Supporting Information

Anion···Anion Coinage Bonds: The Case of Tetrachloridoaurate
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S1. Experimental Details.

S1.1. Chemicals and materials
All starting materials and reagents were purchased from commercial suppliers (Sigma Aldrich, Apollo Scientific) and used without further purification.

S1.2. Synthetic Method.
Adducts 1 and 2 were prepared as follows: A solution of HAuCl₄ (0.3 mmol) in 5 mL of water was added to a 5 mL solution of an equimolar amount of methyl 3-(dimethylsulfonio)propionate chloride (for adduct 1) and acetylcholine chloride (for structure 2) in the same solvent. The mixture was stirred for two hours at room temperature in a clear borosilicate vial. Slow isothermal evaporation of the solvent afforded yellow/golden single crystals suitable for X-Ray diffraction after four days.

S1.3. Characterization.
General Remarks: ¹H and ¹³C NMR spectra were recorded at ambient temperature on Nuclear Magnetic Resonance Spectrometer AVANCE III, Bruker-BioSpin. All the chemical shifts are given in ppm and the Js in Hz. D₂O was used as both solvent and internal standard in ¹H NMR spectra. FT-IR spectra were obtained using a Nicolet Nexus FT-IR spectrometer equipped with UATR unit.

3-(Dimethylsulfonio)methylpropionate tetrachloroaurate (1): golden crystals.
IR (selected bands, cm⁻¹): 1726, 1470, 1379, 1241, 1081, 1046, 1000, 948, 872, 643, 607.
¹H NMR (400 MHz, D₂O): δ 2.89 (s, 6H S⁺-CH₃), 2.97 (t, 2H, 3J = 6.3 Hz), 3.51 (t, 2H, 3J = 6.2 Hz), 3.70 (s, O-CH₃).
¹³C NMR (101 MHz, D₂O): δ 172.04 (C=O), 52.8 (O-CH₃), 38.6 (CH₂-C=O), 28.4 (S⁺-CH₂), 25.1 (CH₃-S⁺).

Acetylcholine tetrachloroaurate (2): golden crystals.
IR (selected bands, cm⁻¹): 1726, 1483, 1471, 1380, 1242, 1046, 944, 874, 812, 643, 607.
¹H NMR (400 MHz, D₂O): δ 2.05 (s, CH₃-C=O), 3.16 (s, 9H, N⁺-CH₃), 3.49 (brt, 2H, N⁺-CH₂), 4.02 (brt, 2H, CH₂-O),
¹³C NMR (101 MHz, D₂O): δ 176.6 (C=O), 67.4 (N⁺-CH₂), 55.7 (CH₂-O), 54.0 (N⁺-CH₃), 20.4 (CH₃-C=O).
S2. Crystallographic Details.

S2.1. General Remarks.
The single crystal data of 1 and 2 were collected at 100 K using a Bruker SMART APEX II CCD area detector diffractometer. Data collection, unit cell refinement and data reduction were performed using Bruker SAINT. Structures were solved by direct methods using SHELXT\textsuperscript{[1]} and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6\textsuperscript{[2]}. Absorption correction was performed based on multi-scan procedure using SADABS. Structure analysis was aided by use of the programs PLATON\textsuperscript{[3]}. The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom.

Table S.1. Crystal data and structure refinement for 1. The Flack parameter of 0.483 is consistent with the obtainment of a racemic crystal.

