Electronic Supplementary Information

# Bismuth···π arene versus bismuth···halide coordination in heterocyclic diorganobismuth(III) compounds with transannular N→Bi interaction

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*4.2. Synthesis of $C_6H_5CH_2N(CH_2C_6H_4Br\text{-}2)_2$* [1]

A reaction mixture of 2-bromo-benzyl bromide (2.17 g, 8.68 mmol), $K_2CO_3$ (2.975 g, 21 mmol) and benzylamine (0.465 g, 4.33 mmol) in dimethylformamide (50 ml) was stirred under reflux for 3 h and then left at room temperature over night. The remained solid was filtered off and to the remained solution diethyl ether was added. The diethyl ether phase was washed with water (2 x 20 ml) and then dried over $MgSO_4$. From the clear solution the solvent was removed in vacuo and the resulted yellowish oil was purified by column chromatography on silica gel, by using a mixture of n-hexane and $CH_2Cl_2$ in 3:1 volume ratio. The solvent was removed at reduced pressure when the title compound resulted as a colorless oil. Yield: 1.25 g (65%). $^1$H NMR ($CDCl_3$, 500 MHz): δ 3.68 (s, 2H, $H_8$), 3.74 (s, 4H, $H_7$), 7.08 (dt, 2H, $H_5$, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.4 Hz), 7.22-7.33 (m, 2H, $C_6H_4$, $H_4$ + 3H, $C_6H_5$-*meta* + *para*), 7.40 (d, 2H, $C_6H_5$-*ortho*, $^3J_{HH}$ 7.9 Hz) 7.50 (dd, $H_6$, $^3J_{HH}$ 7.9, $^4J_{HH}$ 1.2 Hz), 7.68 (dd, 2H, $H_3$, $^3J_{HH}$ 7.8 Hz, $^4J_{HH}$ 1.6 Hz). $^{13}$C NMR ($CDCl_3$, 125.72 MHz): δ 57.76 ($C_7$), 58.78 ($C_8$), 124.48 ($C_1$), 127.20 ($C_6H_5$-*para*), 127.5 ($C_4$), 128.41 ($C_5$), 128.45 ($C_6H_5$-*meta*), 128.90 ($C_6H_5$-*ortho*), 130.47 ($C_3$), 132.79 ($C_6$), 138.67 ($C_2$), 139.11 ($C_6H_5$-*ipso*).

*Synthesis of $C_6H_5CH_2CH_2N(CH_2C_6H_4Br\text{-}2)_2$*

To a solution of 2-bromo-benzyl bromide (3.27 g, 13 mmol) in dimethylformamide (50 ml), $K_2CO_3$ (1.970 g, 14.2 mmol) and 2-phenylethanamine (0.794 g, 6.55 mmol) were added. The reaction mixture was refluxed with stirring for 4 h and then left at room temperature over night. The next day the reaction mixture was diluted with $CH_2Cl_2$ (50 ml) and water (30 ml) and the organic phase was separated. The

aqueous phase was washed with diethyl ether (2 x 15 ml) and the joined organic phases were dried over $MgSO_4$. From the clear solution the solvents were removed at reduced pressure to give a light yellow oil which was purified by column chromatography on silica gel by using a n-hexane: $CH_2Cl_2$ mixture of solvents (1:1 volume ratio) to give the title compound as a colorless oil. Yield: 2.85 g (94%). $^1$H NMR ($CDCl_3$, 500 MHz): δ 2.77-2.81 (m, 2H, $H_{8/9}$), 2.84-2.88 (m, 2H, $H_{8/9}$), 3.82 (s, 4H, $H_7$), 7.07 (dt, 2H, $H_5$, $^3J_{HH}$ 7.51, $^4J_{HH}$ 1.7 Hz), 7.10 (d, 2H, $C_6H_5$-*ortho*, $^3J_{HH}$ 7.8 Hz) 7.16-7.25 (m, 2H, $C_6H_4$, $H_4$ + 3H, $C_6H_5$-*meta* + *para*), 7.46 (dd, 2H, $H_6$, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.6 Hz), 7.50 (dd, 2H, $H_3$, $^3J_{HH}$ 7.9, $^4$J 1.2 Hz). $^{13}$C NMR ($CDCl_3$, 125.72 MHz): δ 33.66 ($C_9$), 56.21 ($C_8$), 58.10 ($C_7$), 124.28 ($C_1$), 126.09 ($C_6H_5$-*para*), 127.43 ($C_4$), 128.35 ($C_5$), 128.41 ($C_6H_5$-*meta*), 129.07 ($C_6H_5$-*ortho*), 130.52 ($C_6$), 132.73 ($C_3$), 138.78 ($C_2$), 140.51 ($C_6H_5$-*ipso*).

*Synthesis of $CH_3OCH_2CH_2N(CH_2C_6H_4Br\text{-}2)_2$*

To a solution of 2-bromobenzyl bromide (1.68 g, 6.7 mmol) in $CH_2Cl_2$ (50 ml) was added a solution of NaOH (0.61 g, 15.25 mmol) in water (12 ml) and 2-methoxyethanamine (0.252 g, 3.35 mmol). The reaction mixture was left with stirring at 0°C for 6h. The organic phase was separated and washed with a $NH_4Cl$ solution in water (0.74 M, 2 x 20 ml) and then dried over $MgSO_4$. From the clear solution the solvent was removed at reduced pressure to give a beige oil which was purified by column chromatography on silica gel by using a n-hexane: $CH_2Cl_2$ mixture of solvents (3:1 volume ratio) to give the title compound as a colorless oil. Yield: 1.255 g (65%). $^1$H NMR ($CDCl_3$, 500 MHz): δ 2.77 (t, 2H, $H_9$, $^3J_{HH}$ 5.2 Hz), 3.29 (s, 3H, $OCH_3$), 3.53 (t, 2H, $H_8$, $^3J_{HH}$ 6.1 Hz, 3.82 (s, 4H, $H_7$), 7.07 (dt, 2H, $H_5$, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.8 Hz), 7.27 (t, 2H, $H_4$, $^3J_{HH}$ 7.5 Hz), 7.50 (dd, 2H, $H_6$, $^3J_{HH}$ 8.1, $^4J_{HH}$ 1.2 Hz), 7.61 (dd, 2H, $H_3$, $^3J_{HH}$ 7.8, $^4$J 1.2 Hz). $^{13}$C NMR ($CDCl_3$, 125.72 MHz): δ 53.70 ($C_9$), 58.75 ($C_7$), 58.91 ($OCH_3$), 71.32 ($C_8$), 124.33 ($C_1$), 127.40 ($C_4$), 128.39 ($C_5$), 130.71 ($C_3$), 132.76 ($C_6$), 138.88 ($C_2$).

