-d:4,5-d']bis(thiazole) **(9)**

To a 5 ml microwave vial under Ar was added 4,8-dibromo-2,6-dihexylbenzo[1,2-d:4,5-d']bis(thiazole) **(16)** (100mg, 0.193 mmol), 2-benzofuranylboronic acid MIDA ester (93 mg, 0.579 mmol), tetrakis(triphenylphosphine) palladium(0) (44.6 mg, 0.039 mmol) and barium hydroxide octahydrate (262 mg, 0.830 mmol) and the flask evacuated several times with Ar. Dry tetrahydrofuran (4 ml) and degassed water (1 ml) were then added and the flask fitted with a cap. The vial was then heated to 120 °C for 2 h in the microwave. The reaction was then cooled before being poured into water (50 ml) and extracted with dichloromethane (3 × 50 ml). The combined organic layers were then washed with (50 ml) water before being dried (MgSO$_4$) and concentrated to dryness. The crude residue was purified by silica gel column chromatography eluting with 20% dichloromethane in hexane. The yellow powder was

recrystallised from hexane to yield fibrous crystals (74 mg, 65% yield; MPt 172°C by DSC).

^{1}H NMR; δ_H (400 MHz CD$_2$Cl$_2$): 8.38 (2H, s, Ar-H), 7.74 (2H, d, J 7.5 Hz, Ar-H), 7.68 (2H, d, J 8.0 Hz, Ar-H), 7.42-7.35 (2H, m, Ar-H), 7.34-7.28 (2H, m, Ar-H), 3.30 (4H, t, J 7.6 Hz, CH$_2$), 2.06 (4H, quin, J 7.0 Hz CH$_2$), 1.61-1.51 (4H, m, CH$_2$), 1.49-1.32 (8H, m, CH$_2$), 0.93 (6H, t, J 7.1 Hz, CH$_3$); ^{13}C NMR; δ_C (125 MHz, CDCl$_3$): 175.3, 154.7, 152.1, 147.8, 131.8, 129.8, 125.1, 123.5, 122.1, 117.6, 111.6, 110.3, 34.8, 32.0, 29.8, 29.4, 23.0, 14.5; m/z (MALDI-TOF): 592; HRMS calculated for C$_{36}$H$_{36}$N$_2$O$_2$S$_2$: 593.2291. Found 593.2286.
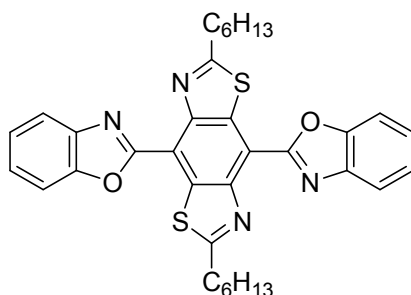
4,8-Bis(benzo[b]thiophen-2-yl)-2,6-dihexylbenzo[1,2-d:4,5-d']bis(thiazole) **(10)**
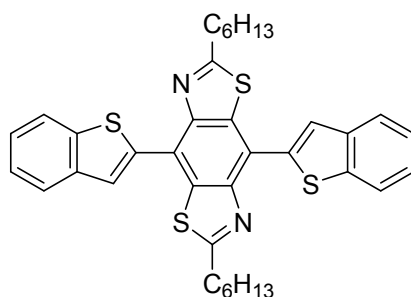
To a 5 ml microwave vial under Ar was added 4,8-dibromo-2,6-dihexylbenzo[1,2-d:4,5-d']bis(thiazole) **(16)** (100mg, 0.193 mmol), benzothiophene-2-boronic acid MIDA ester (102 mg, 0.579 mmol), tetrakis(triphenylphosphine) palladium(0) (44.6 mg, 0.039 mmol) and barium hydroxide octahydrate (262 mg, 0.830 mmol) and the flask evacuated several times with Ar. Dry tetrahydrofuran (4 ml) and degassed water (1 ml) were then added and the flask fitted with a cap. The vial was then heated to 120 °C for 2 h in the microwave. The reaction was then cooled before being poured into water (50 ml) and extracted with dichloromethane (3 × 50 ml). The combined organic layers were then washed with water (50 ml) before being dried (MgSO$_4$) and concentrated to dryness. The crude residue was purified by silica gel column chromatography eluting with 30% dichloromethane in hexane. The resulting yellow

