Supporting Information

Onset of Three-Centre, Four-Electron Bonding in *peri*-Substituted Acenaphthenes: A Structural and Computational Investigation

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1. Experimental Section

All experiments were carried out under an oxygen- and moisture-free nitrogen atmosphere using standard Schlenk techniques and glassware. Reagents were obtained from commercial sources and used as received. Dry solvents were collected from a MBraun solvent system. Elemental analyses were performed by the University of St. Andrews School of Chemistry Microanalysis Service. Infra-red spectra were recorded as KBr discs in the range 4000-300 cm^{-1} on a Perkin-Elmer System 2000 Fourier transform spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with δ(H) and δ(C) referenced to external tetramethylsilane. ^{77}Se and ^{125}Te NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with δ(Se) and δ(Te) referenced to external dimethylselenide and diphenyl ditelluride respectively. Assignments of ^{13}C and ^{1}H NMR spectra were made with the help of H-H COSY and HSQC experiments. All measurements were performed at 25 °C. All values reported for NMR spectroscopy are in parts per million (ppm). Coupling constants (*J*) are given in Hertz (Hz). Mass spectrometry was performed by the University of St. Andrews Mass Spectrometry Service. Electron impact mass spectrometry (EIMS) and Chemical Ionisation Mass Spectrometry (CIMS) was carried out on a Micromass GCT orthogonal acceleration time of flight mass spectrometer. Electrospray Mass Spectrometry (ESMS) was carried out on a Micromass LCT orthogonal accelerator time of flight mass spectrometer. 5,6-dibromoacenaphthene **A13**[1,2,3] and 5,6-diiodoacenaphthene **A14** were prepared following standard literature procedures starting from acenaphthene and 5,6-dibromoacenaphthene respectively.

5-Bromo-6-(phenylsulfanyl)acenaphthene [Acenap(Br)(SPh)] (A1): *Synthesis of* **A1** *from* **A13**: A solution of *n*-butyllithium (2.5 M) in hexane (3.85 mL, 9.62 mmol) was added dropwise to a solution of 5,6-dibromoacenaphthene (3.002 g, 9.62 mmol) in diethyl ether (40 mL) at -78°C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl disulfide (2.100 g, 9.62 mmol) in diethyl ether (30 mL) was added dropwise. The resulting mixture was stirred at -78°C for a further 1 h, then washed with 0.1 N sodium hydroxide (3 x 60 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure affording a yellow solid. Addition of hexane afforded the product as a white precipitate which was collected by filtration and recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give colourless crystals (2.8 g, 87 %); mp 108-110 ºC; elemental analysis (Found C, 63.3, H 3.7. Calc. for $C_{18}H_{13}BrS$: C 63.35; H, 3.8 %); IR (KBr disk): ν_{max} cm^{-1} 2918s, 2825w, 1597vs, 1579vs, 1562s, 1486s, 1475vs, 1436vs, 1417s, 1406s, 1321vs, 1256s, 1229s, 1204w, 1197w, 1107s, 1081vs, 1069s, 1024vs, 996s, 944w, 864s, 839vs, 813vs, 733vs, 687vs, 625s, 603s, 507s, 492s, 466s, 459s, 407w; δ_H(270 MHz; $CDCl_3$, 25 ºC; Me_4Si) 7.68 (1 H, d, $^{3}J_{HH}$ 7.4 Hz, Acenap 4-H), 7.52 (1 H, d, $^{3}J_{HH}$ 7.3 Hz, Acenap 7-H), 7.20-7.11 (3 H, m, Acenap 8-H, S*Ph* 12,16-H), 7.11-7.02 (4 H, m, Acenap 3-H, S*Ph* 13,15-H), 3.33-3.22 (4 H, m, 2 x CH_2); δ_C(67.9 MHz; $CDCl_3$; 25 ºC;

Me_4Si) 148.2(q), 147.0(q), 141.9(q), 139.2(q), 137.8(s), 135.5(s), 130.1(q), 129.1(s), 126.7(q), 125.9(s), 120.90s), 120.6(s), 114.5(q), 30.2(s, CH_2), 30.0(s, CH_2); MS (EI^+): *m/z* 341.95 (M^+, 25 %), 260.15 (100, M - Br).

5-Bromo-6-(phenylselanyl)acenaphthene [Acenap(Br)(SePh) (A2): *Synthesis of* **A2** *from* **A13**: A solution of *n*-butyllithium (2.5 M) in hexane (2.7 mL, 6.76 mmol) was added dropwise to a solution of 5,6-dibromoacenaphthene (1.054 g, 3.378 mmol) in diethyl ether (40 mL) at -78°C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl diselenide (2.109 g, 6.76 mmol) in diethyl ether (30 mL) was added dropwise. The resulting mixture was stirred at -78°C for a further 1 h, then washed with 0.1 N sodium hydroxide (2 x 60 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure affording an orange oil. Addition of hexane afforded the product as a white precipitate which was collected by filtration and recrystallised from dichloromethane to give colourless crystals (0.9 g, 66 %); mp 77-78 ºC; elemental analysis (Found C, 56.05; H, 3.2. Calc. for $C_{18}H_{13}BrSe$: C, 55.7; H, 3.4 %); IR (KBr disk): ν_{max} cm^{-1} 3039w, 2915s, 2822w, 2341w, 1953w, 1886w, 1829w, 1759w, 1651w, 1597s, 1556s, 1470w, 1434s, 1408s, 1344w, 1328s, 1300s, 1248s, 1230s, 1196w, 1173w, 1150w, 1106s, 1060w, 1044w, 1015s, 995s, 969w, 912w, 832vs, 809vs, 740vs, 698vs, 688vs, 600s, 538w, 504w, 473s, 461s, 396w; δ_H(270 MHz, $CDCl_3$, 25 ºC, Me_4Si) 7.59 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 4-H), 7.54-7.45 (2 H, m, Se*Ph* 12-16-H), 7.30-7.19 (3H, m, Se*Ph* 13-15-H), 7.10 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 7-H), 6.95 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 3-H), 6.87 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 8-H), 3.15 (4 H, s, 2 x CH_2); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 146.8(q), 145.7(q), 142.0(q), 135.7(s), 134.2(s), 133.0(s), 132.0(q), 130.1(q), 129.7(s), 128.3(s), 126.5(q), 120.8(s), 120.6(s), 115.4(q), 30.1(s, CH_2), 29.9(s, CH_2); δ_{Se}(51.5 MHz; $CDCl_3$; 25 ºC; PhSeSePh) 423.7(s); MS (EI^+): *m/z* 387.94 (M^+, 100 %).

5-Bromo-6-(phenyltelluro)acenaphthene [Acenap(Br)(TePh)] (A3): *Synthesis of* **A3** *from* **A13**: A solution of *n*-butyllithium (2.5 M) in hexane (2.9 mL, 9.7 mmol) was added dropwise to a solution of 5,6-dibromoacenaphthene (2.026 g, 9.7 mmol) in diethyl ether (40 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl ditelluride (3.971 g, 9.7 mmol) in diethyl ether (30 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further 1 h, then washed with 0.1 N sodium hydroxide (3 x 60 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure affording a yellow oil. Addition of hexane afforded the product as a yellow precipitate which was collected by filtration and recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give yellow crystals (0.7 g, 53 %); mp 135-137 ºC; elemental analysis (Found: C, 49.6; H, 2.8. Calc. for $C_{18}H_{13}BrTe$: C, 49.5; H, 3.0 %); IR (KBr disk): ν_{max} cm^{-1} 2923s, 2839w, 1825w, 1602s, 1555s, 1472w, 1434s, 1408s, 1347w, 1328s, 1250w, 1229s, 1112w, 1097s, 1062w, 1039s, 1014s, 996s, 982w, 913w, 832vs, 803vs, 733vs, 693vs, 598s, 534w, 489w, 456s; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 7.91-7.83 (2 H, m, Te*Ph* 12,16-H), 7.58 (1 H, d, $^4J_{HH}$ 7.4 Hz, Acenap 4-H), 7.41-7.33 (1 H, m, Te*Ph* 14-H), 7.31-7.22 (2 H, m, Te*Ph* 13,15-H), 7.17 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 7-H), 6.99 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 3-H), 6.81 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 8-H), 3.18 (4 H, s, 2 x CH_2); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 147.6(q), 146.1(q), 142.5(q), 141.8(s), 136.0(s), 133.6(s), 132.9(q), 130.4(s), 129.3(s), 121.9(s), 120.9(s), 119.4(q), 117.3(q), 30.4(s, CH_2), 30.2(s, CH_2); δ_{Te}(81.2 MHz; $CDCl_3$; 25 ºC; PhTeTePh) 696.0(s); MS (ES^+): *m/z* 468.89 (100 %, M + OMe,).

5-Iodo-6-(phenylsulfanyl)acenaphthene [Acenap(I)(SPh)] (A4): *Synthesis of* **A4** *from* **A1**: A solution of *n*-butyllithium (2.5 M) in hexane (1.07 mL, 2.66 mmol) was added dropwise to a solution of 5-bromo-6-(phenylsulfanyl)acenaphthene

(0.909 g, 2.66 mmol) in diethyl ether (30 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of iodine (0.676 g, 2.66 mmol) in diethyl ether (30 mL) was added dropwise whilst the temperature of the mixture was maintained between -10-0 °C. The resulting mixture was stirred at -10 °C for 1/2 h and for a further 1 h without cooling. Aqueous 5% sodium thiosulfate (60 mL) was added to the mixture with vigorous stirring. The organic layer was washed with aqueous sodium thiosulfate and then water, dried with magnesium sulfate and concentrated under reduced pressure affording a cream solid. The crude solid was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give the product as colourless crystals (0.8 g, 76 %); mp 92-94 ºC; elemental analysis (Found: C, 55.7; H, 3.0. Calc. for $C_{18}H_{13}IS$: C, 55.7, H, 3.4 %); IR (KBr disk): ν_{max} cm^{-1} 2919s, 2819w, 1936w, 1872w, 1789w, 1722w, 1654w, 1595s, 1578vs, 1474vs, 1434vs, 1415s, 1403s, 1360w, 1341w, 1318vs, 1268w, 1254w, 1228s, 1202s, 1178w, 1150w, 1105s, 1078s, 1022s, 998w, 941w, 894w, 858s, 837vs, 811s, 733vs, 685vs, 624s, 598s, 478w, 463s, 401w; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 8.12 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 4-H), 7.71 (1 H, d, $^3J_{HH}$ 7.2 Hz, Acenap 7-H), 7.19 (1 H, d, $^3J_{HH}$ 7.2 Hz, Acenap 8-H), 7.17-7.09 (2 H, m, S*Ph* 13,15-H), 7.07-7.00 (1 H, m, S*Ph* 14-H), 6.98-6.93 (2 H, m, S*Ph* 12,16-H), 6.91 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 3-H), 3.39-3.20 (4 H, m, 2 x CH_2); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 150.2(q), 148.5(q), 144.8(s), 141.5(q), 140.8(q), 140.4(s), 132.5(q), 129.4(s), 128.1(s), 126.2(q), 125.7(s), 122.2(s), 120.9(s), 85.4(q), 30.6(s, CH_2), 30.5(s, CH_2); MS (ES^+): *m/z* 410.98 (40 %, M + Na).

Synthesis of **A4** *from* **A14**: A solution of *n*-butyllithium (2.5 M) in hexane (0.52 mL, 1.29 mmol) was added dropwise to a solution of 5,6-diiodoacenaphthene (0.525 g, 1.29 mmol) in diethyl ether (30 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl disulfide (0.282 g, 1.29 mmol) in diethyl ether (20 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further 1 h, then washed with 0.1 N sodium hydroxide (3 x 40 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure affording a yellow oil. The crude compound was purified by column chromatography on silica gel (hexane) and the resulting yellow solid was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give the product as colourless crystals (0.3 g, 55 %).

5-Iodo-6-(phenylselanyl)acenaphthene [Acenap(I)(SePh)] (A5): *Synthesis of* **A5** *from* **A2**: A solution of *n*-butyllithium (2.5 M) in hexane (1.10 mL, 2.74 mmol) was added dropwise to a solution of 5-bromo-6-(phenylselenyl)acenaphthene (1.065 g, 2.74 mmol) in diethyl ether (30 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of iodine (0.695 g, 2.74 mmol) in diethyl ether (30 mL) was added dropwise whilst the temperature of the mixture was maintained between -10-0 °C. The resulting mixture was stirred at -10 °C for 1/2 h and for a further 1 h without cooling. Aqueous 5% sodium thiosulfate (60 mL) was added to the mixture with vigorous stirring. The organic layer was washed with aqueous sodium thiosulfate and then water, dried with magnesium sulfate and concentrated under reduced pressure affording a cream solid. The crude solid was purified by column chromatography on silica gel (hexane) and the resulting yellow crystalline solid was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give the product as colourless crystals (0.7 g, 60 %); mp 82-84 ºC; elemental analysis (Found: C, 49.7; H, 2.7. Calc. for $C_{18}H_{13}ISe$: C, 49.7; H, 3.0 %); IR (KBr disk): ν_{max} cm^{-1} 2914s, 2867w, 2824w, 1971w, 1950w, 1898w, 1874w, 1860w, 1803w, 1651w, 1597w, 1552w, 1472s, 1434s, 1403s, 1339w, 1320s, 1299w, 1270w, 1249s, 1230s, 1157w, 1105s, 1062w, 1015s, 1000s, 967w, 953w, 936w, 915w, 835vs, 809vs, 738vs, 690s, 598s, 536w, 498w, 463s, 385w, 363w; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 8.00 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 4-H), 7.42-7.33 (2 H, m, Se*Ph* 12,16-H), 7.31 (1 H,

d, $^3J_{HH}$ 7.4 Hz, Acenap 7-H), 7.22-7.14 (3 H, m, Se*Ph* 13-15-H), 6.90 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 8-H), 6.81 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 3-H), 3.21-3.08 (4 H, m, 2 x CH_2); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 148.3(q), 147.5(q), 143.5(s), 141.8(q), 135.9(s), 134.7(s), 134.2(q), 133.2(q), 130.0(s), 128.1(s), 126.6(q), 122.0(s), 121.2(s), 86.9(q), 30.5(s, *C*H_2), 30.3(s, *C*H_2); δ_{Se}(51.5 MHz; $CDCl_3$; 25 ºC; PhSeSePh) 400.9(s); MS (ES^+): *m/z* 435.91 (3 %, M + H), 308.01 (100, M - I).