[1] F. H. Carre, R. J. P. Corriu, G. F. Lanneau, P. Merle, F. Soulairol, J. Yao, *Organometallics,* 1997, **16***,* 3878.

Table S1. Crystal and structural refinement data for compounds **1 - 5**

| | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| Empirical formula | $C_{21}H_{19}BiBrN$ | $C_{22}H_{21}BiBrN$ | $C_{17}H_{19}BiBrNO$ | $C_{21}H_{19}BiClN$ | $C_{21}H_{19}BiIN$ |
| Formula weight | 574.26 g/mol | 588.29 g/mol | 542.22 g/mol | 529.80 g/mol | 621.25 g/mol |
| Temperature | 110 K | 297(2) K | 297(2) K | 110 K | 110 K |
| Wavelength | 0.71073 Å | 0.71073 Å | 0.71073 Å | 0.71073 Å | 0.71073 Å |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | P 21/c | C 2/c | P 21/c | P 21/c | P 21/c |
| *a* [Å] | 7.5186(5) | 27.200(2) | 16.777(4) | 10.0394(4) | 7.3565(2) |
| *b* [Å] | 10.6718(7) | 10.1132(9) | 13.537(4) | 11.5616(4) | 10.8639(4) |
| *c* [Å] | 22.4700(16) | 19.7239(17) | 16.910(4) | 15.0742(6) | 23.1182(7) |
| *α* [°] | 90 | 90 | 90 | 90 | 90 |
| *β* [°] | 94.532(7) | 132.9980(10) | 114.416(4) | 90.277(4) | 92.701(3) |
| *γ* [°] | 90 | 90 | 90 | 90 | 90 |
| Volume | 1797.3(2)Å$^3$ | 3968.2(6) Å$^3$ | 3497.0(16) Å$^3$ | 1749.66(12) Å$^3$ | 1845.56(10) Å$^3$ |
| Z | 4 | 8 | 8 | 4 | 4 |
| Density (calculated) | 2.122 g/cm$^3$ | 1.969 g/cm$^3$ | 2.060 g/cm$^3$ | 2.011 g/cm$^3$ | 2.236 g/cm$^3$ |
| Absorption coefficient | 12.034 mm$^{-1}$ | 10.904 mm$^{-1}$ | 12.367 mm$^{-1}$ | 10.231mm$^{-1}$ | 11.228 mm$^{-1}$ |
| F(000) | 1080 | 2224 | 2032 | 1008 | 1152 |
| Crystal size | 0.4 x 0.35 x 0.25 mm | 0.39 x 0.33 x 0.26mm | 0.38 x 0.30 x 0.26 mm | 0.40 x 0.40 x 0.20 mm | 0.30 x 0.20 x 0.20 mm |
| Theta range for data collection | 3.149 to 25.993° | 2.047 to 24.996° | 1.333 to 24.999 ° | 3.003 to 25.998 ° | 3.215 to 24.999 ° |
| Index ranges | -8<=h<=9<br>-13<=k<=13<br>-27<=l<=24 | -32<=h<=32<br>-12<=k<=12<br>-23<=l<=23 | -19<=h<=19<br>-16<=k<=16<br>-20<=l<=20 | -12<=h<=11<br>-14<=k<=14<br>-8<=l<=18 | -8<=h<=8<br>-12<=k<=12<br>-27<=l<=27 |
| Reflections collected/unique | 8333 / 3525<br>[R(int) = 0.0381] | 18397 / 3492<br>[R(int) = 0.0646] | 32639 / 6146<br>[R(int) = 0.0959] | 8593 / 3439<br>[R(int) = 0.0402] | 6828 / 3243<br>[R(int) = 0.0304] |
| Completeness to theta max. | 99.7% | 99.9% | 100.0% | 99.7 % | 99.7 % |
| Absorption correction | multi-scan | | | | |
| Refinement method | Full-matrix least-squares on F^2 | | | | |
| Data / restrains / parameters | 3525 / 0 / 217 | 3492 / 24 / 226 | 6146 / 0 / 381 | 3439 / 0 / 217 | 3243 / 0 / 217 |
| Goodness-of-fit on $F^2$ -S | 1.060 | 1.094 | 1.058 | 1.031 | 1.045 |
| Final R indices [I>2sigma(I)] | R1 = 0.0339<br>wR2 = 0.0658 | R1 = 0.0677<br>wR2 = 0.1896 | R1 = 0.0526<br>wR2 = 0.0917 | R1 = 0.0281<br>wR2 = 0.0592 | R1 = 0.0262<br>wR2 = 0.0507 |
| R indices (all data) | R1 = 0.0423<br>wR2 = 0.0686 | R1 = 0.0862<br>wR2 = 0.2010 | R1 = 0.0792<br>wR2 = 0.0987 | R1 = 0.0363<br>wR2 = 0.0615 | R1 = 0.0311<br>wR2 = 0.0525 |
| Largest diff. peak and hole | 1.668 and-1.397e/Å$^3$ | 6.058 and -2.388e/Å$^3$ | 1.479 and -1.489 e/Å3 | 0.920 and -1.935 e/Å3 | 1.236 and -0.764 e/Å3 |