powder was recrystallised from hot ethanol with small additions of tetrahydrofuran to yield the product as yellow crystals (52 mg, 43% yield; MPt 148°C by DSC). ^{1}H NMR; δ_H (400 MHz CD$_2$Cl$_2$): 8.11 (2H, s, Ar-H), 7.95-7.9 (4H, m, Ar-H), 7.45-7.37 (4H, m, Ar-H), 3.20 (4H, t, J 7.6 Hz, CH$_2$), 1.96 (4H, quin, J 7.5 Hz CH$_2$), 1.50 (4H, q, J 6.9 Hz, CH$_2$), 1.43-1.28 (8H, m, CH$_2$), 0.89 (6H, t, J 7.0 Hz, CH$_3$); ^{13}C NMR; δ_C (125 MHz, CDCl$_3$): 173.4, 148.7, 141.4, 139.9, 139.8, 135.2, 125.8, 125.2, 124.7, 124.4, 122.4; m/z (MALDI-TOF): 624; HRMS calculated for C$_{36}$H$_{36}$N$_2$S$_4$: 625.1834. Found 625.1829.

4,8-Bis(benzo[d]thiazol-2-yl)-2,6-dihexylbenzo[1,2-d:4,5-d']bis(thiazole) **(11)**

To a 50 ml oven dried flask under Ar was added 4,8-dibromo-2,6-dihexylbenzo[1,2-d:4,5-d']bis(thiazole) **(16)** (150 mg, 0.289 mmol), 2-(tributylstannyl)benzo[d]thiazole **(18)** (307 mg, 0.723 mmol) and tetrakis(triphenylphosphine) palladium(0) (66.9 mg, 0.058 mmol) and the flask purged with Ar several times. Dry toluene (20 ml) was then added and the flask heated to reflux for 48 h under Ar. The reaction was then poured into water (100 ml) and extracted with dichloromethane (3 × 50 ml) before being washed with water (2 × 50 ml), dried (MgSO$_4$) and concentrated to a deep red residue. The crude residue was then purified via silica gel column chromatography eluting with 40% dichloromethane in hexane to yield a bright yellow powder which was then recrystallised from toluene:ethanol to yield yellow fibrous crystals (122 mg, 67% yield; MPt 223°C by DSC). ^{1}H NMR; δ_H (400 MHz CD$_2$Cl$_2$):

8.27 (2H, d, J 8.08 Hz, Ar-H), 8.11 (2H, d, J 7.9 Hz, Ar-H), 7.62 (2H, ddd, ^4J = 1.2, ^3J = 7.2, ^3J = 8.1, Hz, Ar-H), 7.52 (2H, ddd, ^4J = 1.2, ^3J = 7.2, ^3J = 8.1, Hz, Ar-H), 3.39 (4H, t, J 7.6 Hz, CH$_2$) 2.18 (4H, quin, J 7.5 Hz CH$_2$), 1.66 (4H, q, J 6.9 Hz, CH$_2$), 1.52-1.4 (8H, m, CH$_2$), 0.99 (6H, t, J 7.0 Hz, CH$_3$); ^{13}C NMR; δ_C (125 MHz, CDCl$_3$): 178.2, 162.7, 152.5, 148.8, 137.9, 132.9, 126.4, 125.7, 123.7, 122.1, 121.9, 34.6, 32.0, 29.5, 29.4, 23.0, 14.5; m/z (MALDI-TOF): 627; HRMS calculated for C$_{34}$H$_{34}$N$_4$S$_4$: 627.1739. Found 627.1735.