Synthesis of **A5** *from* **A14**: A solution of *n*-butyllithium (2.5 M) in hexane (0.58 mL, 1.45 mmol) was added dropwise to a solution of 5,6-diiodoacenaphthene (0.589 g, 1.45 mmol) in diethyl ether (30 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl diselenide (0.453 g, 1.45 mmol) in diethyl ether (30 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further 1 h, then washed with 0.1 N sodium hydroxide (3 x 40 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure affording a yellow oil. The crude compound was purified by column chromatography on silica gel (hexane) and the resulting yellow solid was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give the product as colourless crystals (0.2 g, 30 %).

5-Iodo-6-(phenyltelluro)acenaphthene [Acenap(I)(TePh)] (A6): *Synthesis of* **A6** *from* **A14**: A solution of *n*-butyllithium (2.5 M) in hexane (0.50 mL, 1.26 mmol) was added dropwise to a solution of 5,6-diiodoacenaphthene (0.510 g, 1.26 mmol) in diethyl ether (40 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl ditelluride (0.514 g, 1.26 mmol) in diethyl ether (30 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further 1 h, then washed with 0.1 N sodium hydroxide (3 x 60 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure affording a yellow oil. The crude compound was purified by column chromatography on silica gel (hexane/dichloromethane 9:1) and the resulting yellow solid was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give the product as colourless crystals (0.1 g, 22 %); mp 77-79 ºC; IR (KBr disk): ν_{max} cm^{-1} 2922w, 2834w, 1599w, 1547s, 1469w, 1431s, 1405s, 1341w, 1316s, 1263w, 1248s, 1228s, 1176w, 1154w, 1112w, 1095s, 1062w, 1036w, 1009s, 996s, 984w, 951w, 932w, 913w, 832vs, 801vs, 732vs, 691vs, 594s, 532w, 484w, 454s, 378w, 359w; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 8.08 (1 H, d, $^3J_{HH}$ 7.3 Hz, Acenap 4-H), 7.96-7.89 (2 H, m, Te*Ph* 12,16-H), 7.49-7.31 (4 H, m, Acenap 7-H, Te*Ph* 13-15-H), 7.00 (1 H, d, $^3J_{HH}$ 7.3 Hz, Acenap 3-H), 6.92 (1 H, d, $^3J_{HH}$ 7.3 Hz, Acenap 8-H), 3.36-3.26 (4 H, m, 2 x CH_2); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 147.0(q), 141.9(s), 141.2(s),138.4(q), 137.3(s), 130.4(s), 129.2(s), 128.0(q), 121.9(s), 121.8(s), 121.7(q), 113.9(q), 30.4(s, *C*H_2), 30.0(s, *C*H_2); δ_{Te}(81.2 MHz; $CDCl_3$; 25 ºC; PhTeTePh) 662.0(s); MS (ES^+): *m/z* 516.75 (100 %, M + OMe).

5-Iodo-6-bromoacenaphthene [Acenap(I)(Br)] (A15): *Synthesis of* **A15** *from* **A3**: A solution of *n*-butyllithium (2.5 M) in hexane (0.33 mL, 0.829 mmol) was added dropwise to a solution of 5-bromo-6-(phenyltelluro)acenaphthene (0.362 g, 0.829 mmol) in diethyl ether (30 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of iodine (0.210 g, 0.829 mmol) in diethyl ether (30 mL) was added dropwise whilst the temperature of the mixture was maintained between -10-0°C. The resulting mixture was stirred at -10 °C for 1/2 h and for a further 1 h without cooling. Aqueous 5% sodium thiosulfate (60 mL) was added to the mixture with vigorous stirring. The organic layer was washed with aqueous sodium thiosulfate and then water, dried with magnesium sulfate and concentrated under reduced pressure affording a cream solid. The crude solid was washed with hexane and the white precipitate was collected by filtration. Recrystallisation by diffusion of hexane into a saturated solution of the compound in dichloromethane gave the product as

colourless crystals (0.05 g, 17 %); mp 144-146 ºC; elemental analysis (Found: C, 40.7; H, 2.0. Calc. for $C_{12}H_8IBr$: C, 40.15; H, 2.25 %); IR (KBr disk): ν_{max} cm^{-1} 2938w, 2924w, 2819w, 1855w, 1595s, 1554w, 1434w, 1403s, 1344w, 1316s, 1249w, 1225s, 1142w, 1100s, 1067w, 1041w, 1014s, 939w, 887w, 834vs, 809s, 768w, 733w, 695w, 681w, 595s, 539w, 489w, 456w, 361w, 328w; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 8.16 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 7-H), 7.74 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 4-H), 7.03 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 3-H), 6.87 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 8-H), 3.30-3.16 (4 H, m, 2 x CH_2); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 148.6(q), 148.1(q), 145.0(s), 141.6(q), 136.1(s), 129.7(q), 122.3(s), 121.3(s), 116.6(q), 85.6(q), 30.5(s, CH_2), 30.3(s, CH_2); MS (ES^-): *m/z* 380.68 (100 %, M + Na – H).

5,6-Bis(phenylsulfanyl)acenaphthene [Acenap(SPh)$_2$] (A7): *Synthesis of* **A7** *from* **A1**: A solution of *n*-butyllithium (2.5 M) in hexane (0.66 mL, 1.65 mmol) was added dropwise to a solution of 5-bromo-6-(phenylsulfanyl)acenaphthene (0.562 g, 1.65 mmol) in diethyl ether (20 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl disulfide (0.360 g, 1.65 mmol) in diethyl ether (20 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further 1 h, then washed with 0.1 N sodium hydroxide (2 x 20 mL). The organic layer was dried with magnesium sulphate and concentrated under reduced pressure. The residual crude oil was purified by column chromatography on silica gel (hexane/dichloromethane 9:1) and the resulting white solid was recrystallised by diffusion of pentane into a saturated solution of the compound in dichloromethane to give the product as colourless crystals (0.4 g, 69%); mp 108-110 ºC; elemental analysis (Found: C, 77.9; H, 4.9. Calc. for $C_{24}H_{18}S_2$: C, 77.8; H, 4.9 %); IR (KBr disk): ν_{max} cm^{-1} 2908w, 1655w, 1637w, 1597w, 1580s, 1475s, 1436s, 1415s, 1341w, 1322s, 1296w, 1256w, 1230w, 1199w, 1084s, 1067w, 1022s, 955w, 882w, 839s, 733vs, 686s, 622w, 569w, 505w, 463w; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 7.40 (2 H, d, $^3J_{HH}$ 7.3 Hz, Acenap 4,7-H), 7.16-7.10 (6 H, m, Acenap 3,8-H, S*Ph* 12,16,18,22-H), 7.10-7.02 (6 H, m, S*Ph* 13-15,19-21-H), 3.31 (4 H, s, 2 x CH_2); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 147.5(q), 141.4(q), 139.2(q), 136.4(s), 129.9(s), 129.1(s), 129.0(s), 127.8(q), 126.1(s), 120.4(s), 30.2(s, 2 x CH_2); MS (ES^+): *m/z* 393.02 (100, M + Na).

Synthesis of **A7** *from* **A4**: A solution of *n*-butyllithium (2.5 M) in hexane (0.2 mL, 0.51 mmol) was added dropwise to a solution of 5-iodo-6-(phenylsulfanyl)acenaphthene (0.199 g, 0.51 mmol) in diethyl ether (20 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl disulfide (0.112 g, 0.51 mmol) in diethyl ether (20 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further 1 h, then washed with 0.1 N sodium hydroxide (2 x 20 mL). The organic layer was dried with magnesium sulphate and concentrated under reduced pressure. The residual crude oil was purified by column chromatography on silica gel (hexane/dichloromethane 9:1) and the resulting white solid was recrystallised by diffusion of pentane into a saturated solution of the compound in dichloromethane to give the product as colourless crystals (0.05 g, 28%).

Synthesis of **A7** *from* **A13**: A solution of 5,6-dibromoacenaphthene (0.592 g, 1.897 mmol) in diethyl ether (40 mL) was cooled to -10 – 0 °C on an ice-ethanol bath and to this was added a solution of TMEDA (0.8 mL, 5.04 mmol). The mixture was allowed to stir for 15 min before a solution of *n*-butyllithium (2.5 M) in hexane (1.8 mL, 4.56 mmol) was added dropwise over a period of 15 min. During these operations, the temperature of the mixture was maintained at -10 – 0 °C. The mixture was stirred at this temperature for a further 1 h, before being cooled to -78 °C. A solution of diphenyl disulfide (0.829 g, 3.79 mmol) in diethyl ether (30 mL) was then added dropwise and the resulting solution was stirred at -78 °C for a further 1 h. The mixture was allowed to warm to room temperature and then washed with 0.1 N sodium hydroxide (3 x 60

mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure to afford a yellow solid. The crude product was purified by column chromatography on silica gel (hexane/dichloromethane) and the resulting cream powder was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give colourless crystals (0.4 g, 54 %).

5,6-Bis(phenylselanyl)acenaphthene [Acenap(SePh)$_2$] (A8): *Synthesis of* **A8** *from* **A2**: A solution of *n*-butyllithium (2.5 M) in hexane (0.94 mL, 2.35 mmol) was added dropwise to a solution of 5-bromo-6-(phenylselenyl)acenaphthene (0.912 g, 2.35 mmol) in diethyl ether (20 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl diselenide (0.734 g, 2.35 mmol) in diethyl ether (20 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further 1 h, then washed with 0.1 N sodium hydroxide (2 x 20 mL). The organic layer was dried with magnesium sulphate and concentrated under reduced pressure. The residual crude oil was purified by column chromatography on silica gel (hexane) and the resulting white solid was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give the product as colourless crystals (0.7 g, 60%); mp 104-106 ºC; elemental analysis (Found: C, 62.12; H, 3.68. Calc. for $C_{24}H_{18}Se_2$: C, 62.08; H, 3.91 %); IR (KBr disk): ν_{max} cm^{-1} 2924w, 2872w, 2829w, 1957w, 1881w, 1857w, 1651w, 1637w, 1597s, 1573s, 1545w, 1474s, 1433s, 1410s, 1326s, 1301w, 1254w, 1232w, 1171w, 1157w, 1103s, 1069w, 1019s, 998w, 913w, 901w, 856w, 836vs, 811vs, 745vs, 732vs, 691s, 666w, 605s, 574w, 541w, 503w, 469s, 337w; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 7.45 (2 H, d, $^3J_{HH}$ 7.3 Hz, Acenap 4,7-H), 7.40-7.34 (4 H, m, Se*Ph* 12,16,18,22-H), 7.34-7.20 (6 H, m, Se*Ph* 13-15,19-21-H), 7.04 (2 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 3,8-H), 3.27 (4 H, s, 2 x CH_2); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 147.0(q), 141.3(q), 136.4(s), 134.6(q), 133.5(q), 133.3(s), 129.3(s), 127.2(s), 125.6(q), 120.6(s), 30.1(s, *C*H_2); δ_{Se}(51.5 MHz; $CDCl_3$; 25 ºC; PhSeSePh) 408.3(s); MS (ES$^+$): *m/z* 465.96 (100 %, M + H).

Synthesis of **A8** *from* **A5**: A solution of *n*-butyllithium (2.5 M) in hexane (0.17 mL, 0.427 mmol) was added dropwise to a solution of 5-iodo-6-(phenylselanyl)acenaphthene (0.186 g, 0.427 mmol) in diethyl ether (30 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl diselenide (0.133 g, 0.427 mmol) in diethyl ether (20 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further 1 h, then washed with 0.1 N sodium hydroxide (2 x 20 mL). The organic layer was dried with magnesium sulphate and concentrated under reduced pressure. The residual crude oil was purified by column chromatography on silica gel (hexane/dichloromethane 9:1) and the resulting white solid was recrystallised by diffusion of pentane into a saturated solution of the compound in dichloromethane to give the product as colourless crystals (0.06 g, 28%).