| Identification code | 1 |
|---------------------|---|
| **Empirical formula** | C\textsubscript{6}H\textsubscript{13}AuCl\textsubscript{4}O\textsubscript{2}S |
| **Formula weight** | 487.99 |
| **Temperature/K** | 100(2) |
| **Crystal system** | orthorhombic |
| **Space group** | P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1} |
| a/Å | 7.8771(14) |
| b/Å | 8.6445(15) |
| c/Å | 19.740(4) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| **Volume/Å\textsuperscript{3}** | 1344.2(4) |
| **Z** | 4 |
| **ρ\textsubscript{calc} g/cm\textsuperscript{3}** | 2.411 |
| **μ/mm\textsuperscript{-1}** | 11.869 |
| **F(000)** | 912.0 |
| **Crystal size/mm\textsuperscript{3}** | 0.020 × 0.020 × 0.020 |
| **Radiation** | MoKα (λ = 0.71073) |
| **2Θ range for data collection/°** | 6.618 to 59.722 |
| **Index ranges** | -10 ≤ h ≤ 11, -12 ≤ k ≤ 8, -27 ≤ l ≤ 27 |
| **Reflections collected** | 27994 |
| **Independent reflections** | 3857 [R\textsubscript{int} = 0.0606, R\textsubscript{sigma} = 0.0396] |
| **Data/restraints/parameters** | 3857/0/131 |
| **Goodness-of-fit on F\textsuperscript{2}** | 1.015 |
| **Final R indexes [I>=2σ (I)]** | R\textsubscript{1} = 0.0218, wR\textsubscript{2} = 0.0376 |
| **Final R indexes [all data]** | R\textsubscript{1} = 0.0257, wR\textsubscript{2} = 0.0388 |
| **Largest diff. peak/hole / e Å\textsuperscript{3}** | 0.81/-0.50 |
| **Flack parameter** | 0.483(8) |
| **CCDC Number** | 2075035 |
Table S.2. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 1. U(eq) is defined as 1/3 of the trace of the orthogonalised Uₐ tensor.

| Atom | x        | y        | z        | U(eq)       |
|------|----------|----------|----------|-------------|
| C(6) | -796(8)  | 10875(8) | 5074(3)  | 33.8(15)    |
| C(1) | 4945(8)  | 6578(5)  | 3189(2)  | 24.7(11)    |
| C(4) | 2119(6)  | 8831(7)  | 3889(3)  | 20.5(12)    |
| Cl(1)| 2764.5(13)| 3044.1(19)| 3340.4(8)| 20.3(3)     |
| Cl(2)| -164(2)  | 1292.6(12)| 2500.0(6)| 20.4(3)     |
| Cl(3)| -127(2)  | 4803.3(14)| 4237.6(6)| 26.3(3)     |
| Cl(4)| 4003(6)  | 9068(6)  | 4020(3)  | 17.7(11)    |
| Cl(2)| 199(5)   | 10442(4) | 4476.1(16)| 23.7(8)     |
| Cl(4)| -3039.3(14)| 2939.4(19)| 3410.3(8)| 20.3(3)     |
| C(5) | 1143(6)  | 9171(6)  | 4532(3)  | 16.6(11)    |
| Au(1)| -141.2(2)| 3034.6(2)| 3374.9(2)| 13.18(5)    |
| S(1) | 5231.0(17)| 8628.4(13)| 3271.7(6)| 17.3(3)     |
| O(2) | 1020(5)  | 8386(4)  | 5037(2)  | 25.5(9)     |
| C(2) | 7337(6)  | 8693(7)  | 3612(3)  | 23.9(13)    |

Table S.3. Anisotropic Displacement Parameters (Å²×10³) for 1. The Anisotropic displacement factor exponent takes the form: -2π²[h²a*²U₁₁+2hka*b*U₁₂+…].