Table S2. Crystal and structural refinement data for compounds **6 - 10**

| | **6** | **7** | **8** | **9** | **10** |
|---|---|---|---|---|---|
| Empirical formula | $C_{22}H_{21}BiClN$ | $C_{22}H_{21}BiIN$ | $C_{17}H_{19}BiFNO$ | $C_{17}H_{19}BiClNO$ | $C_{17}H_{19}BiINO$ |
| Formula weight | 543.83 g/mol | 635.28 g/mol | 481.31g/mol | 497.76 g/mol | 589.21 g/mol |
| Temperature | 293(2) K | 110 K | 297(2) K | 110 K | 297(2) K |
| Wavelength | 0.71073 Å | 0.71073 Å | 0.71073 Å | 0.71073 Å | 0.71073 Å |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | C 2/c | P 21/c | P 21/n | P 21/c | C 2/c |
| *a* [Å] | 27.197(3) | 19.5719(6) | 12.506(7) | 9.0546(3) | 14.942(2) |
| *b* [Å] | 10.0324(11) | 20.7636(6) | 18.658(5) | 18.9853(6) | 13.8911(19) |
| *c* [Å] | 19.709(3) | 19.6683(6) | 18.119(12) | 19.0771(6) | 17.153(2) |
| $\alpha$ [°] | 90 | 90 | 90 | 90 | 90 |
| $\beta$ [°] | 132.929(4) | 93.297(3) | 110.129(9) | 90.059(3) | 98.306(2) |
| $\gamma$ [°] | 90 | 90 | 90 | 90 | 90 |
| Volume | 3937.4(9) $Å^3$ | 7979.6(4) $Å^3$ | 1842.0(19) $Å^3$ | 3279.43(18) $Å^3$ | 3522.9(8) $Å^3$ |
| Z | 8 | 16 | 4 | 8 | 8 |
| Density (calculated) | 1.835 $g/cm^3$ | 2.115 $g/cm^3$ | 1.736 $g/cm^3$ | 2.016 $g/cm^3$ | 2.222 $g/cm^3$ |
| Absorption coefficient | 9.095 $mm^{-1}$ | 10.390 $mm^{-1}$ | 9.579 $mm^{-1}$ | 10.913 $mm^{-1}$ | 11.761 $mm^{-1}$ |
| F(000) | 2080 | 4736 | 912 | 1888 | 2176 |
| Crystal size | 0.40 x 0.30 x 0.20mm | 0.30 x 0.30 x 0.20mm | 0.39 x 0.33 x 0.24 mm | 0.40 x 0.40 x 0.20 mm | 0.37 x 0.32 x 0.23 mm |
| Theta range for data collection | 2.070 to 25.493° | 2.856 to 24.998 ° | 1.333 to 24.999 ° | 3.109 to 25.998 ° | 2.012 to 24.999 ° |
| Index ranges | -32<=h<=32<br>-12<=k<=12<br>-23<=l<=23 | -22<=h<=23<br>-24<=k<=24<br>-23<=l<=21 | -15<=h<=15<br>-10<=k<=10<br>-21<=l<=21 | -11<=h<=11<br>-23<=k<=23,<br>-23<=l<=23 | -17<=h<=17<br>-16<=k<=16<br>-20<=l<=20 |
| Reflections collected/unique | 18798 / 3655<br>[R(int) = 0.1023] | 46954 / 14024<br>[R(int) = 0.0566] | 17537 / 3425<br>[R(int) = 0.0718] | 33575 / 6413<br>[R(int) = 0.0622] | 16224 / 3109<br>[R(int) = 0.1500] |
| Completeness to theta max. | 99.7% | 99.8% | 99.9% | 99.7 % | 99.9 % |
| Absorption correction | multi-scan | | | | |
| Refinement method | Full-matrix least-squares on F^2 | | | | |
| Data / restrains / parameters | 3655 / 0 / 227 | 14024 / 0 / 889 | 3425 / 0 / 191 | 6413 / 0 / 379 | 3109 / 6 / 190 |
| Goodness-of-fit on $F^2$ -S | 0.998 | 0.996 | 1.068 | 1.059 | 0.981 |
| Final R indices [I>2sigma(I)] | R1 = 0.0432<br>wR2 = 0.0952 | R1 = 0.0399<br>wR2 0.0734 | R1 = 0.0383<br>wR2 = 0.0765 | R1 = 0.0323<br>wR2 = 0.0691 | R1 = 0.0631<br>wR2 = 0.1320 |
| R indices (all data) | R1 = 0.0630<br>wR2 = 0.1009 | R1 = 0.0616<br>wR2 = 0.0792 | R1 = 0.0553<br>wR2 = 0.0814 | R1 = 0.0414<br>wR2 = 0.0718 | R1 = 0.0937<br>wR2 = 0.1444 |
| Largest diff. peak and hole | 2.513 and -1.516e/$Å^3$ | 1.983 and -1.702e/$Å^3$ | 0.988 and -1.243 e/Å3 | 2.407 and -1.625 e/Å3 | 2.903 and -3.469e/Å3 |

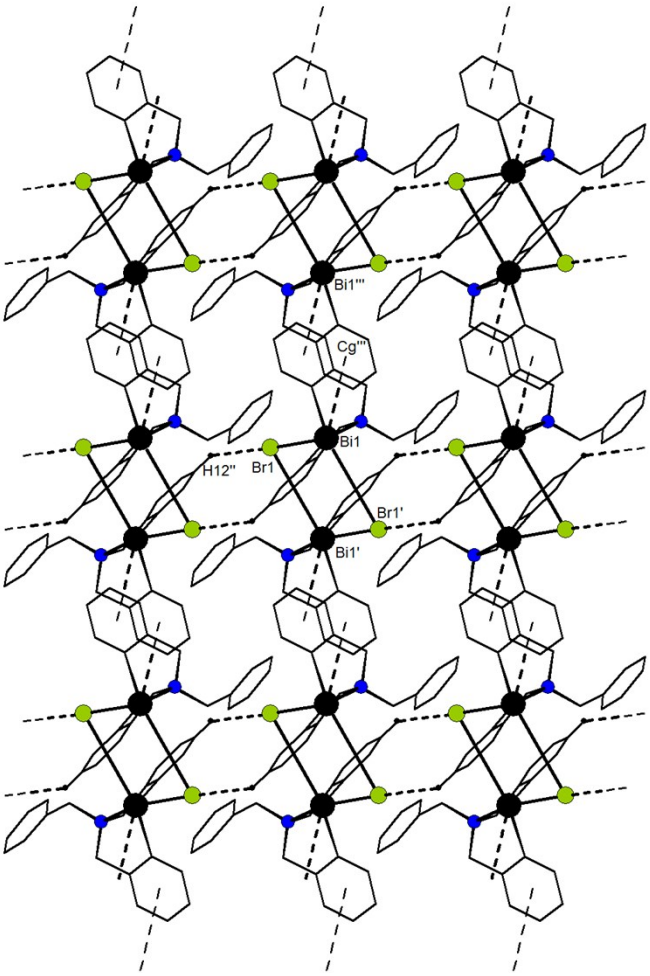


**Figure S1.** View along axis *c* of a 2D layer in **1**

| | | |
|---|---|---|
| Inter-dimers interactions | Br1···H12" | 3.025 Å (*-x, 1-y, 2-z*), $\Sigma r_{vdW}$(H,Br) 3.15 Å |
| Inter-chains interactions | Bi1···Cg'''(C1'''-C6''') | 4.097 Å (*1-x, 2-y, 2-z*) |