Synthesis of **A8** *from* **A13**: A solution of 5,6-dibromoacenaphthene (0.676 g, 2.167 mmol) in diethyl ether (40 mL) was cooled to -10 – 0 °C on an ice-ethanol bath and to this was added a solution of TMEDA (0.9 mL, 5.76 mmol). The mixture was allowed to stir for 15 min before a solution of *n*-butyllithium (2.5 M) in hexane (2.1 mL, 5.21 mmol) was added dropwise over a period of 15 min. During these operations, the temperature of the mixture was maintained at -10 – 0 °C. The mixture was stirred at this temperature for a further 1 h, before being cooled to -78 °C. A solution of diphenyl diselenide (1.353 g, 4.33 mmol) in diethyl ether (30 mL) was then added dropwise and the resulting solution was stirred at -78 °C for a further 1 h. The mixture was allowed to warm to room temperature and then washed with 0.1 N sodium hydroxide (3 x 60 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure to

afford a red solid. The crude product was purified by column chromatography on silica gel (hexane/dichloromethane) and the resulting cream powder was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give colourless crystals (0.5 g, 52 %).

5,6-Bis(phenyltelluro)acenaphthene [Acenap(TePh)$_2$] (A9): *Synthesis of* **A9** *from* **A13**: A solution of 5,6-dibromoacenaphthene (0.548 g, 1.756 mmol) in diethyl ether (40 mL) was cooled to -10 – 0 °C on an ice-ethanol bath and to this was added a solution of TMEDA (0.7 mL, 4.67 mmol). The mixture was allowed to stir for 15 min before a solution of *n*-butyllithium (2.5 M) in hexane (1.7 mL, 4.22 mmol) was added dropwise over a period of 15 min. During these operations, the temperature of the mixture was maintained at -10 – 0 °C. The mixture was stirred at this temperature for a further 1 h, before being cooled to -78 °C. A solution of diphenyl ditelluride (1.438 g, 3.51 mmol) in diethyl ether (30 mL) was then added dropwise and the resulting solution was stirred at -78 °C for a further 1 h. The mixture was allowed to warm to room temperature and then washed with 0.1 N sodium hydroxide (3 x 60 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure to afford a red solid. The crude product was purified by column chromatography on silica gel (hexane/dichloromethane) and the resulting cream powder was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give colourless crystals (0.5 g, 55 %); mp 146-148 ºC; elemental analysis (Found: C, 51.5; H, 2.95. Calc. for $C_{24}H_{18}Te_2$: C, 51.3; H, 3.2 %); IR (KBr disk): ν_{max} cm^{-1} 2914w, 2867w, 2824w, 1599w, 1588w, 1567s, 1483w, 1469s, 1429s, 1403s, 1320s, 1261w, 1247w, 1230s, 1176w, 1150w, 1112w, 1097s, 1057s, 1013s, 996s, 896w, 834s, 806s, 729vs, 690vs, 650w, 598s, 534w, 484w, 449s, 311w; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 7.81 (2 H, d, $^3J_{HH}$ 7.3 Hz, Acenap 4,7-H), 7.64-7.54 (4 H, m, Te*Ph* 12,16,18,22-H), 7.24-7.07 (6 H, m, Te*Ph* 13-15,19-21-H), 6.97 (2 H, d, $^3J_{HH}$ 7.3 Hz, Acenap 3,8-H), 3.27 (4 H, s, 2 x CH_2); δ_C(67.9 MHz; $CDCl_3$; 25ºC; Me_4Si) 148.5(q), 142.5(s), 141.2(q), 139.0(q), 138.1(s), 129.9(s), 128.2(s), 122.9(q), 121.5(s), 113.5(q), 30.3(s, 2 x *C*H_2); δ_{Te}(81.2 MHz; $CDCl_3$; 25 ºC; PhTeTePh) 585.9(s); MS (ES$^+$): *m/z* 592.94 (100, M + OMe).

5-(Phenylsulfanyl)-6-(phenylselanyl)acenaphthene [Acenap(SePh)(SPh)] (A10): *Synthesis of* **A10** *from* **A1**: A solution of *n*-butyllithium (2.5 M) in hexane (0.54 mL, 1.35 mmol) was added dropwise to a solution of 5-bromo-6-(phenylsulfanyl)acenaphthene (0.460 g, 1.35 mmol) in diethyl ether (20 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl diselenide (0.421 g, 1.35 mmol) in diethyl ether (20 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further 1 h, then washed with 0.1 N sodium hydroxide (2 x 20 mL). The organic layer was dried with magnesium sulphate and concentrated under reduced pressure. The residual crude oil was purified by column chromatography on silica gel (hexane) and the resulting white solid was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give the product as colourless crystals (0.2 g, 37%); mp 106-108 ºC; elemental analysis (Found: C, 69.15; H, 4.6. Calc. for $C_{24}H_{18}SSe$: C, 69.1; H, 4.35 %); IR (KBr disk): ν_{max} cm^{-1} 2914w, 2829w, 1959w, 1936w, 1860w, 1654w, 1595s, 1578s, 1475s, 1436s, 1408s, 1331vs, 1301w, 1254w, 1230w, 1216w, 1176w, 1152w, 1107w, 1082s, 1062w, 1021s, 998w, 936w, 915w, 894w, 865w, 836vs, 816s, 778w, 747vs, 732vs, 690vs, 624w, 608w, 579w, 555w, 510w, 466s, 404w, 311w; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 7.79 (1 H, d, $^3J_{HH}$ 7.2 Hz, Acenap 4-H), 7.64-7.59 (2 H, m, Se*Ph* 12,16-H), 7.41-7.33 (3 H, m, Se*Ph* 13-15-H), 7.31 (1 H, d, $^3J_{HH}$ 7.2 Hz, Acenap 3-H), 7.26-7.19 (2 H, m, S*Ph* 18,22-H), 7.16-7.09 (4 H, m, Acenap 7-H, S*Ph* 19-21-H), 7.06 (1 H, d, $^3J_{HH}$ 7.0 Hz, Acenap 8-H), 3.46-3.40 (2 H, m, CH_2), 3.40-3.33 (2 H, m, CH_2); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 149.3(q), 145.0(q), 141.4(q), 140.6(q), 139.7(s), 136.3(s), 132.9(q), 132.4(q), 131.7(s), 129.5(s), 128.9(s), 128.2(s),

128.0(q), 127.4(s), 125.3(s), 125.1(q), 120.7(s), 120.3(s), 30.4(s, CH_2), 29.8(s, CH_2); δ_{Se}(51.5 MHz; $CDCl_3$; 25 ºC; PhSeSePh) 433.7(s); MS (ES^+): *m/z* 441.05 (100 %, M + Na), 418.05 (25, M + H).

Synthesis of **A10** *from* **A2**: A solution of *n*-butyllithium (2.5 M) in hexane (0.30 mL, 0.783 mmol) was added dropwise to a solution of 5-bromo-6-(phenylselanyl)acenaphthene (0.304 g, 0.783 mmol) in diethyl ether (40 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl disulfide (0.171 g, 0.783 mmol) in diethyl ether (30 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further 1 h, then washed with 0.1 N sodium hydroxide (2 x 60 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure. The residual crude oil was purified by column chromatography on silica gel (hexane) and the resulting white solid was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give colourless crystals (0.03 g, 36 %).

Synthesis of **A10** *from* **A4**: A solution of *n*-butyllithium (2.5 M) in hexane (0.23 mL, 0.583 mmol) was added dropwise to a solution of 5-iodo-6-(phenylsulfanyl)acenaphthene (0.226 g, 0.583 mmol) in diethyl ether (20 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl diselenide (0.182 g, 0.583 mmol) in diethyl ether (20 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further 1 h, then washed with 0.1 N sodium hydroxide (2 x 40 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure. The residual crude oil was purified by column chromatography on silica gel (hexane) and the resulting white solid was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give colourless crystals (0.05 g, 21 %).

Synthesis of **A10** *from* **A5**: A solution of *n*-butyllithium (2.5 M) in hexane (0.37 mL, 0.783 mmol) was added dropwise to a solution of 5-iodo-6-(phenylselanyl)acenaphthene (0.397 g, 0.912 mmol) in diethyl ether (30 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl disulfide (0.199 g, 0.912 mmol) in diethyl ether (30 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further 1 h, then washed with 0.1 N sodium hydroxide (2 x 40 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure. The residual crude oil was purified by column chromatography on silica gel (hexane) and the resulting white solid was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give colourless crystals (0.2 g, 52 %).

5-(Phenyltelluro)-6-(phenylsulfanyl)acenaphthene [Acenap(TePh)(SPh)] (A11): *Synthesis of* **A11** *from* **A1**: A solution of *n*-butyllithium (2.5 M) in hexane (0.59 mL, 1.47 mmol) was added dropwise to a solution of 5-bromo-6-(phenylsulfanyl)acenaphthene (0.501 g, 1.47 mmol) in diethyl ether (40 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl ditelluride (0.602 g, 1.47 mmol) in diethyl ether (30 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further 1 h, then washed with 0.1 N sodium hydroxide (2 x 60 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure. The residual crude oil was purified by column chromatography on silica gel (hexane) and the resulting cream powder was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give colourless crystals (0.2 g, 30 %); mp 110-112 ºC; elemental analysis (Found: C, 62.12; H, 3.68. Calc. for $C_{24}H_{18}STe$: C, 61.85; H, 3.89 %); IR (KBr disk):

ν_{max} cm^{-1} 2923w, 2824w, 1957w, 1931w, 1855w, 1637w, 1595s, 1578s, 1475s, 1434s, 1427s, 1407s, 1331s, 1299w, 1254w, 1232w, 1202w, 1178w, 1154w, 1105w, 1078w, 1058w, 1020s, 996w, 913w, 863w, 836s, 809s, 736vs, 693s, 624w, 602w, 487w, 455w, 397w; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 7.88-7.81 (2 H, m, Te*Ph* 12,16-H), 7.72 (1 H, d, $^3J_{HH}$ 7.2 Hz, Acenap 4-H), 7.37-7.30 (1 H, m, Te*Ph* 14-H), 7.28-7.19 (3 H, m, Acenap 3-H, Te*Ph* 13,15-H), 7.18-7.07 (3 H, m, Acenap 7-H, S*Ph* 18,22-H), 7.05-6.95 (3 H, m, S*Ph* 19-21-H), 6.90 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 8-H), 3.39-3.22 (4 H, m, 2 x CH_2); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 150.2(q), 145.4(q), 141.4(q), 141.3(s), 140.4(q), 139.9(s), 135.6(q), 134.9(s), 129.7(s), 129.1(q), 129.0(s), 128.6(s), 126.9(s), 125.7(s), 124.8(q), 121.5(s), 120.2(s), 111.7(q), 30.5(s, CH_2), 29.8(s, CH_2); δ_{Te}(81.2 MHz; $CDCl_3$; 25 ºC; PhTeTePh) 689.4(s); MS (ES^+): *m/z* 499.03 (100 %, M + OMe).

Synthesis of **A11** *from* **A4**: A solution of *n*-butyllithium (2.5 M) in hexane (0.29 mL, 0.737 mmol) was added dropwise to a solution of 5-iodo-6-(phenylsulfanyl)acenaphthene (0.286 g, 0.737 mmol) in diethyl ether (30 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl ditelluride (0.302 g, 0.737 mmol) in diethyl ether (30 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further 1 h, then washed with 0.1 N sodium hydroxide (2 x 40 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure. The residual crude oil was purified by column chromatography on silica gel (hexane) and the resulting yellow solid was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give colourless crystals (0.1 g, 35 %).

5-(Phenyltelluro)-6-(phenylselanyl)acenaphthene [Acenap(TePh)(SePh)] (A12): *Synthesis of* **A12** *from* **A2**: A solution of *n*-butyllithium (2.5 M) in hexane (0.75 mL, 1.88 mmol) was added dropwise to a solution of 5-bromo-6-(phenylselanyl)acenaphthene (0.731 g, 1.88 mmol) in diethyl ether (40 mL) at -78 °C. The mixture was stirred at this temperature for 1 h, after which a solution of diphenyl ditelluride (0.771 g, 1.88 mmol) in diethyl ether (30 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further 1 h, then washed with 0.1 N sodium hydroxide (2 x 60 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure. The residual crude oil was purified by column chromatography on silica gel (hexane) and the resulting yellow solid was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give colourless crystals (0.6 g, 62%); mp 138-140 ºC; elemental analysis (Found: C, 56.4; H, 3.5. Calc. for $C_{24}H_{18}SeTe$: C, 56.2; H, 3.5 %); IR (KBr disk): ν_{max} cm^{-1} 2947w, 2909w, 2834w, 1950w, 1876w, 1855w, 1595s, 1573s, 1474s, 1432s, 1405s, 1324s, 1299w, 1249w, 1230s, 1154w, 1112w, 1097s, 1065s, 1018s, 998w, 896w, 837vs, 807w, 764w, 729vs, 687vs, 664s, 614w, 600s, 539w, 489w, 451s, 399w, 333w; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 7.98 (1 H, d, $^3J_{HH}$ 7.2 Hz, Acenap 4-H), 7.96-7.91 (2 H, m, Te*Ph* 12,16-H), 7.46-7.41 (1 H, m, Te*Ph* 14-H), 7.38-7.31 (3 H, m, Acenap 7-H, Te*Ph* 13,15-H), 7.31-7.24 (3 H, m, Acenap 3-H, Se*Ph* 18,22-H), 7.24-7.14 (3 H, m, Se*Ph* 19-21-H), 7.00 (1 H, d, $^3J_{HH}$ 7.4 Hz, Acenap 8-H), 3.44-3.34 (4 H, m, 2 x CH_2); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 149.8(q), 145.8(q), 141.3(q), 141.1(s), 140.8(s), 136.0(q), 135.8(s), 135.7(q), 129.8(s), 129.7(s), 129.2(s), 128.4(s), 126.4(s), 123.2(q), 122.3(q), 121.3(s), 120.4(s), 113.0(q), 30.4(s, CH_2), 29.7(s, CH_2); δ_{Se}(51.5 MHz; $CDCl_3$; 25 ºC; PhSeSePh) 340.7 (s, $^4J_{SeTe}$ ±715.6 Hz); δ_{Te}(81.2 MHz; $CDCl_3$; 25 ºC; PhTeTePh) 663.4 (s, $^4J_{TeSe}$ ±715.6 Hz); MS (ES^+): *m/z* 544.87 (100 %, M + OMe).