2,2'-(2,6-Dihexylbenzo[1,2-d:4,5-d']bis(thiazole)-4,8-diyl)bis(benzo[d]oxazole) **(12)**

To a 50 ml oven dried flask under Ar was added 4,8-dibromo-2,6-dihexylbenzo[1,2-d:4,5-d']bis(thiazole) **(16)** (150 mg, 0.289 mmol), 2-(tributylstannyl)benzo[d]oxazole **(19)** (295 mg, 0.723 mmol) and tetrakis(triphenylphosphine) palladium(0) (66.9 mg, 0.058 mmol) and the flask purged with Ar several times. Dry toluene (20 ml) was then added and the flask heated to reflux for 24 h under Ar. Once cool the reaction mixture was poured into water (100 ml) and extracted with dichloromethane (3 × 50 ml) before being dried (MgSO$_4$) and concentrated to a deep orange residue. The crude product was purified by silica gel column chromatography eluting with dichloromethane to remove the impurities then THF to elute the product. Evaporation of solvent afforded the title compound as a bright yellow crystalline solid (86 mg, 50%; MPt 220°C by DSC). ^{1}H NMR; δ_H (400 MHz CDCl$_3$): 8.02-7.98 (2H, m,

Ar-H), 7.92-7.88 (2H, m, Ar-H), 7.61-7.50 (4H, m, Ar-H), 3.46 (4H, t, J 8.0 Hz, CH$_2$), 2.11 (4H, quin, J 7.9 Hz CH$_2$), 1.68-1.58 (4H, m, CH$_2$), 1.52-1.38 (8H, m, CH$_2$), 0.97 (6H, t, J 7.0 Hz, CH$_3$); ^{13}C NMR; δ_C (125 MHz, CDCl$_3$): 178.6, 161.2, 151.6, 148.9, 141.8, 136.7, 126.3, 125.2, 120.9, 116.7, 111.8; m/z (MALDI-TOF): 595; HRMS calculated for C$_{34}$H$_{34}$N$_4$O$_2$S$_2$: 594.2196. Found 595.2191.
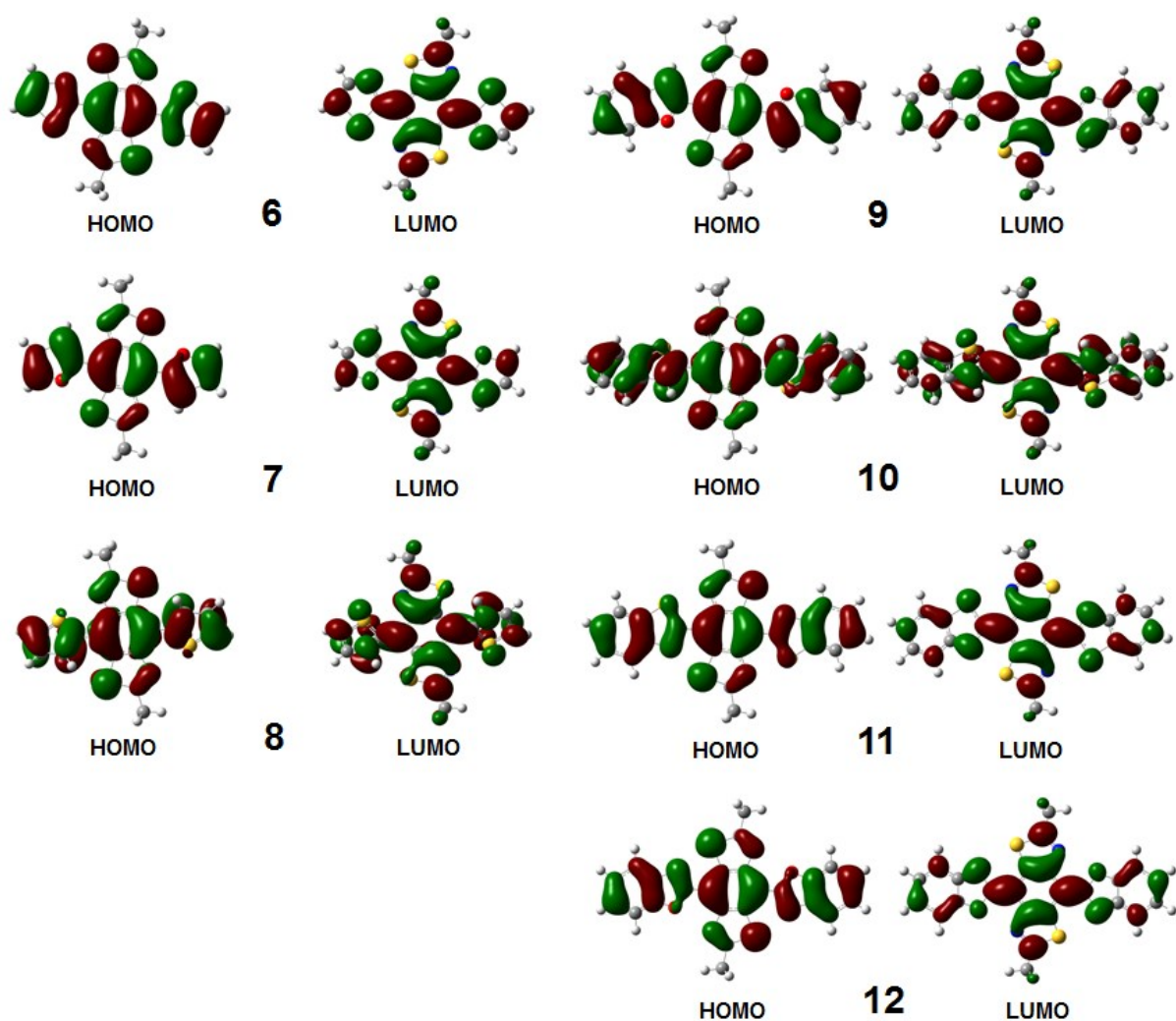
Figure SI1. HOMO and LUMO plots (isosurface 0.031) of compounds **6-12** calculated at the M06-2X/6-311G** level of theory.
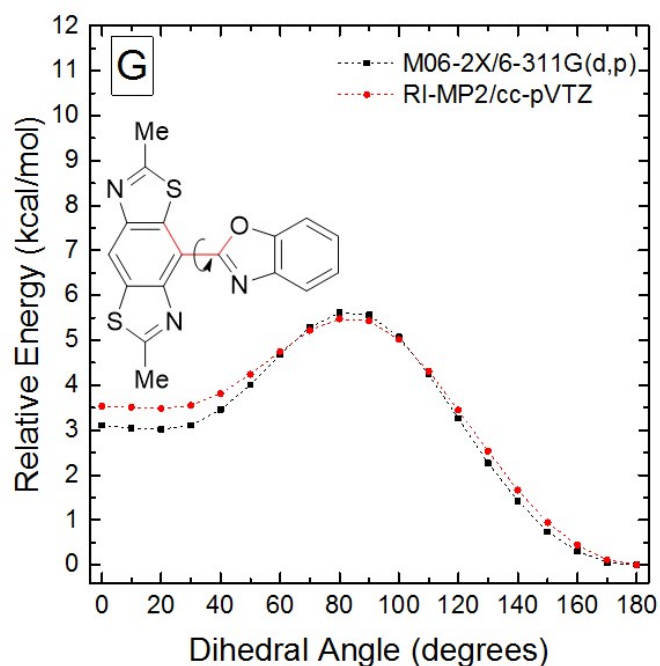
Figure SI2. Torsional potential surfaces for the fragment **12s** calculated at the M06-2X/6-311G** (black) and RI-MP2/cc-pVTZ (red) levels of theory. Rotation occurs around the inter-ring C−C bond marked in red, starting from the conformation shown (0°).