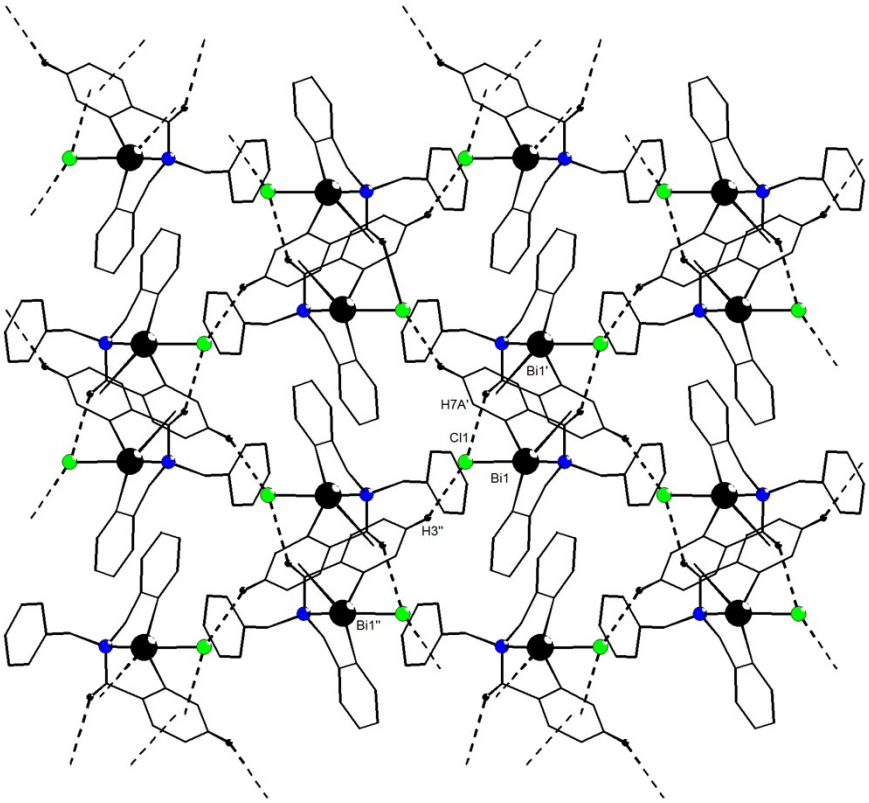


**Figure S2.** View along axis *a* of a 2D layer in **4**

| | | |
|---|---|---|
| Inter-dimers interactions | Cl1···H3" | 2.787 Å (*-x, -0.5+y, 0.5-z*), $\Sigma r_{vdW}$(H,Cl) 3.01 Å |
| Inter-chains interactions | Cl1···H7A' | 2.868 Å (*-x, 2-y, -z*) |
| Inter-layers interactions | Cl1'"···H19 | 2.857 Å (*1+x, 1.5-y, -0.5+z*) |

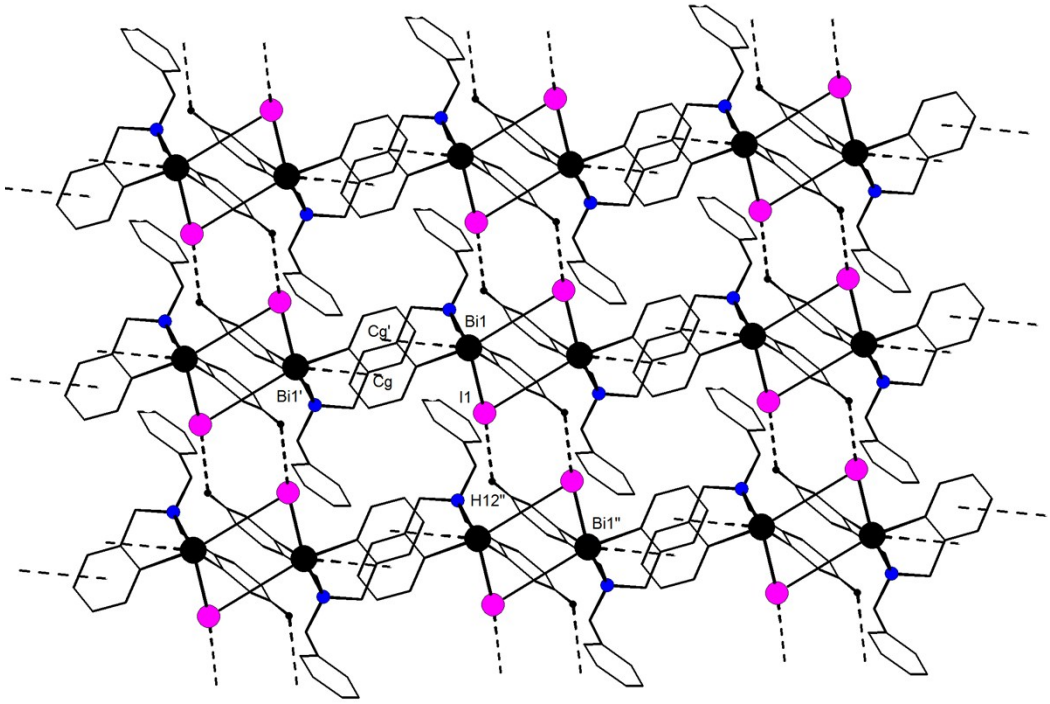


**Figure S3.** Best view of a 2D layer in **5**

| | | |
|---|---|---|
| Inter-dimers interactions | H12''···I1 | 3.296 Å (*-x, -y, 1-z*), $\Sigma r_{vdW}$(H,I) 3.35 Å |
| Inter-chains interactions | Bi1···Cg'(C1'-C6') | 4.137 Å (*1-x, 1-y, 1-z*) |