Synthesis of **A12** *from* **A5**: A solution of *n*-butyllithium (2.5 M) in hexane (0.26 mL, 0.657 mmol) was added dropwise to a solution of 5-iodo-6-(phenylselanyl)acenaphthene (0.286 g, 0.657 mmol) in diethyl ether (40 mL) at -78 °C. The mixture

was stirred at this temperature for 1 h, after which a solution of diphenyl ditelluride (0.269 g, 0.657 mmol) in diethyl ether (30 mL) was added dropwise. The resulting mixture was stirred at -78 °C for a further 1 h, then washed with 0.1 N sodium hydroxide (2 x 30 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure. The residual crude oil was purified by column chromatography on silica gel (hexane) and the resulting yellow solid was recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give colourless crystals (0.1 g, 32%).

5,6-diiodoacenaphthene(Acenap(I)$_2$] (A14): *Synthesis of* **A14** *from* **A13**: A solution of TMEDA (6.42 mL, 42.7 mmol) was added to a solution of 5,6-dibromoacenaphthene (5.005 g, 16.04mmol) in diethyl ether (300 mL). To this *n*-butyllithium (2.5 M) in hexane (15.4 mL, 38.50 mmol) was added dropwise at -78 °C and stirred at this temperature for a further 1 h. The temperature of the reaction mixture was allowed to warm to -10 °C after which a solution of iodine (9.038 g, 35.61 mmol) in diethyl ether (80 mL) was added dropwise. The resulting mixture was stirred at -10 °C for a further 1/2 h and for a further 1 h without cooling. Aqueous 5% sodium thiosulfate (300 mL) was added to the mixture with vigorous stirring. The organic layer was washed with aqueous sodium thiosulfate and then water, dried with magnesium sulfate and concentrated under reduced pressure affording a pale brown solid. The title compound was purified by column chromatography on silica gel (hexane) and the resulting brown crystalline solid recrystallised by diffusion of hexane into a saturated solution of the compound in dichloromethane to give colourless crystals (1.9 g, 28 %); mp 158-159 ºC (lit.,[ref]; 159-160 ºC); IR (KBr disk): ν_{max} cm^{-1} 2938s, 2924s, 2862s, 2815s, 2625w, 2563w, 2436w, 2308w, 2232w, 2127w, 2023w, 1933w, 1857s, 1808w, 1770w, 1739w, 1649w, 1595s, 1550s, 1486w, 1431s, 1405s, 1355w, 1339w, 1311s, 1261s, 1249s, 1223s, 1142w, 1097s, 1007s, 955w, 941w, 882w, 832vs, 806vs, 738s, 678s, 648w, 593s, 534w, 482s, 458w, 394w, 380w; δ_H(270 MHz; $CDCl_3$; 25 ºC; Me_4Si) 8.23 (2 H, d, $^3J_{HH}$ 7.5 Hz, Acenap 4,7-H), 6.91 (2 H, d, $^3J_{HH}$ 7.5 Hz, Acenap 3,8-H), 3.26 (4 H, s, 2 x CH_2); δ_C(67.9 MHz; $CDCl_3$; 25 ºC; Me_4Si) 149.0(q), 144.7(s), 131.3(q), 121.9(s), 121.0(q), 89.5(q), 30.0(s, 2 x CH_3).

2. Computational Details

Geometries were fully optimised in the gas phase at the B3LYP level[4] using Curtis and Binning's 962(d) basis[5] on Se and Br (augmented with a set of diffuse s and p functions on Br), the Stuttgart-Dresden effective core potentials along with their double zeta valence basis sets for Te and I[6] (augmented with d-polarisation functions with exponents of 0.237 and 0.241, respectively),[7] and 6-31+G(d) basis elsewhere. Wiberg bond indices[8] were obtained in a natural bond orbital analysis[9] at the same level. The optimisations were started from a number of different conformers for those compounds containing a phenylchalcogen substituent. For the mono-phenyl chalcogens these were A and B. For the di-phenylchalcogens these were AAc, AAt, AB, and BB. Mixed chalcogen structures also included the BA conformer. For the dichalcogen compounds, experimental structures from X-ray crystallography were used as one of the starting conformers. The computations were performed using the Gaussian 03 suite of programs.[10]

The $J(^{77}Se,^{125}Te)$ spin-spin coupling constants of **A12** and **N12** were computed[11] at the BP86 level[12] using the relativistic zeroth-order regular approximation both in its scalar formulation (ZORA)[13] and with spin-orbit coupling (ZORA-SO),[14] together with a TZ2P basis of Slater-type orbitals. A fine integration grid was used (Integration 6), as well as a finite nuclear size. These calculations were performed with the ADF program.[15,16] Employing the B3LYP-optimised geometries

(BA conformations), *J* values of –490 Hz and –658 Hz were obtained for **A12** and **N12**, respectively, at the ZORA level (–480 Hz and –647 Hz , respectively, at ZORA-SO). While the observed values of $|J|$ = 715.6 Hz (**A12**) and 834.0 Hz (**N12**) are underestimated in absolute terms, the signs (which stem from the negative sign of the ^{125}Te gyromagnetic ratio) should be reliable and were used to assign a negative sign to the observed $J(^{77}Se,^{125}Te)$ values.

Table S1: Selected optimised parameters WBIs, and relative energies (kJ/mol) of mono-phenylchalcogen acenaphthene derivatives **A1-A6** (B3LYP level), including structural data from X-ray crystallography, where available)

Compound	**A1 XRD-A**	**A1-A**	**A1-B**	**A2 XRD-B**	**A2-A**	**A2-B**
X, EPh	Br, S	Br, S	Br, S	Br, Se	Br, Se	Br, Se
Energy(rel)* / kJ/mol	-	0.00	0.32	-	6.05	0.00
X(1)···E(1) / Å	3.297(3)	3.3538	3.1888	3.1588(16)	3.4301	3.2231
WBI X(1)···E(1)	-	0.0060	0.0254	-	0.0079	0.0413
X(1)-C(1) / Å	1.926(7)	1.9255	1.9293	1.905(5)	1.9250	1.9295
E(1)-C(9) / Å	1.777(7)	1.7963	1.8093	1.943(5)	1.9456	1.9631
C(10)-C(9)-E(1)-C(13); θ1 / °	-89.44(1)	-81.399	170.□85	159.92(1)	-80.291	179.726
C(9)-E(1)-C(13)-C(14); γ1 / °	170.06(1)	168.816	102.258	95.94(1)	-2□.195	92.910

Compound	**A3 XRD-B**	**A3-A**	**A3-B**	**A4 XRD-A**	**A4-A**	**A4-C**
X, EPh	Br, Te	Br, Te	Br, Te	I, S	I, S	I, S
En□rgy(rel)* / kJ/mol	-	15.11	0.00	-	0.00	1.□4
X(1)···E(1) / Å	3.2503(14)	3.5625	3.3189	3.428(4)	3.4799	3.3620
WBI X(1)···E(1)	-	0.0111	0.0620	-	0.0115	0.0290
X(1)-C(1) / Å	1.919(10)	1.9255	1.9309	2.129(13)	2.1514	2.1512
E(1)-C(9) / Å	2.148(10)	2.1499	2.1661	1.773(14)	1.7947	1.8074
C(10)-C(9)-E(1)-C(13); θ1 / °	162.39(1)	-77.267	175.394	90.15(1)	-85.000	150.547
C(9)-E(1)-C(13)-C(14); γ1 / °	100.03(1)	153.061	96.172	151.86(1)	174.347	116.508

Compound	**A5 XRD-B**	**A5-A**	**A5-B**	**A6 XRD-B**	**A6-A**	**A6-B**
X, EPh	I, Se	I, Se	I, Se	I, Te	I, Te	I, Te
Ener□y(rel)* / kJ/mol	-	4.82	0.00	-	15.13	0.00
X(1)···E(1) / Å	3.3291(11)	3.5653	3.3842	3.3721(17)	3.7054	3.4553
WBI X(1)···E(1)	-	0.0141	0.0504	-	0.0181	0.0841
X(1)-C(1) / Å	2.110(7)	2.1517	2.1497	2.058(16)	2.1517	2.1497
E(1)-C(9) / Å	1.930(7)	1.9435	1.9622	2.176(17)	2.1474	2.1693
C(10)-C(9)-E(1)-C(13); θ1 / °	-165.87(1)	-80.612	161.047	-161.42(1)	-84.399	179.978
C(9)-E(1)-C(13)-C(14); γ1 / °	-92.60(1)	163.542	-80.713	-101.61(1)	160.161	92.576

[a] Distances in Å, angles in degrees, relative energies in kJ/mol.

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Table S2 Selected optimised parameters WBIs, and relative energies (kJ/mol) of di-phenylchalcogen acenaphthene derivatives **A7-A12** (B3LYP level), including structural data from X-ray crystallography, where available)

Compound	**A7 XRD-AAt**	**A7-AAt**	**A7-AB**	**A7-CCt**
Eph, E'Ph	S, S	S, S	S, S	S, S
Energy(rel)* / kJ/mol	-	3.21	0.00	3.21
E(1)···E(2) / Å	3.274(4)	3.3227	3.1351	3.0862
WBI E(1)···E(2)	-	0.0065	0.0314	0.0364
E(1)-C(1) / Å	1.812(12)	1.7912	1.8068	1.8060
E(2)-C(9) / Å	1.782(11)	1.7912	1.7952	1.8070
C(10)-C(1)-E(1)-C(13)□ θ1 / °	75.64(1)	82.320	164.523	139.201
C(10)-C(9)-E(2)-C(19); θ2 / °	92.07(1)	82.337	-86.587	144.087
C(1)-E(1)-C(13)-C(14); γ1 / °	-4.51(1)	8.688	-79.244	-57.640
C(9)-E(2)-C(19)-C(20); γ2 / °	30.56(1)	8.635	-9.636	-62.374

Compound	**A8 XRD-AB**	**A8-AAt**	**A8-AB**
Eph, E'Ph	Se, Se	Se, Se	Se, Se
Energy(rel)* / kJ/mol	-	11.00	0.00
E(1)···E(2) / Å	3.1834(10)	3.4720	3.2170
WBI E(1)···E(2)	-	0.0123	0.0660
E(1)-C(1) / Å	1.928(9)	1.9358	1.9382
E(2)-C(9) / Å	1.932(8)	1.9358	1.9614
C(10)-C(1)-E(1)-C(13); θ1 / °	-□7.70(1)	81.607	92.012
C(10)-C(9)-E(2)-C(19); θ2 / °	163.05(1)	81.610	-174.155
C(1)-E(1)-C(13)-C(14); γ1 / °	-148.68(1)	-168.996	-177.769
C(9)-E(2)-C(19)-C(20); γ2 / °	-84.31(1)	-168.992	-97.683

Compound	**A9 XRD-AB**	**A9-AAt**	**A9-AB**
Eph, E'Ph	Te, Te	Te□ Te	Te, Te
Energy(rel)* / kJ/mol	-	22.77	0.00
E(1)···E(2) / Å	3.3674(19)	3.7237	3.4228
WBI E(1)···E(2)	-	0.0234	0.1404
E(1)-C(1) / Å	2.180(17)	2.1320	2.1674
E(2)-C(9) / Å	2.155(17)	2.1346	2.1426
C(10)-C(1)-E(1)-C(13); θ1 / °	166.60(1)	74.708	161.011
C(10)-C(9)-E(2)-C(19); θ2 / °	79.56(1)	75.924	95.269
C(1)-E(1)-C(13)-C(14); γ1 / °	86.37(1)	22.353	103.489
C(9)-E(2)-C(19)-C(20); γ2 / °	-167.34(1)	-149.017	113.643

Compound	**A10 XRD-BA**	**A10-AAt**	**A10-AB**	**A10-BA**
Eph, E'Ph	Se, S	Se, S	Se, S	Se, S
Energy(□el)* / kJ/mol	-	11.53	8.74	0.00
E(1)···E(2) / Å	3.113(4)	3.3946	3.2127	3.1313
WBI E(1)···E(2)	-	0.0107	0.0386	0.0565
E(1)-C(1) / Å	1.953(10)	1.9452	1.9418	1.9600
E(2)-C(9) / Å	1.798(11)	1.7962	1.8076	1.7932
C(10)-C(1)-E(1)-C(13); θ1 / °	156.26(1)	79.□07	85.260	-176.246
C(10)-C(9)-E(2)-C(19); θ2 / °	-100.46(1)	84.009	-168.158	93.960
C(1)-E(1)-C(13)-C(14); γ1 / °	-82.12(1)	-167.224	-166.930	-96.424
C(9)-E(2)-C(19)-C(20); γ2 / °	5.36(1)	5.482	83.269	-1.233

Compound	**A11 XRD-BA**	**A11-AAt**	**A11-BA**	**A11-AC□**
Eph, E'Ph	Te, S	Te, S	Te, S	Te, S
Energy(rel)* / kJ/mol	-	22.70	0.00	22.2534978
E(1)···E(2) / Å	3.1576(15)	3.5077	3.1908	3.3768
WBI E(1)···E(2)	-	0.0149	0.0905	0.0387
E(1)-C(1) / Å	2.138(6)	2.1477	2.1608	2.1438
E(2)-C(9) / Å	1.781(7)	1.7960	1.7945	1.8071
C(10)-C(1)-E(1)-C(13); θ1 / °	166.03(1)	73.351	-179.857	83.607
C(10)-C(9)-E(2)-C(19); θ2 / °	-95.67(1)	88.092	100.995	-154.366
C(1)-E(1)-C(13)-C(14); γ1 / °	-83.57(1)	30.354	91.648	30.520
C(9)-E(2)-C(19)-C(20); γ2 / °	-150.20(1)	176.838	159.248	-114.342

Compound	**A12 XRD-BA**	**A12-AAt**	**A12AB**	**A12-BA**
Eph, E'Ph	Te, Se	Te, Se	Te, Se	Te, Se
Energy(rel)* / kJ/mol	-	23.88	16.22	0.00
E(1)···E(2) / Å	3.2479(19)	3.5863	3.3733	3.2668
WBI E(1)···E(2)	-	0.0176	0.0704	0.1156
E(1)-C(1) / Å	2.152(10)	2.1484	2.1386	2.1638
E(2)-C(9) / Å	1.943(11)	1.9439	1.9638	1.9405
C(10)-C(1)-E(1)-C(13); θ1 / °	-168.14(1)	75.092	81.843	-173.618
C(10)-C(9)-E(2)-C(19); θ2 / °	101.19(1)	85.768	169.922	-98.243
C(1)-E(1)-C(13)-C(14); γ1 / °	83.63(1)	-151.654	-152.943	88.938
C(9)-E(2)-C(19)-C(20); γ2 / °	160.85(1)	176.127	99.097	-149.412

[a] Distances in Å, angles in degrees, relative energies in kJ/mol.