Discussion of potential 3-centre-2-electron interactions

The nature of these interactions is not entirely clear, but one possible source of an attractive potential is a 3-centre-2-electron interaction between lone pairs and relatively low-lying antibonding orbitals,[7] although these are likely to be counteracted, at least to some extent, by significant lone pair − lone pair repulsions. In order to investigate this hypothesis experimentally, we synthesised the compounds shown in Figure SI3; the molecular structures of all these compounds were determined by X-ray crystallographic studies (manuscript in preparation to be published elsewhere). The chosen compounds were designed to encourage S⋯O interactions and the structural variation across the series focussed on the local environment of the potential S⋯O contacts: ring size fused to the back of the thiophene/furan

rings (5, 6 and 7-membered); a Csp^2 bridge in the fused ring in place of Csp^3, and additional electron donating groups to vary the electron density around the molecules; unsubstituted thiophene. From the crystallographic data, we extracted the bond lengths within the molecules to see if we could identify any correlations between the degree of non-covalent bonding. To this end, we plotted the distance between sulfur and oxygen atoms against the bond-lengths of all the common bonds in the series (Figure SI4). If 3-centre-2-electron interactions were predominant then we would have seen a correlation in one or more of the common bonds, but it is clear that there is no such trend observed with the data points scattered randomly or with no meaningful difference (Fig. SI4 bottom right).
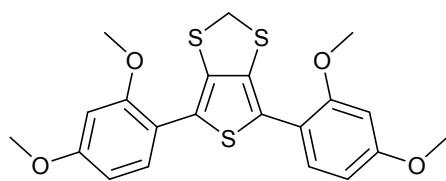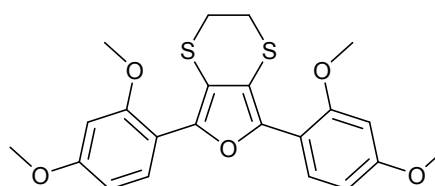
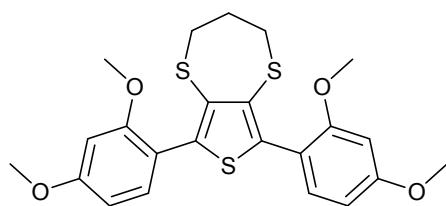Inter-ring torsion angles 41.2, 48.5
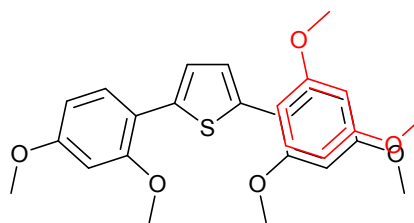
Two molecules in the asymmetric unit
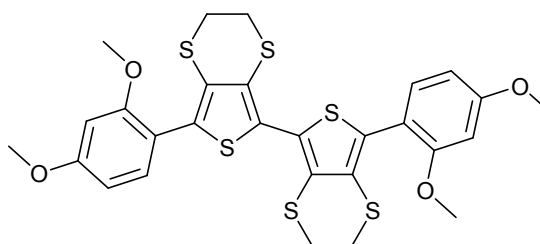Inter-ring torsion angles 2.5, 3.6, 3.8, 8.1
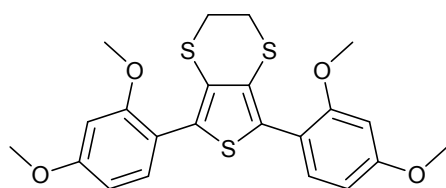
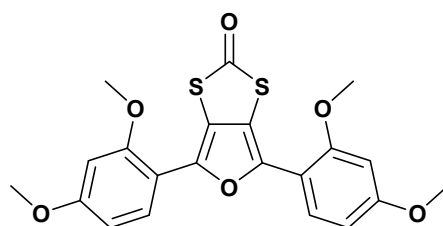Inter-ring torsion angles 47.3, 73.1