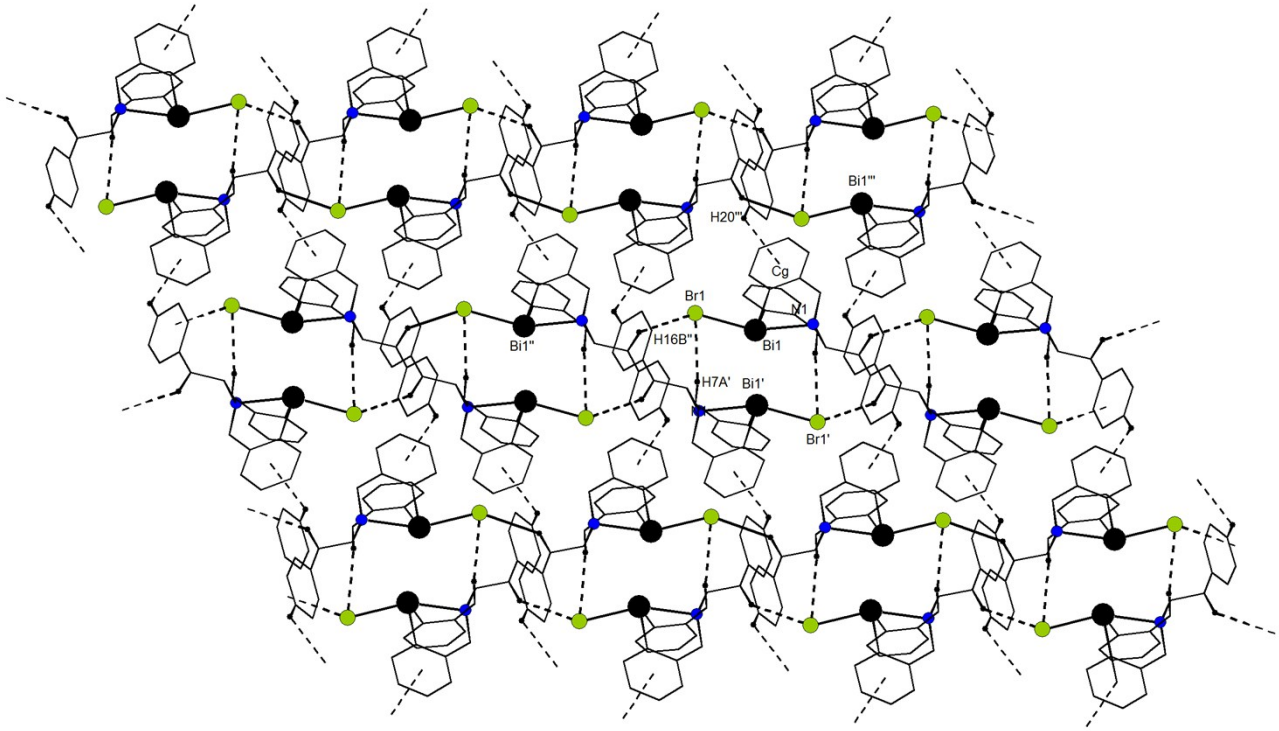


**Figure S4.** Best view of a 2D layer in **2**

| | | |
|---|---|---|
| Intra-dimers interactions | Br1···H7A' | 3.037 Å (*-x, 1-y, -z*), $\Sigma r_{vdW}$(H,Br) 3.15 Å |
| Inter-dimers interactions | Br1···H16B" | 2.889 Å (*x, 1+y, z*) |
| Inter-chains interactions | H20'''···Cg(C9-C14) | 2.993 Å (*0.5+x, 0.5-y, 0.5+z*) |

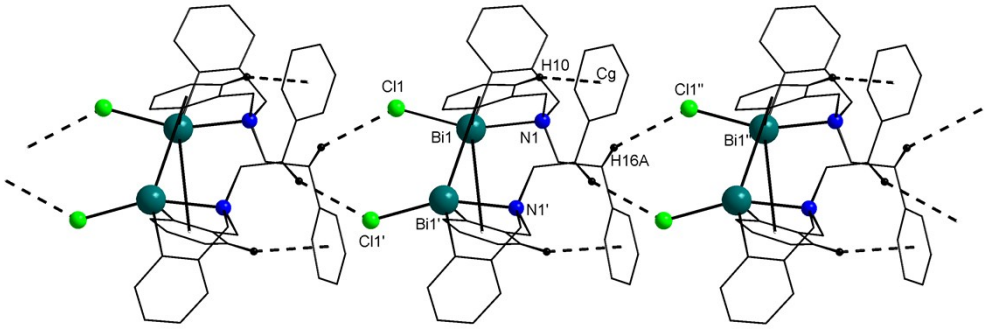


**Figure S5.** Polymeric chain of $R^1,R^2$-**6** and $S^1,S^2$-**6** isomers.

| | | |
|---|---|---|
| Cl1'···H16A | 2.867 Å (*x, -1+y, z*) | $\Sigma r_{vdW}$(H,Cl) 3.01 Å |
| H10···Cg'(C17'-C22') | 2.972 Å (*1-x, y, 1.5-z*) | |

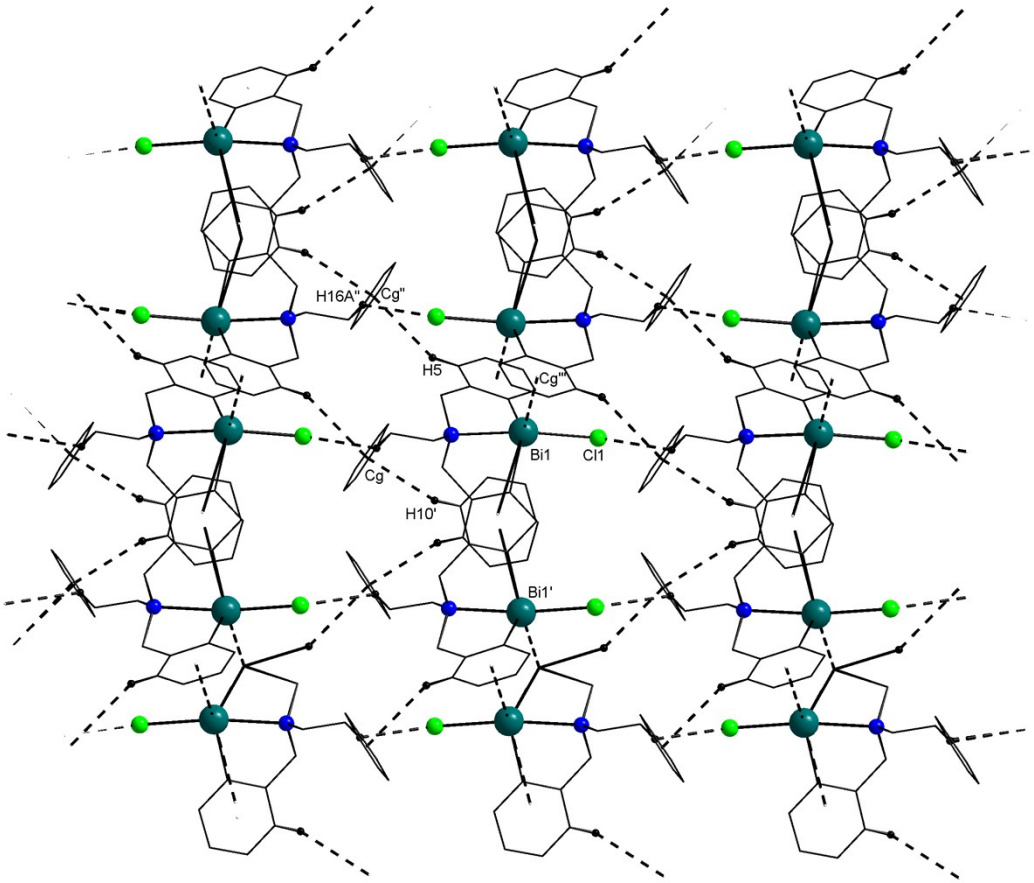


**Figure S6.** Best view of a 2D layer in **6**

| | | | |
|---|---|---|---|
| Intra-dimers interactions: | Bi1'···Cg(C9-C14) | 4.481 Å (*1-x, y, 1.5-z*) | |
| | H10'···Cg(C17-C22) | 2.972 Å (*1-x, y, 1.5-z*) | |
| Inter-dimers interactions: | Cl1···H16A" | 2.867 Å (*x, 1+y, z*) | $\Sigma r_{vdW}$(H,Cl) 3.01 Å |
| Inter-chains interactions: | H5···Cg"(C17"-C22") | 2.972 Å (*1-x, -y, 2-z*) | |
| | Bi1···Cg'''(C1'''-C6''') | 4.791 Å (*1-x, 1-y, 2-z*) | |