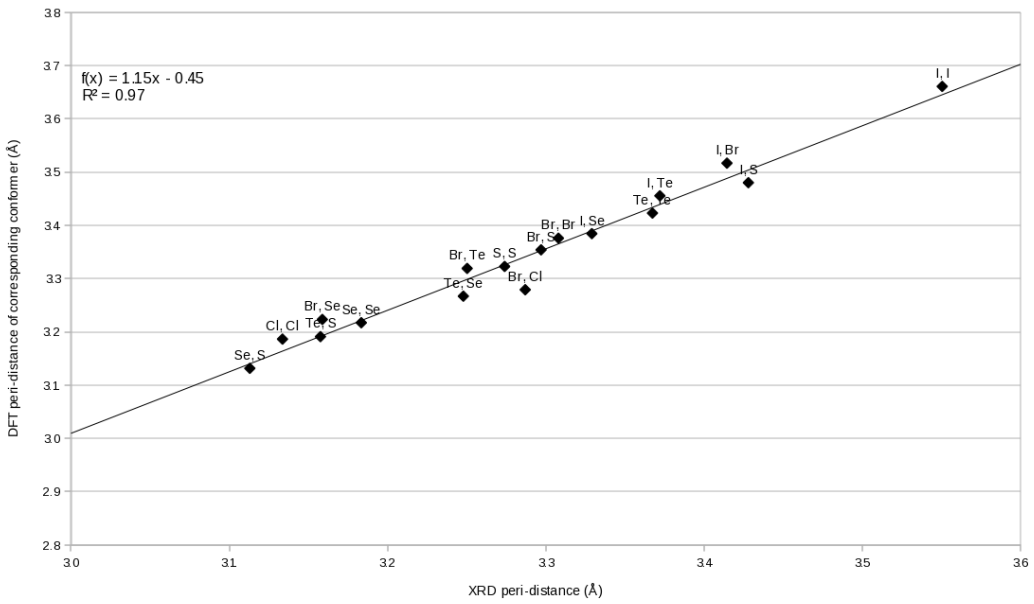

Figure S1: Plot of optimised (B3LYP) vs. observed (X-ray diffraction) *peri*-distances in acenaphthene derivatives.

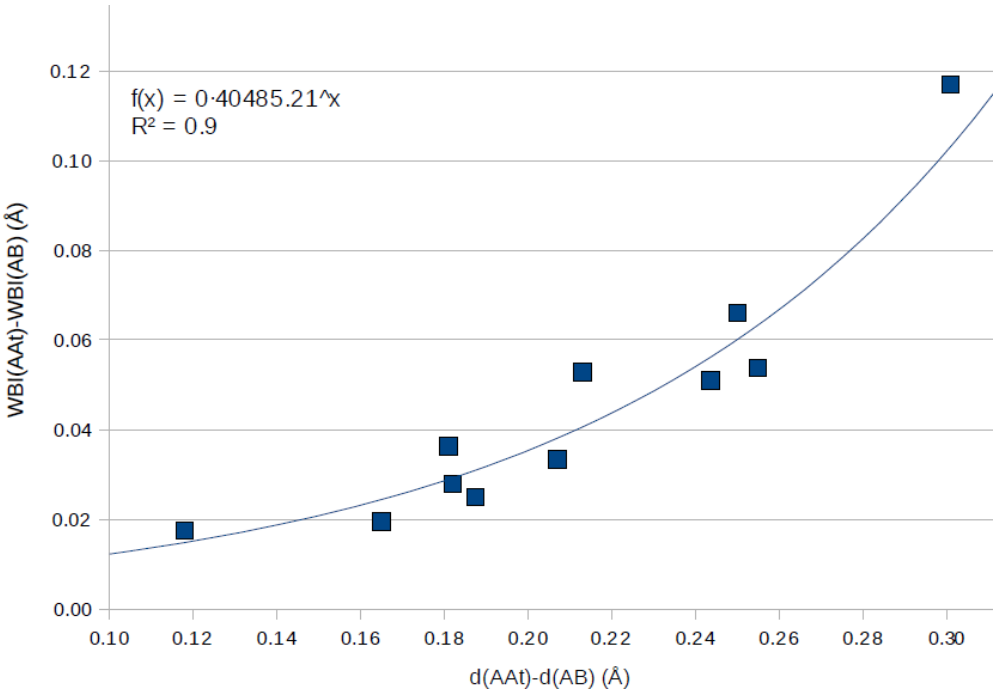

Figure S2: Plot of the increase in the Wiberg bond index on going from AAt to AB conformers vs the concomitant contraction of the peri-distance (in Å, acenapthene series). The more pronounced this bond contraction, the higher the covalent contribution.

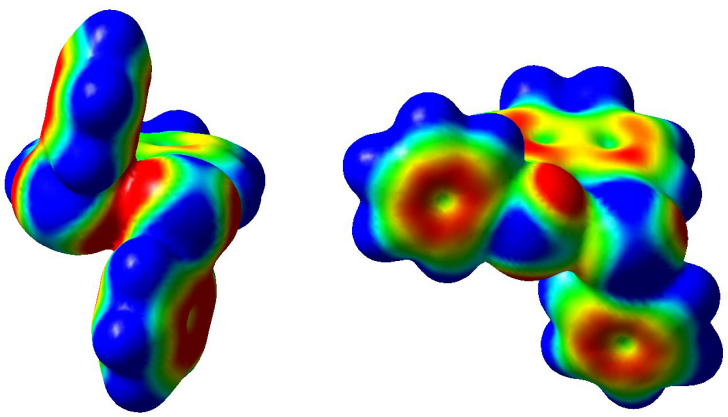

Figure S3: Plot of the electrostatic potential of **A9**-AAt (left) and **A9**-AB (right), mapped onto isodensity surfaces ($\rho = 4 \cdot 10^{-3}$ au); color code: red 50 kJ/mol; green: zero; blue –50 kJ/mol.

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Table S3: Selected optimised parameters, WBIs, and relative energies of naphthalene derivatives **N1-N6** (B3LYP level), including structural data from X-ray crystallography, where available).

Compound	**N1 (Oil)**	**N1-A**	**N1-B**
X, EPh	Br, SPh	Br, SPh	Br, SPh
Energy(rel)* / kJ/mol	-	3.04	0.00
X(1)···E(1)	-	3.2879	3.1314
WBI X(1)···E(1)	-	0.0066	0.0290
X(1)-C(1)	-	1.9280	1.9303
E(1)-C(9)	-	1.8001	1.8109
C(10)-C(9)-E(1)-C(11); θ1 / °	-	76.897	158.707
C(9)-E(1)-C(11)-C(12); γ1 / °	-	18.536	109.227

Compound	**N2 XRD-B**	**N2-A**	**N2-B**	**N3 XRD-B**	**N3-B**
X, EPh	Br, SePh	Br, SePh	Br, SePh	Br, TePh	Br, TePh
Energy(rel)* / kJ/mol	-	9.85	0.00	-	0.00
X(1)···E(1)	3.1136(6)	3.3689	3.1731	3.1909(10)	3.2664
WBI X(1)···E(1)	-	0.0086	0.0454	-	0.0675
X(1)-C(1)	1.919(3)	1.9268	1.9297	1.917(6)	1.9316
E(1)-C(9)	1.948(3)	1.9505	1.9655	2.153(6)	2.1704
C(10)-C(9)-E(1)-C(11); θ1 / °	-159.2(3)	-71.119	159.200	-160.0(6)	162.873
C(9)-E(1)-C(11)-C(12); γ1 / °	-96.0(3)	-25.459	105.765	-99.4(5)	100.731

Compound	**N4 XRD-A**	**N4-C**	**N5 XRD-B**	**N5-C**
X, EPh	I, Sph	I, SPh	I, SePh	I, SePh
Energy(rel)* / kJ/mol	-	0.00	-	0.00
X(1)···E(1)	3.338(11)	3.2973	3.2524(8)	3.3355
WBI X(1)···E(1)	-	0.0354	-	0.0566
X(1)-C(1)	2.118(11)	2.1538	2.122(4)	1.9641
E(1)-C(9)	1.765(11)	1.8096	1.958(4)	2.1519
C(10)-C(9)-E(1)-C(11); θ1 / °	83.6(10)	148.508	-157.0(4)	151.829
C(9)-E(1)-C(11)-C(12); γ1 / °	1.4(10)	116.268	-89.4(4)	-76.273

Compound	**N6 XRD-B**	**N6-B**
X, EPh	I, TePh	I, TePh
Energy(rel)* / kJ/mol	-	0.00
X(1)···E(1)	3.3146(6)	3.4253
WBI X(1)···E(1)	-	0.0867
X(1)-C(1)	2.108(6)	2.1518
E(1)-C(9)	2.151(6)	2.1687
C(10)-C(9)-E(1)-C(11); θ1 / °	-158.1(6)	152.606
C(9)-E(1)-C(11)-C(12); γ1 / °	-86.5(5)	-78.210

[a] Distances in Å, angles in degrees, relative energies in kJ/mol.

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Table S4: Selected optimised parameters, WBIs, and relative energies of naphthalene derivatives **N7-N12** (B3LYP level), including structural data from X-ray crystallography, where available).

Compound	**N7 XRD-AB**	**N7-AAt**	**N7-AB**	**N7-CCt**
Eph, E'Ph	SPh, SPh	SPh, SPh	SPh, SPh	SPh, SPh
Energy(rel)* / kJ/mol	-	5.93	0.00	0.69
E(1)···E(2)	3.0036(13)	3.2533	3.0498	3.0071
WBI E(1)···E(2)	-	0.0099	0.0396	0.0446
E(1)-C(1)	1.794(3)	1.8000	1.8099	1.8092
E(2)-C(9)	1.783(4)	1.8000	1.7977	1.8095
C(10)-C(1)-E(1)-C(11); θ1 / °	159.8(2)	76.041	-179.798	138.628
C(10)-C(9)-E(2)-C(17); θ2 / °	95.0(3)	76.040	81.680	138.761
C(1)-E(1)-C(11)-C(12); γ1 / °	-73.62(1)	13.345	92.056	-60.353
C(9)-E(2)-C(17)-C(18); γ2 / °	-24.10(1)	13.351	12.741	124.984

Compound	**N8 XRD-AB**	**N8-AAt**	**N8-AB**	**N8-CCt**
Eph, E'Ph	SePh, SePh	SePh, SePh	SePh, SePh	SePh, SePh
Energy(rel)* / kJ/mol	-	15.18	1.52	0.00
E(1)···E(2)	3.1332(9)	3.4140	3.1522	3.1171
WBI E(1)···E(2)	-	0.0140	0.0□81	0.0821
E(1)-C(1)	1.922(7)	1.9494	1.9660	1.9594
E(2)-C(9)	1.930(7)	1.9494	1.9449	1.9576
C(10)-C(1)-E(1)-C(11); θ1 / °	155.35(1)	65.404	159.999	136.310
C(10)-C(9)-E(2)-C(17); θ2 / °	-109.990	65.402	-107.051	131.088
C(1)-E(1)-C(11)-C(12); γ1 / °	-83.57(1)	35.143	-80.441	-63.715
C(9)-E(2)-C(17)-C(18); γ2 / °	10.88(1)	35.068	-155.136	-59.079