Inter-ring torsion angles 41.6, 44.5

Inter-ring torsion angles 41.9, 60.0

Inter-ring torsion angles 50.4, 52.3

Inter-ring torsion angles 0.8, 1.5

Figure SI3. Structures of thiophene and furan derivatives bearing dimethoxybenzene rings synthesised to probe the possibility of 3-centre-2-electron interactions. The conformations are given relative to those observed from single crystal x-ray diffraction studies, along with the torsion angles between thiophene (or furan) and benzene rings.
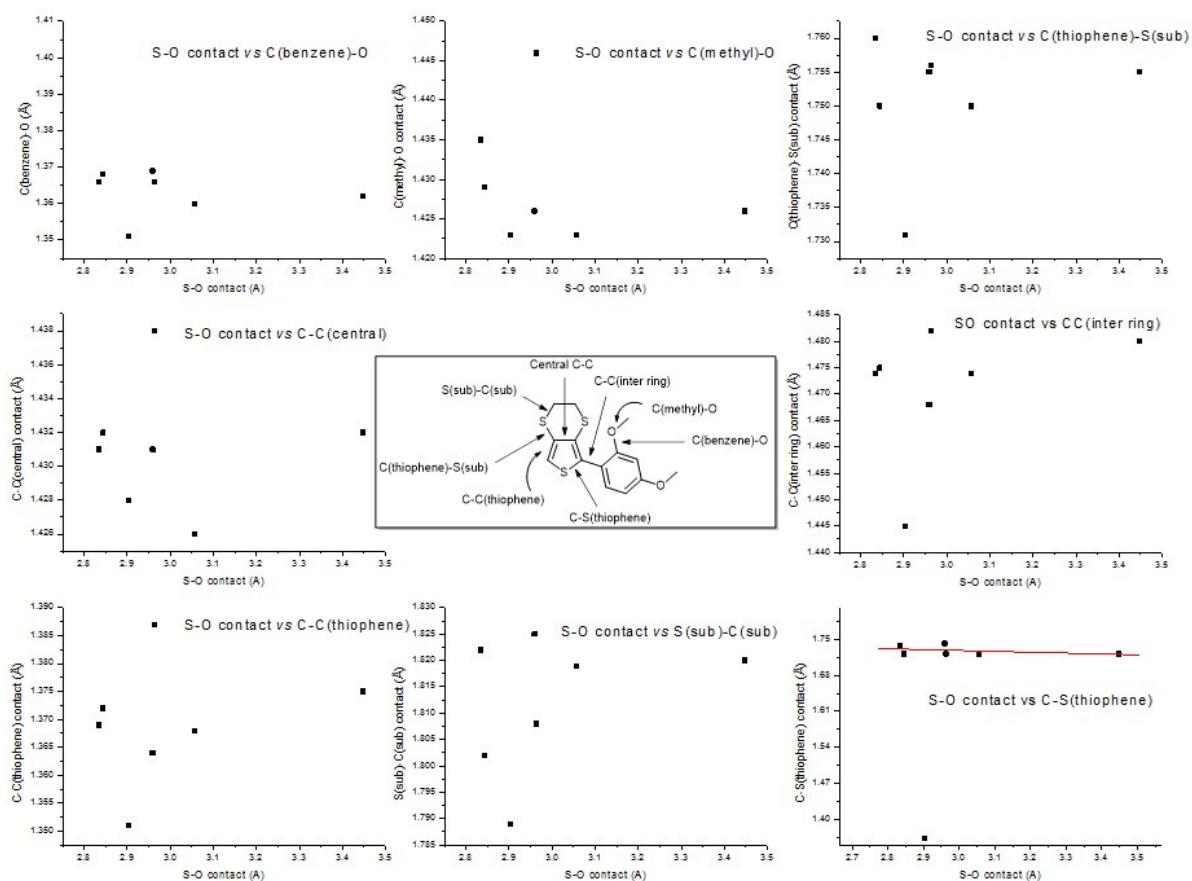
Figure SI4. Plots of the non-covalent S⋯O distances versus bond lengths in common bonds (see central graphic for the key) in the structures given in Fig. SI3.
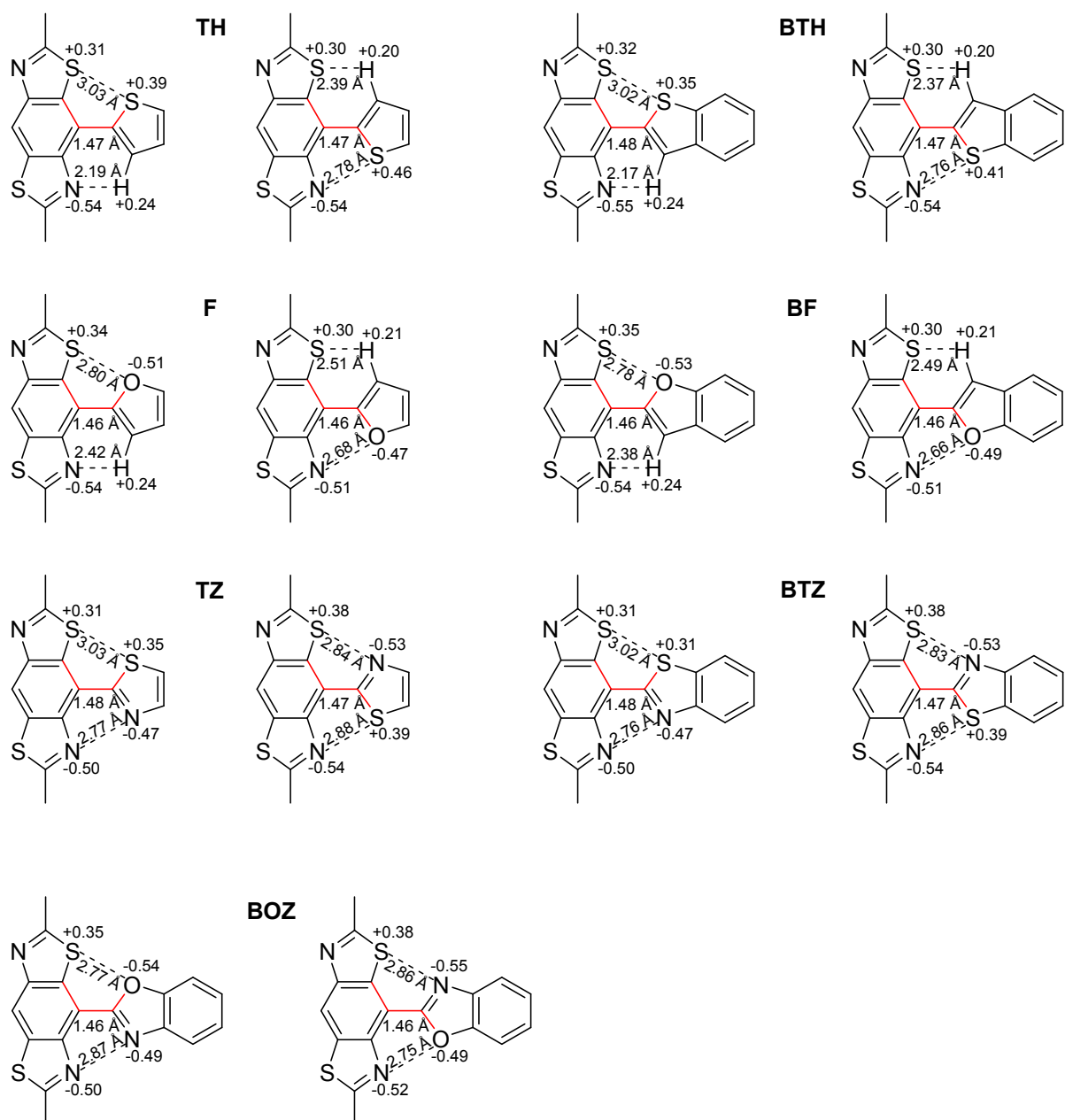
Figure SI5. Natural Bond Orbital (NBO) population analysis (net atomic charges in |e|) calculated at the RI-MP2/cc-pVTZ level of theory

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