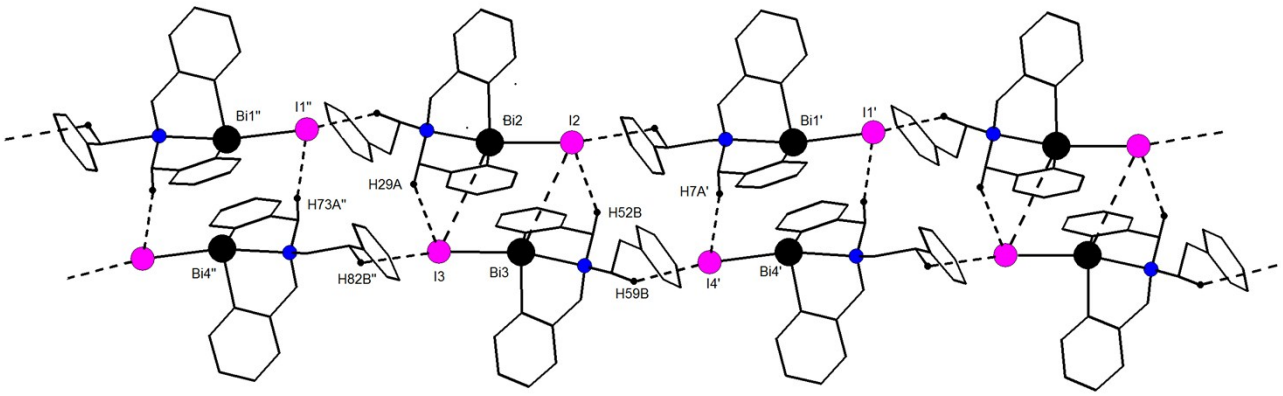


**Figure S7.** Polymeric chain of **7a/7d** and **7b/7c** dimers (hydrogen atoms are omitted for clarity). Bi1–C1 2.262(7) Å, Bi1–C14 2.242(7) Å, Bi1–I1 2.9890(6) Å, Bi1–N1 2.490(6) Å; Bi2–C23 2.256(7) Å, Bi2–C36 2.250(7) Å, Bi2–I2 2.9909(6) Å, Bi2–N2 2.513(5) Å; Bi3–C45 2.268(8) Å, Bi3–C58 2.260(7) Å, Bi3–I3 3.0043(6) Å, Bi3–N3 2.509(5) Å; Bi4–C67 2.258(7) Å, Bi4–C80 2.225(7) Å, Bi4–I4 2.9791(6) Å, Bi4–N4 2.496(5) Å; C1–Bi1–C14 96.9(3)$^0$, C1–Bi1–I1 93.93(18)$^0$, C14–Bi1–I1 93.07(18)$^0$, C1–Bi1–N1 72.6(2)$^0$, C14–Bi1–N1 74.6(2)$^0$, I1–Bi1–N1 160.08(14)$^0$, C23–Bi2–C36 97.1(3)$^0$, C23–Bi2–I2 93.87(18)$^0$, C36–Bi2–I2 91.45(18)$^0$, C23–Bi2–N2 71.6(2)$^0$, C36–Bi2–N2 73.9(2)$^0$, I2–Bi2–N2 157.44(14)$^0$, C29–N2–C30 110.6(6)$^0$, C45–Bi3–C58 96.7(3)$^0$, C45–Bi3–I3 90.82(18)$^0$, C58–Bi3–I3 94.47(18)$^0$, C45–Bi3–N3 74.3(2)$^0$, C58–Bi3–N3 71.8(2)$^0$, I3–Bi3–N3 157.94(13)$^0$, C51–N3–C52 110.3(6)$^0$. C67–Bi3–C80 98.9(3)$^0$, C67–Bi4–I4 93.45(18)$^0$, C80–Bi4–I4 92.49(17)$^0$, C67–Bi4–N4 72.0(2)$^0$, C80–Bi4–N4 74.3(2)$^0$, I4–Bi4–N4 158.05(14)$^0$, C73–N4–C74 112.4(6)$^0$. Bi2···I3 4.440 Å, Bi3···I2 4.443 Å.