Compound	**N9 XRD-CCt**	**N9-CCc**	**N9-CCt**
Eph, E'Ph	TePh, TePh	TePh, TePh	TePh, TePh
Energy(rel)* / kJ/mol	-	3.25	0.00
E(1)···E(2)	3.287(1)	3.3907	3.3408
WBI E(1)···□(2)	-	0.1407	0.1497
E(1)-C(1)	2.14(1)	2.1720	2.1574
E(2)-C(9)	2.14(2)	2.1449	2.1575
C(10)-C(1)-E(1)-C(11); θ1 / °	-124.79(1)	-118.985	-129.438
C(10)-C(9)-E(2)-C(17); θ2 / °	-132.46(1)	152.358	-129.469
C(1)-E(1)-C(11)-C(12); γ1 / °	100.88(1)	-127.785	□117.102
C(9)-E(2)-C(17)-C(18); γ2 / °	57.21(1)	-77.057	65.924

Compound	**N10 XRD-BA**	**N10-AAt**	**N10-BA**
Eph, E'Ph	SePh, SPh	SePh, SPh	SePh, SPh
Energy(rel)* / kJ/mol	-	15.11	0.00
E(1)···E(2)	3.063(2)	3.3326	3.0567
WBI E(1)···E(2)	-	0.0118	0.0676
E(1)-C(1□	1.907(9)	1.9517	1.9642
E(2)-C(9)	1.813(8)	1.7985	1.7959
C(10)-C(1)-E(1)-C(11); θ1 / °	-156.4(7)	66.787	168.716
C(10)-C(9)-E(2)-C(17); θ2 / °	111.3(7)	69.547	91.079
C(1)-E(1)-C(11)-C(12); γ1 / °	-98.0(8)	-145.834	100.267
C(9)-E(2)-C(17)-C(18); γ2 / °	-9.3(9)	-157.852	174.732

Compound	N11 XRD-BA	N11-BA	N12 XRD-BA	N12-BA
Eph, E'Ph	TePh, SPh	TePh, SPh	TePh, SePh	TePh, SePh
Energy(rel)* / kJ/mol	-	0.00	-	0.00
E(1)···E(2)	3.0684(13)	3.1202	3.1919(11)	3.2035
WBI E(1)···E(2)	-	0.1028	-	0.1295
E(1)-C(1)	2.141(5)	2.1649	2.137(11)	2.1681
E(2)-C(9)	1.770(5)	1.7954	1.920(12)	1.9444
C(10)-C(1)-E(1)-C(11); θ1 / °	-160.5(11)	169.653	-165.3(5)	164.033
C(10)-C(9)-E(2)-C(17); θ2 / °	-83.1(11)	94.898	-84.0(5)	95.389
C(1)-E(1)-C(11)-C(12); γ1 / °	108.0(11)	97.895	-89.5(4)	-83.532
C(9)-E(2)-C(17)-C(18); γ2 / °	-12.3(9)	-10.877	-12.5(□)	-32.494

[a] Distances in Å, angles in degrees, relative energies in kJ/mol.

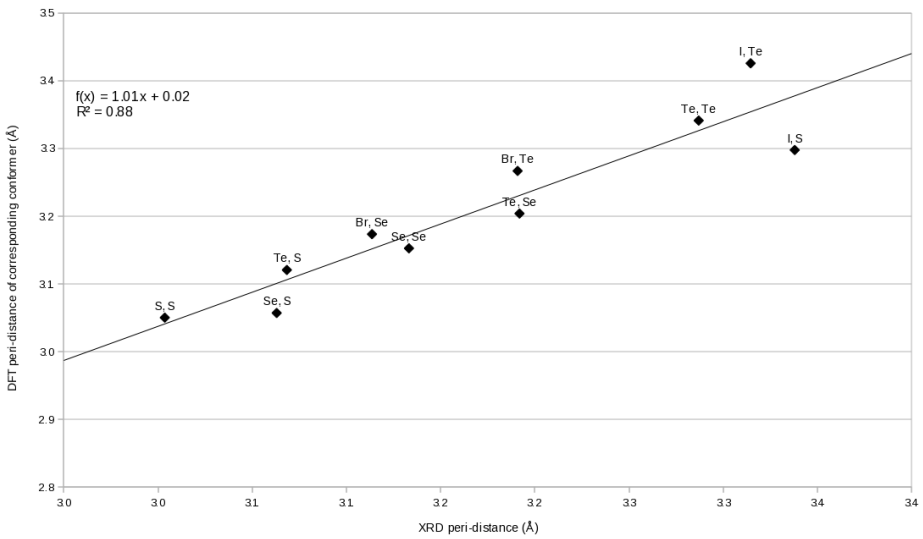

Figure S4: Plot of optimised (B3LYP) vs. observed (X-ray diffraction) *peri*-distances in naphthalene derivatives.

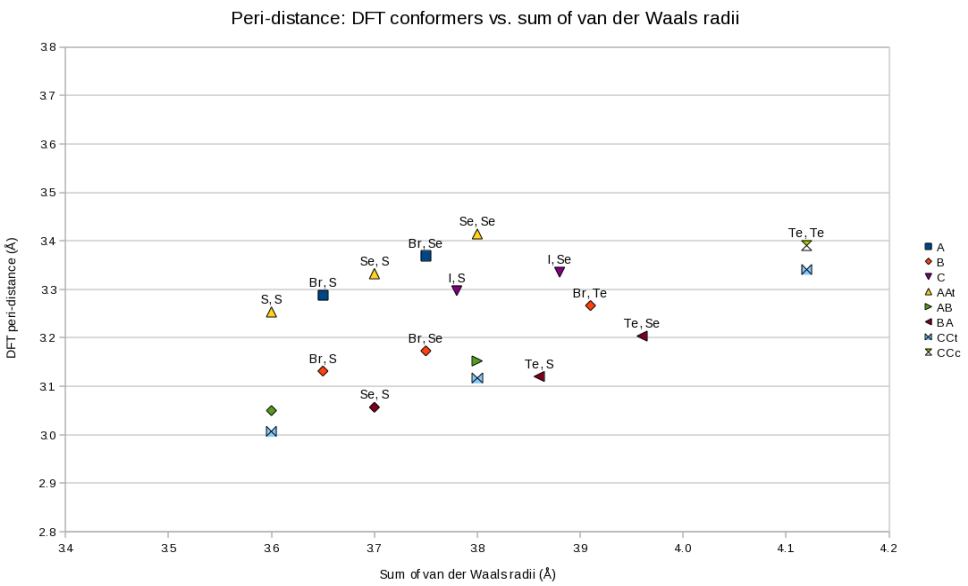

Figure S5: Plot of B3LYP optimised *peri*-distances vs. sum of van der Waals radii in the naphthalene series. Note that no A or AA minima could be located for any of the I and Te compounds - the optimisations went directly to B, C, AB or CC conformers.

3. Crystal structure analyses

X-ray crystal structures for **A1-A7**, **A9**, **A10**, **A12**, **A14** and **A15** were determined at -148(1) °C on the St Andrews Robotic Diffractometer[17] a Rigaku ACTOR-SM, Saturn 724 CCD area detector with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data for compound **A8** were collected at -180(1) °C by using a Rigaku MM007 High brilliance RA generator (Mo Kα radiation, confocal optic) and Mercury CCD system. At least a full hemisphere of data was collected using ω scans. Data for compound **A11** were collected at -180(1) °C by using a Rigaku MM007 High brilliance RA generator (Mo Kα radiation, confocal optic) and Saturn CCD system. At least a full hemisphere of data was collected using ω scans. Data for compound **A16** were collected at -148(1) °C on a Rigaku SCXmini CCD area detector with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). All data had intensities corrected for Lorentz, polarisation and absorption. The data for the complexes was collected and processed using CrystalClear (Rigaku).[18] The structures were solved by Patterson or direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model. All calculations were performed using the CrystalStructure[19] and SHELXL-97.[20] These X-ray data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk CCDC Nos: A1-A12 816080-81691, A14-A16 816091-816094.

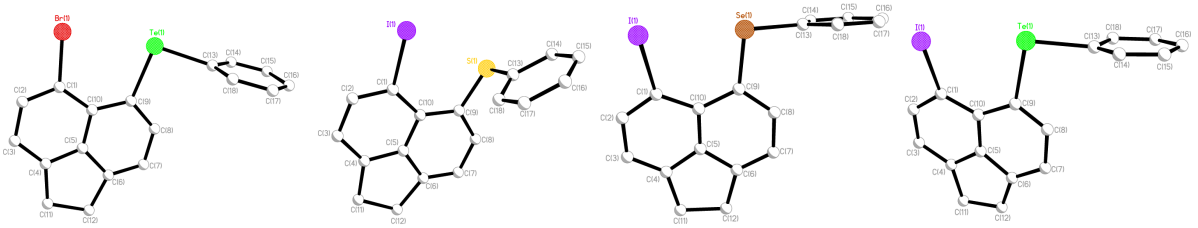

Fig. S6 Molecular structures of **A3-A6** (H atoms omitted for clarity).

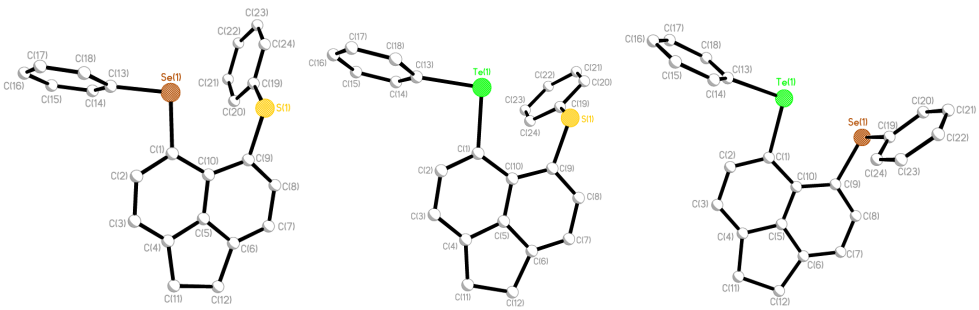

Fig. S7 Molecular structures of **A10-A12** (H atoms omitted for clarity).

Electronic Supplementary Material (ESI) for Dalton Transactions

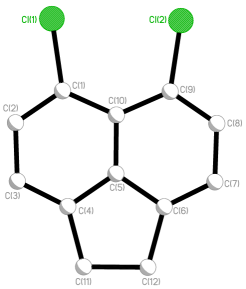

Fig. S8 Molecular structures of **A14** and **A16** (H atoms omitted for clarity).

Table S5 Selected interatomic distances [Å] and angles [°] for Acenap[X][EPh] compounds **A1-A6** [values in parentheses are for independent molecules]

Compound	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
X, EPh	Br,SPh	Br,SePh	Br,TePh	I,SPh	I,SePh	I,TePh
Peri-region-distances						
X(1)···E(1)	**3.297(3)**	**3.1588(16)**	**3.2503(14)**	**3.428(4)**	**3.3291(11)**	**3.3721(17) [3.3774(17)]**
Σr_{vdW} - X···E [a]	0.353	0.5912	0.6597	0.352	0.5509	0.6679 [0.6626]
% Σr_{vdW} [a]	90	84	83	91	86	83 [84]
X(1)-C(1)	1.926(7)	1.905(5)	1.919(10)	2.129(13)	2.110(7)	2.058(16) [2.067(16)]
E(1)-C(9)	1.777(7)	1.943(5)	2.148(10)	1.773(14)	1.930(7)	2.176(17) [2.151(18)]
Acenaphthene bond lengths						
C(1)-C(2)	1.383(10)	1.361(8)	1.369(14)	1.388(17)	1.360(10)	1.37(2) [1.40(2)]
C(2)-C(3)	1.387(10)	1.429(8)	1.389(16)	1.42(2)	1.407(11)	1.37(3) [1.37(3)]
C(3)-C(4)	1.355(11)	1.362(8)	1.376(16)	1.399(18)	1.368(11)	1.39(3) [1.45(2)]
C(4)-C(5)	1.411(9)	1.416(8)	1.415(14)	1.423(17)	1.401(9)	1.41(2) [1.39(2)]
C(5)-C(10)	1.421(9)	1.423(7)	1.434(14)	1.438(17)	1.417(9)	1.43(2) [1.42(2)]
C(5)-C(6)	1.434(10)	1.405(8)	1.420(15)	1.433(17)	1.428(9)	1.42(2) [1.40(2)]
C(6)-C(7)	1.358(10)	1.367(8)	1.364(15)	1.344(19)	1.361(10)	1.40(2) [1.37(2)]
C(7)-C(8)	1.385(10)	1.405(8)	1.409(14	1.422(20)	1.390(10)	1.44(2) [1.39(2)]
C(8)-C(9)	1.396(11)	1.377(8)	1.396(14)	1.378(18)	1.391(10)	1.34(2) [1.38(2)]
C(9)-C(10)	1.437(9)	1.438(8)	1.434(13)	1.444(17)	1.444(9)	1.44(2) [1.47(2)]
C(10)-C(1)	1.442(10)	1.431(8)	1.411(13)	1.444(17)	1.433(10)	1.44(2) [1.43(2)]
C(4)-C(11)	1.536(10)	1.514(8)	1.505(15)	1.53(2)	1.513(10)	1.50(3) [1.50(2)]
C(11)-C(12)	1.536(11)	1.562(9)	1.538(17)	1.563(19)	1.545(11)	1.48(3) [1.53(3)]
C(12)-C(6)	1.535(9)	1.510(8)	1.488(17)	1.529(17)	1.510(10)	1.45(2) [1.52(2)]
Peri-region bond angles						
X(1)-C(1)-C(10)	122.3(5)	121.8(4)	121.6(7)	125.3(9)	123.8(5)	124.6(12) [123.7(11)]
C(1)-C(10)-C(9)	132.5(6)	131.4(5)	131.7(9)	132.6(12)	131.4(6)	130.5(15) [130.3(14)]
E(1)-C(9)-C(10)	125.5(6)	121.4(4)	123.5(7)	124.4(10)	122.3(5)	123.2(12) [124.4(10)]
Σ of bay angles	**380.3(11)**	**74.6(9)**	**376.8(15)**	**382.3(20)**	**377.5(11)**	**378.3(32) [378.4(28)]**
Splay angle [b]	20.3	14.6	16.8	22.3	17.5	18.3 [18.4]
C(4)-C(5)-C(6)	112.1(6)	111.4(5)	110.8(9)	111.9(10)	111.1(6)	110.4(15) [109.8(14)]
X(1)-E(1)-C(13)	87.4(1)	172.83(1)	169.0(1)	86.46(1)	177.69(1)	171.31(1) [171.48(1)]
Out-of-plane displacement						
X(1)	0.149(1)	0.287(1)	0.307(1)	-0.201(1)	-0.439(1)	-0.425(1) [0.333(1)]
E(1)	-0.121(1)	-0.359(1)	-0.298(1)	0.092(1)	0.364(1)	0.334(1) [-0.395(1)]
Central naphthalene ring torsion angles						
C:(6)-(5)-(10)-(1)	178.76(1)	175.27(1)	178.17(1)	179.40(1)	174.34(1)	175.29(1) [175.81(1)]
C:(4)-(5)-(10)-(9)	176.84(1)	177.24(1)	176.39(1)	177.51(1)	177.91(1)	-177.33(1) [178.08(1)]

[a] van der Waals radii used for calculations: r_{vdW}(S) 1.80Å, r_{vdW}(Se) 1.90Å, r_{vdW}(Te) 2.06Å, r_{vdW}(Br) 1.85 Å, r_{vdW}(I) 1.98 Å;[21] [b] Splay angle: Σ of the three bay region angles – 360.

Table S6 Selected interatomic distances [Å] and angles [°] for Acenap[EPh][E`Ph] compounds **A7-A12** [values in parentheses are for independent molecules]

Compound	**A7**	**A8**	**A9**	**A10**	**A11**	**A12**
EPh, E`Ph	SPh,SPh	SePh,SePh	TePh,TePh	SePh,SPh	TePh,SPh	TePh,SePh
Peri-region-distances						
E(1)···E(2)	**3.274(4) [3.289(4)]**	**3.1834(10)**	**3.3674(19)**	**3.113(4)**	**3.1576(15)**	**3.2479(19)**
Σr_{vdW} - E···E` [a]	0.326 [0.311]	0.6166	0.7526	0.5870	0.7024	0.7121
% Σr_{vdW} [a]	91 [91]	84	82	84	82	82
E(1)-C(1)	1.812(12) [1.776(11)]	1.928(9)	2.180(17)	1.953(10)	2.138(6)	2.152(10)
E(2)-C(9)	1.782(11) [1.804(12)]	1.932(8)	2.155(17)	1.798(11)	1.781(7)	1.943(11)
Acenaphthene bond lengths						
C(1)-C(2)	1.393(16) [1.402(15)]	1.372(12)	1.367(19)	1.393(15)	1.363(8)	1.397(14)
C(2)-C(3)	1.411(17) [1.405(17)]	1.411(12)	1.43(3)	1.424(14)	1.417(9)	1.404(15)
C(3)-C(4)	1.313(18) [1.380(17)]	1.371(12)	1.36(2)	1.350(16)	1.371(9)	1.351(16)
C(4)-C(5)	1.432(16) [1.406(15)]	1.420(12)	1.410(17)	1.404(15)	1.420(8)	1.422(16)
C(5)-C(10)	1.437(17) [1.431(15)]	1.423(12)	1.43(2)	1.450(14)	1.427(8)	1.428(14)
C(5)-C(6)	1.431(16) [1.403(16)]	1.425(12)	1.443(20)	1.423(16)	1.415(8)	1.409(16)
C(6)-C(7)	1.372(18) [1.383(17)]	1.364(12)	1.318(19)	1.367(16)	1.354(9)	1.371(17)
C(7)-C(8)	1.415(18) [1.458(18)]	1.412(12)	1.42(3)	1.406(15)	1.416(9)	1.405(17)
C(8)-C(9)	1.411(17) [1.365(17)]	1.372(12)	1.38(2)	1.361(17)	1.371(9)	1.395(16)
C(9)-C(10)	1.400(16) [1.472(16)]	1.444(12)	1.430(18)	1.451(15)	1.426(9)	1.424(15)
C(10)-C(1)	1.442(17) [1.458(15)]	1.425(12)	1.43(2)	1.434(16)	1.446(8)	1.447(15)
C(4)-C(11)	1.548(16) [1.516(17)]	1.520(12)	1.50(2)	1.522(15)	1.499(9)	1.538(15)
C(11)-C(12)	1.536(17) [1.572(16)]	1.570(12)	1.545(18)	1.568(17)	1.557(9)	1.547(17)
C(12)-C(6)	1.529(16) [1.470(16)]	1.509(12)	1.55(2)	1.525(15)	1.505(9)	1.506(15)
Peri-region bond angles						
E(1)-C(1)-C(10)	124.3(9) [126.3(8)]	123.4(6)	123.9(10)	120.7(7)	121.5(4)	123.1(7)
C(1)-C(10)-C(9)	131.8(11) [129.2(10)]	131.1(8)	131.7(16)	131.3(9)	131.2(5)	130.6(9)
E(2)-C(9)-C(10)	125.1(9) [124.3(9)]	122.0(6)	122.8(12)	120.7(8)	122.3(5)	123.4(8)
Σ of bay angles	**381.2(24) [379.8(22)]**	**376.5(13)**	**378.4(24)**	**372.7(16)**	**375.0(10)**	**377.1(16)**
Splay angle [b]	21.2 (19.8)	16.5	18.4	12.7	15.0	17.1
C(4)-C(5)-C(6)	111.4(10) [111.8(10)]	110.5(7)	113.3(14)	113.4(9)	111.1(5)	112.2(9)
E(2)-E(1)-C(13)	75.14(1) [73.91(1)]	171.28(1)	174.0(4)	167.95(1)	167.86(1)	172.82(1)
E(1)-E(2)-C(19)	85.76(1) [84.55(1)]	91.48(1)	94.1(4)	86.58(1)	91.70(1)	94.13(1)
Out-of-plane displacement						
E(1)	-0.132(1) [0.194(1)]	0.176(1)	0.310(1)	0.274(1)	0.176(1)	-0.403(1)
E(2)	0.161(1) [-0.128(1)]	-0.193(1)	-0.404(1)	-0.416(1)	-0.063(1)	0.032(1)
Central naphthalene ring torsion angles						
C:(6)-(5)-(10)-(1)	-176.50(1) [177.94(1)]	178.40(1)	176.19(1)	175.14(1)	179.22(1)	179.41(1)
C:(4)-(5)-(10)-(9)	178.82(1) [-176.17(1)]	179.23(1)	179.03(1)	174.65(1)	176.81(1)	176.12(1)

[a] van der Waals radii used for calculations: r_{vdW}(S) 1.80Å, r_{vdW}(Se) 1.90Å, r_{vdW}(Te) 2.06Å;[21] [b] Splay angle: Σ of the three bay region angles – 360.

Table S7 Selected interatomic distances [Å] and angles [°] for Acenap[X][X`] (X/X` = I/I, I/Br, ClCl) compounds **A14-A16** [compared to known structures Acenap[X][X`] (X/X` = Br/Br, Br/Cl) **A13** and **A17**]

Compound	**A14**	**A15**	**A16**	**A13**[22]	**A17**[23]
X X`	I I	I Br	Cl Cl	Br Br	Br Cl

Peri-region-distances					
X(1)···X(2)	**3.5505(12)**	**3.4145(18)**	**3.1336(11)**	**3.308(1)**	**3.287(1)**
Σr_{vdW} - X···X` [a]	0.4095	0.4155	0.3664	0.392	0.313
% Σr_{vdW} [a]	90	89	90	89	91
X(1)-C(1)	2.108(6)	2.041(10)	1.750(2)	1.905(1)	1.893(1)
X(2)-C(9)	2.107(6)	2.032(9)	1.754(2)	1.906(1)	1.938(1)
Acenaphthene bond lengths					
C(1)-C(2)	1.371(10)	1.340(19)	1.376(4)	1.381(1)	1.384(1)
C(2)-C(3)	1.389(10)	1.413(18)	1.411(3)	1.407(1)	1.450(1)
C(3)-C(4)	1.386(11)	1.352(17)	1.367(4)	1.364(1)	1.370(1)
C(4)-C(5)	1.405(10)	1.426(14)	1.412(4)	1.415(1)	1.447(1)
C(5)-C(10)	1.427(8)	1.389(12)	1.418(3)	1.425(1)	1.508(1)
C(5)-C(6)	1.419(10)	1.398(16)	1.417(3)	1.415(1)	1.462(1)
C(6)-C(7)	1.359(11)	1.402(16)	1.364(4)	1.366(1)	1.415(1)
C(7)-C(8)	1. 411(10)	1.438(14)	1.408(3)	1.411(1)	1.420(1)
C(8)-C(9)	1.397(11)	1.373(16)	1.370(3)	1.377(1)	1.419(1)
C(9)-C(10)	1.420(10)	1.414(15)	1.424(4)	1.432(1)	1.420(1)
C(10)-C(1)	1.443(10)	1.492(15)	1.430(3)	1.427(1)	1.446(1)
C(4)-C(11)	1.508(10)	1.562(16)	1.507(3)	1.511(1)	1.435(1)
C(11)-C(12)	1.559(12)	1.530(19)	1.554(4)	1.549(1)	1.563(1)
C(12)-C(6)	1.503(10)	1.500(14)	1.512(4)	1.509(1)	1.421(1)
Peri-region bond angles					
X(1)-C(1)-C(10)	125.6(5)	124.4(7)	122.5(2)	123.94(1)	119.77(1)
C(1)-C(10)-C(9)	132.7(6)	131.2(8)	132.1(2)	132.65(1)	138.25(1)
X(2)-C(9)-C(10)	126.9(5)	125.9(7)	122.51(17)	124.20(1)	120.10(1)
Σ of bay angles	**385.2(13)**	**381.5(18)**	**377.1(5)**	**380.79(1)**	**378.12(3)**
Splay angle [b]	25.2	21.5	17.1	20.8	18.1
C(4)-C(5)-C(6)	110.2(6)	110.1(8)	111.3(2)	110.89(1)	109.40(1)
Out-of-plane displacement					
X(1)	0.098(1)	-0.067(1)	-0.067(1)	-0.027(1)	-0.117(1)
X(2)	-0.146(1)	0.098(1)	0.114(1)	0.074(1)	0.053(1)
Central naphthalene ring torsion angles					
C:(6)-(5)-(10)-(1)	179.13(1)	179.12(1)	-178.19(1)	-179.29(1)	179.35(1)
C:(4)-(5)-(10)-(9)	179.25(1)	-179.66(1)	-179.12(1)	-178.71(1)	-172.53(1)

[a] van der Waals radii used for calculations: r_{vdW}(Cl) 1.75Å, r_{vdW}(Br) 1.85Å, r_{vdW}(I) 1.98Å;[21] [b] Splay angle: Σ of the three bay region angles – 360.

Table S8: Crystallographic data for compounds **A1-A4**.

	A1	**A2**	**A3**	**A4**
Empirical Formula	$C_{18}H_{13}BrS$	$C_{18}H_{13}BrSe$	$C_{18}H_{13}BrTe$	$C_{18}H_{13}IS$
Formula Weight	341.26	388.16	436.80	388.27
Temperature (°C)	-148(1)	-148(1)	-148(1)	-148(1)
Crystal Colour, Habit	colourless, platelet	colourless, prism	yellow, platelet	colourless, platelet
Crystal Dimensions (mm^3)	0.15 X 0.09 X 0.02	0.20 X 0.20 X 0.20	0.12 X 0.03 X 0.03	0.15 X 0.15 X 0.02
Crystal System	triclinic	triclinic	orthorhombic	monoclinic
Lattice Parameters	a = 7.400(5) Å	a = 5.645(3) Å	a = 5.8486(17) Å	a = 5.109(4)Å
	b = 9.253(6) Å	b = 11.096(5) Å	b = 21.983(7) Å	b = 15.850(12)Å
	c = 10.744(6) Å	c = 11.508(5) Å	c = 22.637(6) Å	c = 17.810(14) Å
	α = 79.67(4)º	α = 97.849(11)º	-	-
	β = 77.28(4)º	β = 95.044(11)º	-	β = 93.721(19)º
	γ = 87.54(5)º	γ = 97.960(13)º	-	-
Volume ($Å^3$)	V = 705.9(8)	V = 703.0(6)	V = 2910.4(14)	V = 1439.0(19)
Space Group	P-1	P-1	Pbca	$P2_1/c$

Z value	2	2	8	4
Dcalc (g/cm^3)	1.605	1.834	1.994	1.792
F000	344	380	1664	760
μ(MoKα) (cm^{-1})	30.531	55.071	47.845	23.571
No. of Reflections Measured	5704	6071	21021	11043
Rint	0.0574	0.0298	0.0744	0.1431
Min and Max Transmissions	0.464 - 0.941	0.220 - 0.332	0.525 - 0.866	0.192 - 0.954
Independ. Reflection (No. Variables)	2790(181)	3040(181)	2908(181)	3262(181)
Reflection/Parameter Ratio	15.41	16.80	16.07	18.02
Residuals: R_1 (I>2.00σ(I))	0.0716	0.0456	0.0703	0.1043
Residuals: R (All reflect□ons)	0.0903	0.0579	0.1047	0.1361
Residuals: wR_2 (All reflections)	0.2237	0.1876	0.2862	0.3414
Goodness of Fit Indicator	1.181	1.197	1.284	1.141
Flack Parameter	-	-	-	-
Maximum peak in Final Diff. Map	0.58 e-/Å^3	1.46 e-/Å^3	2.42 e-/Å^3	1.88 e-/Å^3
Minimum peak in Final Diff. Map	-0.82 e-/Å^3	-1.53 e-/Å^3	-3.79 e-/Å^3	-3.17 e-/Å^3

Table S9: Crystallographic data for compounds **A5-A6**.