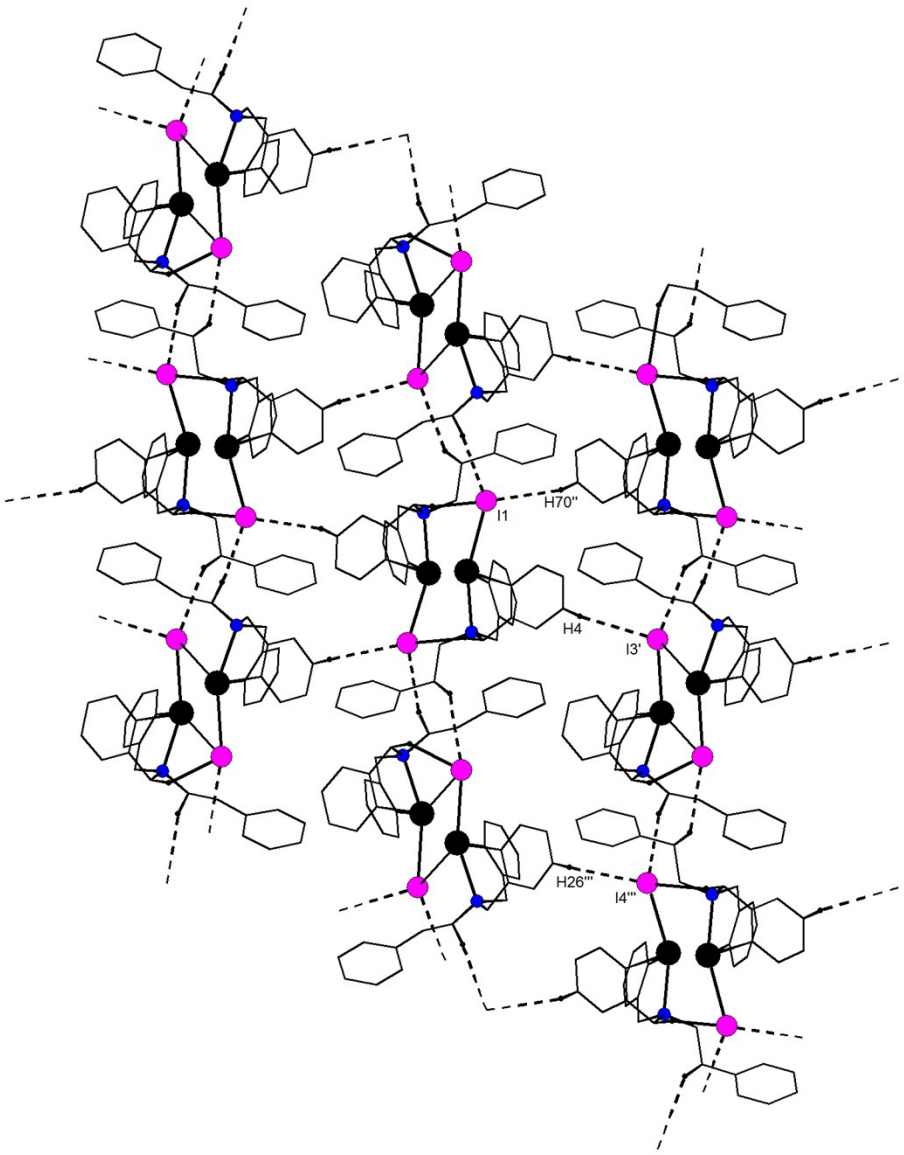


**Figure S8.** View along axis *a* of a 2D layer in **7**

| | | | |
|---|---|---|---|
| Inter-chains interactions: | I1···H70" | 3.113 Å (*-x, 0.5+y, 1.5-z*) | $\Sigma r_{vdW}$(H,I) 3.35 Å |
| | I3'···H4 | 3.327 Å (*-x, 0.5+y, 1.5-z*) | |
| | I4'''···H26''' | 3.259 Å (*-x, -0.5+y, 1.5-z*) | |

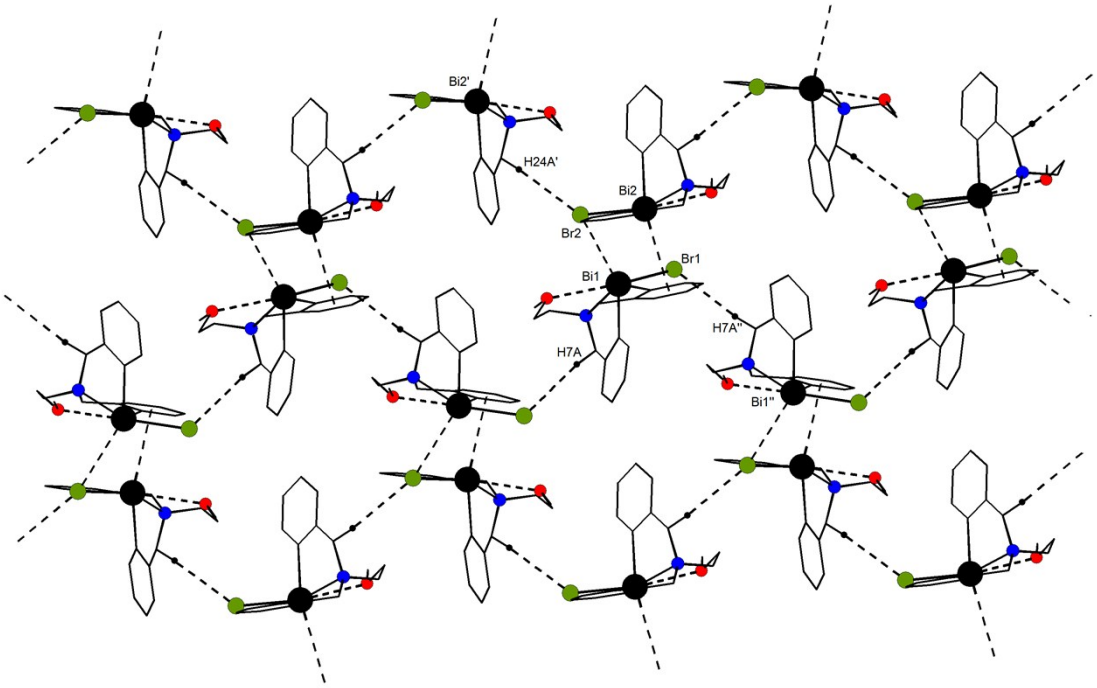


**Figure S9.** Best view of a 2D layer in **3**.

| | | | |
|---|---|---|---|
| Inter-dimers interactions | Br1···H7A" | 3.083 Å (*1-x, 0.5+y, 0.5-z*) | $\Sigma r_{vdW}$(H,Br) 3.15 Å |
| | Br2··· H24A' | 3.133 Å (*-x, -0.5+y, 0.5-z*) | |

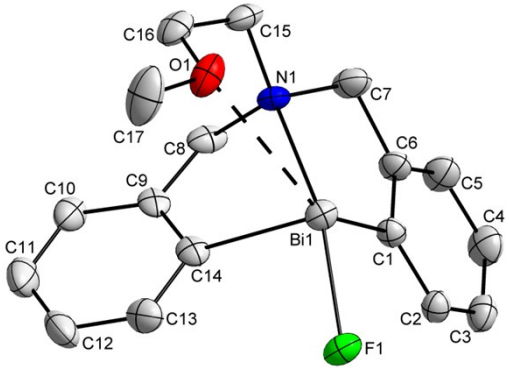


**Figure S10.** Thermal ellipsoids representation at 50% probability and atom numbering scheme in $S^1,S^2$-**8** (hydrogen atoms are omitted for clarity). Bi1–C1 2.237(7) Å, Bi1–C14 2.229(7) Å, Bi1–F1 2.213(4) Å, Bi1–N1 2.583(6) Å, Bi1···O1 3.005 Å; C1–Bi1–C14 97.3(3)$^0$, C1–Bi1–F1 92.2(2)$^0$, C14–Bi1–F1 88.9(2)$^0$, C1–Bi1–N1 71.1(2)$^0$, C14–Bi1–N1 72.8(2)$^0$, F1–Bi1–N1 152.82(17)$^0$, C7–N1–C8 109.7(6)$^0$.

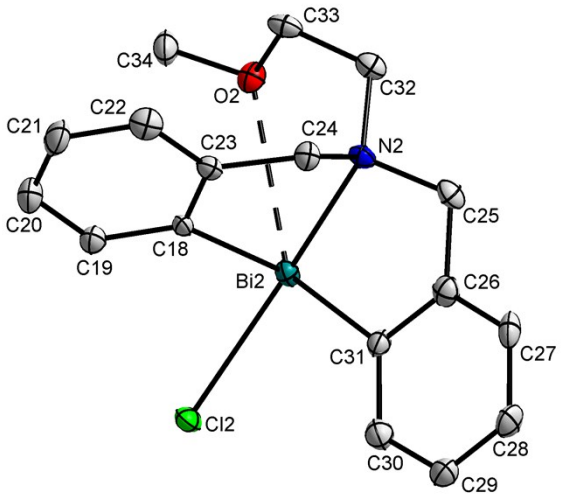


**Figure S11.** Thermal ellipsoids representation at 30% probability and atom numbering scheme in $S^1,S^2$-**9b** (hydrogen atoms are omitted for clarity). Bi2–C18 2.239(5) Å, Bi2–C31 2.261(5) Å, Bi2–Cl2 2.6926(14) Å, Bi1–N1 2.540(5) Å, Bi2···O2 3.074 Å; C18–Bi2–C31 99.77(19)$^0$, C18–Bi2–Cl2 87.90(15)$^0$, C31–Bi2–Cl2 92.71(15)$^0$, C18–Bi2–N2 74.07(17)$^0$, C31–Bi2–N2 71.76(18)$^0$, Cl2–Bi2–N2 153.30(10)$^0$, C25–N2–C32 109.8(4)$^0$.