	A5	**A6**	**A7**	**A8**
Empirical Formula	$C_{18}H_{13}ISe$	$C_{18}H_{13}ITe$	$C_{24}H_{18}S_2$	$C_{24}H_{18}Se_2$
Formula Weight	435.17	483.81	370.53	464.33
Temperature (°C)	-148(1)	-148(1)	-148(1)	-180(1)
Crystal Colour, Habit	colourless, prism	yellow, plate	colourless, platelet	colourless, platelet
Crystal Dimensions (mm^3)	0.09 X 0.09 X 0.03	0.27 X 0.03 X 0.02	0.18 X 0.09 X 0.03	0.20 X 0.10 X 0.01
Crystal System	monoclinic	monoclinic	monoclinic	orthorhombic
Lattice Parameters	a = 7.3312(19) Å	a = 5.9391(18) Å	a = 11.794(6) Å	a = 22.1470(15) Å
	b = 10.845(3) Å	b = 22.301(6) Å	b = 10.806(6) Å	b = 5.221(4) Å
	c = 18.220(5) Å	c = 22.556(6) Å	c = 28.856(17) Å	c = 15.829(6) Å
	-	-	-	-
	β = 95.673(8)º	β = 90.069(9)º	β = 93.435(15)º	-
	-	-	-	-
Volume (Å^3)	V = 1441.5(6)	V = 2987.5(15)	V = 3671(4)	V = 1830.3(15)
Space Group	$P2_1/c$	$P2_1/c$	Cc	$Pca2_1$
Z value	4	8	8	4
Dcalc (g/cm^3)	2.005	2.151	1.341	1.685
F000	832	1808	1552	920
μ(MoKα) (cm^{-1})	47.340	40.460	2.943	40.454
No. of Reflections Measured	11619	25496	13181	10530
Rint	0.0665	0.0779	0.1058	0.0591
Min and Max Transmissions	0.518 - 0.868	0.509 - 0.922	0.364 - 0.991	0.656 - 0.960
Independ. Reflection (No. Vari□bles)	2926(181)	6960(361)	6408(469)	3200(235)
Reflection/Parameter Ratio	16.17	19.28	13.66	13.62
Residuals: R_1 (I>2.00σ(I))	0.0511	0.0953	0.1115	0.0406
Residuals: R (All reflections)	0.0694	0.1276	0.1540	0.0943
Residuals: wR_2 (All reflections)	0.1582	0.3271	0.3075	0.1333
Goodness of Fit Indicator	1.264	1.260	1.063	0.765
Flack Parameter	-	-	-	0.011(18)
Maximum peak in Final Diff. Map	1.70 e-/Å^3	2.79 e-/Å^3	0.80 e-/Å^3	0.59 e-/Å^3
Minimum peak in Final Diff. Map	-2.00 e-/Å^3	-3.55 e-/Å^3	-0.74 e-/Å^3	-0.67 e-/Å^3

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Table S10: Crystallographic data for compounds **A9-A12**.

	A9	**A10**	**A11**	**A12**
Empirical Formula	$C_{24}H_{18}Te_2$	$C_{24}H_{18}SSe$	$C_{24}H_{18}STe$	$C_{24}H_{18}SeTe$
Formula Weight	561.61	417.43	466.07	512.97

Temperature (°C)	-148(1)	-148(1)	-180(1)	-148(1)
Crystal Colour, Habit	yellow, platelet	colourless, platelet	colourless, prism	colourless, prism
Crystal Dimensions (mm^3)	0.12 X 0.09 X 0.03	0.24 X 0.02 X 0.03	0.12 X 0.03 X 0.03	0.20 X 0.20 X 0.20
Crystal System	monoclinic	monoclinic	orthorhombic	monoclinic
Lattice Parameters	a = 10.050(6)Å	a = 5.606(4) Å	a = 22.326(3) Å	a = 5.641(2) Å
	b = 21.750(11) Å	b = 16.173(9) Å	b = 5.272(10) Å	b = 22.249(10) Å
	c = 9.843(5) Å	c = 20.919(13) Å	c = 15.640(14) Å	c = 15.272(7) Å
	-	-	-	-
	β = 116.242(12)°	β = 97.126(14)°	-	β = 100.477(18)°
	-	-	-	-
Volume ($Å^3$)	V = 1929.8(19)	V = 1881.8(19)	V = 1841(4)	V = 1884.7(14)
Space Group	$P2_1/c$	$P2_1/n$	$Pca2_1$	$P2_1/n$
Z value	4	4	4	4
Dcalc (g/cm^3)	1.933	1.473	1.681	1.808
F000	1064	848	920	992
μ(MoKα) (cm^{-1})	30.281	21.108	17.338	35.146
No. of Reflections Measured	15461	16208	17293	16286
Rint	0.1036	0.1434	0.0682	0.1052
Min and Max Transmissions	0.298 - 0.913	0.484 - 0.959	0.558 - 0.949	0.299 - 0.495
Independ.Reflection (No. Variables)	4448(235)	4381 (235)	3322 (235)	4318(235)
Reflection/Parameter Ratio	18.93	18.64	14.14	18.37
Residuals: R_1 (I>2.00σ(I))	0.0948	0.1324	0.0409	0.0835
Residuals: R (All reflections)	0.1393	0.1948	0.0430	0.1251
Residuals: wR_2 (All reflections)	0.3803	0.3364	0.0985	0.2644
Goodness of Fit Indicator	1.421	1.218	1.084	1.148
Flack Parameter	-	-	-0.01(4)	-
Maximum peak in Final Diff. Map	2.90 e-/$Å^3$	0.73 e-/$Å^3$	1.58 e-/$Å^3$	1.38 e-/$Å^3$
Minimum peak in Final Diff. Map	-4.99 e-/$Å^3$	-1.16 e-/$Å^3$	-1.39 e-/$Å^3$	-2.35e-/$Å^3$

Table S11: Crystallographic data for compounds **A14-A16**.

	A14	**A15**	**A16**
Empirical Formula	$C_{12}H_8I_2$	$C_{12}H_8BrI$	$C_{12}H_8Cl_2$
Formula Weight	406.00	359.00	223.10
Temperature (°C)	-148(1)	-148(1)	-148(1)
Crystal Colour, Habit	colourless, prism	colourless, platelet	colourless, prism
Crystal Dimensions (mm^3)	0.20 X 0.20 X 0.20	0.15 X 0.12 X 0.03	0.37 X 0.12 X 0.10
Crystal System	monoclinic	monoclinic	triclinic
Lattice Parameters	a = 8.062(3)Å	a = 7.912(3) Å	a = 7.6529(7) Å
	b = 11.733(4) Å	b = 11.715(5) Å	b = 8.2912(8) Å
	c = 11.966(4) Å	c = 11.771(5) Å	c = 8.8382(8) Å
	-	-	α = 64.174(2)°
	β = 107.480(8)°	β = 107.423(9)°	β = 78.781(2)°
	-	-	γ = 69.709(2)°
Volume ($Å^3$)	V = 1079.6(6)	V = 1041.0(8)	V = 472.83(8)
Space Group	$P2_1/n$	$P2_1/n$	P-1
Z value	4	4	2
Dcalc (g/cm^3)	2.498	2.290	1.567
F000	744	672	228

μ(MoKα) (cm^{-1})	57.831	68.804	6.330
No. of Reflections Measured	8943	8650	4081
Rint	0.0337	0.0382	0.0256
Min and Max Transmissions	0.235 - 0.315	0.492 - 0.813	0.821 - 0.939
Independ.Reflection (No. Variables)	2471(127)	2412(127)	1663(127)
Reflection/Parameter Ratio	19.46	18.99	13.09
Residuals: R_1 (I>2.00σ(I))	0.0421	0.1031	0.0384
Residuals: R (All reflections)	0.0549	0.1121	0.0506
Residuals: wR_2 (All reflections)	0.1786	0.3718	0.0853
Goodness of Fit Indicator	1.201	1.735	1.168
Flack Parameter	-	-	-
Maximum peak in Final Diff. Map	3.04 e-/$Å^3$	8.24 e-/$Å^3$	0.27 e-/$Å^3$
Minimum peak in Final Diff. Map	-2.94 e-/$Å^3$	-3.49 e-/$Å^3$	-0.27 e-/$Å^3$

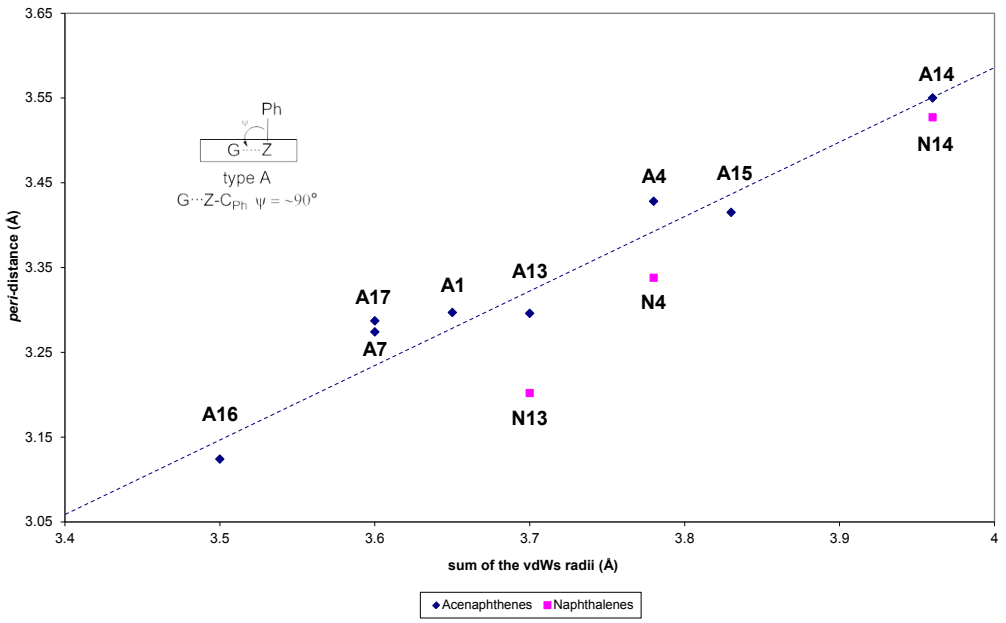

Fig. S9 The relationship between heteroatom size (sum of van der Waals radii) versus *peri*-distance in compounds adopting type A/AA conformations and bis-halides.

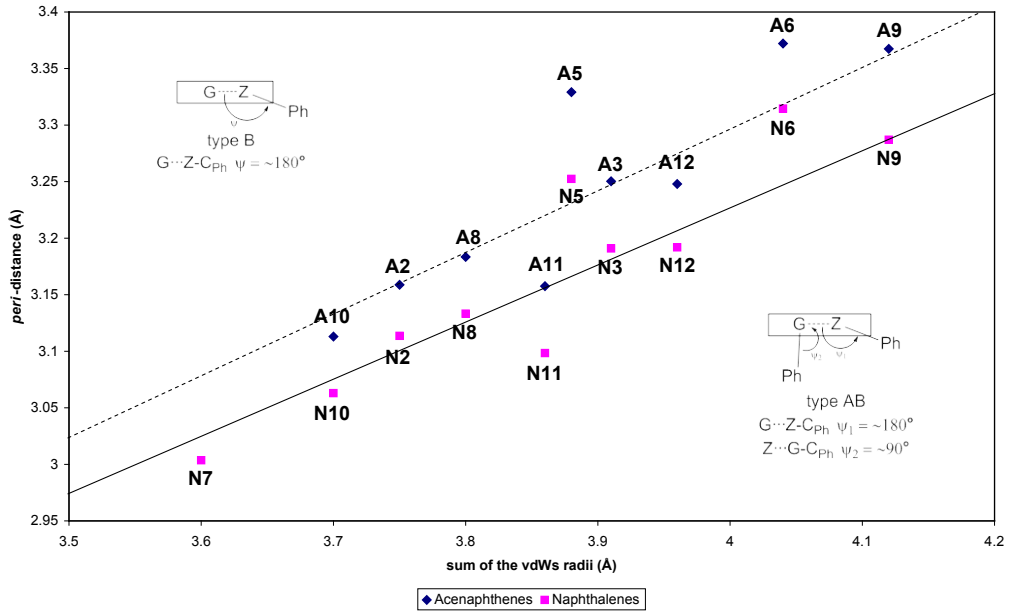

Fig. S10 The relationship between heteroatom size (sum of van der Waals radii) versus *peri*-distance in compounds adopting type B/AB conformations.

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