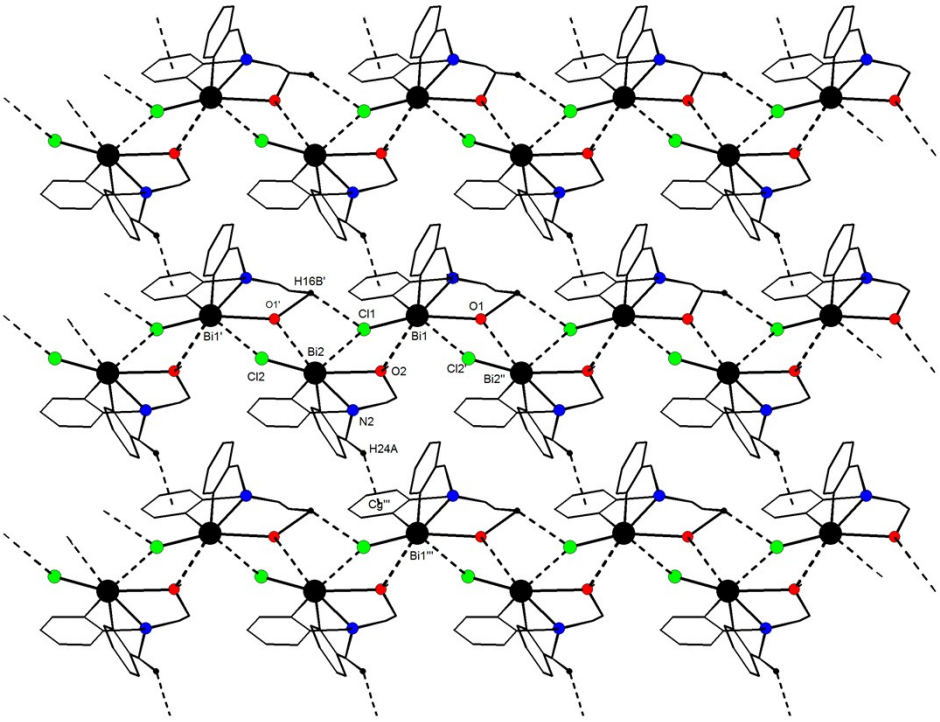


**Figure S12.** View along axis *b* of a 2D layer in **9**

| | | | |
|---|---|---|---|
| Intra-chain interactions: | Bi1···O2 | 3.642 Å; | $\Sigma r_{vdW}$(Bi,O) 3.80 Å |
| | Bi2···Cl1 | 3.728 Å | $\Sigma r_{vdW}$(Bi,Cl) 4.21 Å |
| | Bi2'···O1 | 3.556 Å (*1+x, y, z*) | |
| | Bi1···Cl2' | 3.765 Å (*1+x, y, z*) | |
| | Cl1···H16B' | 2.906 Å (*-1+x, y, z*) | |
| Inter-chains interactions: | H24A···Cg'''(C9'''-C14''') | 2.669 Å (*x, 1.5-y, 0.5+z*) | |

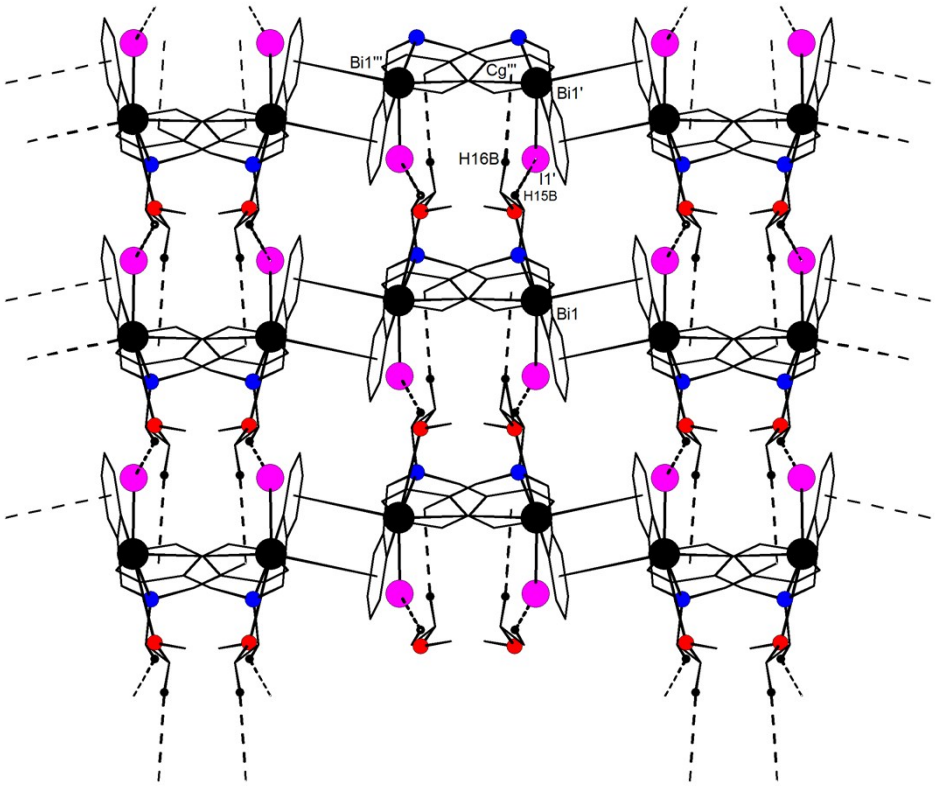


**Figure S13.** View along axis *a* of the supramolecular network in **10**

| | | | |
|---|---|---|---|
| Inter-dimers interactions: | I1"···H15B | 3.320 Å (0.5+x, 0.5+y, z) | $\Sigma r_{vdW}$(H,I) 3.35 Å |
| Inter-chains interactions: | H16B···Cg'''(C1'''-C6''') | 2.879 Å (0.5-x, 0.5+y, 0.5-z) | |