| Atom | U₁₁ | U₂₂ | U₃₃ | U₁₂ | U₁₃ | U₂₃ |
|------|-----|-----|-----|-----|-----|-----|
| C(6) | 40(4)| 43(4)| 19(3)| 4(3)| 13(3)| 16(3)|
| C(1) | 34(3)| 14(2)| 25(3)| -4.0(18)| 4(3)| 1(3)|
| C(4) | 21(3)| 23(3)| 18(3)| -2(2)| -1(2)| 1(2)|
| Cl(1)| 13.6(5)| 24.9(7)| 22.4(7)| -3.7(11)| -0.9(5)| -3.4(5)|
| Cl(2)| 24.6(7)| 19.8(5)| 16.8(6)| -5.0(4)| -1.6(6)| -0.1(6)|
| Cl(3)| 34.0(8)| 24.3(6)| 20.7(6)| -9.3(5)| 0.6(7)| 1.1(7)|
| C(3) | 18(3)| 18(3)| 17(3)| 0(2)| 3(2)| 1(2)|
| O(2) | 27(2)| 30.5(19)| 13.5(17)| 4.2(14)| 4.9(18)| 9(2)|
| Cl(4)| 13.7(5)| 29.2(8)| 34.0(8)| 0.8(13)| 0.4(6)| 4.3(6)|
| C(5) | 13(3)| 20(3)| 17(3)| -1(2)| -1(2)| -4(2)|
| Au(1)| 13.50(8)| 13.16(8)| 12.89(8)| -0.16(7)| -0.37(8)| 0.60(8)|
| S(1) | 20.7(6)| 15.7(5)| 15.3(6)| 1.8(4)| 2.6(6)| 0.6(5)|
| O(2) | 27(2)| 26(2)| 23(2)| 8.0(17)| 0.7(17)| -1.7(16)|
| C(2) | 19(3)| 28(3)| 25(3)| -1(3)| 4(2)| -2(2)|
### Table S.4. Bond Lengths for 1.

| Atom | Atom | Length/Å |
|------|------|----------|
| C(6) | O(2) | 1.465(6) |
| C(1) | S(1) | 1.794(4) |
| C(4) | C(3) | 1.520(7) |
| C(4) | C(5) | 1.514(7) |
| Cl(1) | Au(1) | 2.2886(11) |
| Cl(2) | Au(1) | 2.2855(12) |

### Table S.5. Bond Angles for 1.

| Atom | Atom | Atom | Angle/˚ |
|------|------|------|---------|
| C(5) | C(4) | C(3) | 109.1(4) |
| C(4) | C(3) | S(1) | 110.8(4) |
| C(5) | O(2) | C(6) | 116.2(4) |
| O(2) | C(5) | C(4) | 112.0(4) |
| O(1) | C(5) | C(4) | 124.3(5) |
| O(1) | C(5) | O(2) | 123.7(5) |
| Cl(1) | Au(1) | Cl(2) | 89.31(6) |
| Cl(3) | Au(1) | Cl(1) | 90.85(6) |

### Table S.6. Hydrogen Atom Coordinates (Å$x10^4$) and Isotropic Displacement Parameters (Å$^2$x10$^3$) for 1.

| Atom | x | y | z | U(eq) |
|------|---|---|---|-------|
| H(6A) | -1429.63 | 11826.54 | 4979.16 | 51 |
| H(6B) | -32.03 | 11046.42 | 5458.22 | 51 |
| H(6C) | -1593.26 | 10041.34 | 5183.65 | 51 |
| H(1A) | 5790.6 | 6163.25 | 2873.87 | 37 |
| H(1B) | 3802.7 | 6363.88 | 3016.23 | 37 |
| H(1C) | 5084.62 | 6086.23 | 3633.29 | 37 |
| H(4A) | 1735.2 | 9529.42 | 3522.35 | 25 |
| H(4AB) | 1908.38 | 7750.8 | 3744.69 | 25 |
| H(3A) | 4370.72 | 8391.32 | 4396.88 | 21 |
| H(3AB) | 4208.11 | 10155 | 4155.52 | 21 |
| H(2A) | 8142.8 | 8307.63 | 3273.31 | 36 |
| H(2B) | 7396.65 | 8045.3 | 4018.54 | 36 |
| H(2C) | 7625.49 | 9762.74 | 3730.01 | 36 |
Figure S.1. Unit cell content and thermal ellipsoid for structure 1 along the three crystallographic axis \( a \) (top), \( b \) (middle) and \( c \) (bottom). Color code: gray, carbon; whitish, hydrogen; ochre, gold; red, oxygen; yellow, sulfur.
Table S.7. Crystal data and structure refinement for 2.

| Identification code | 2 |
|---------------------|---|
| **Empirical formula** | C₇H₁₆NO₂Cl₄Au |
| **Formula weight** | 484.97 |
| **Temperature/K** | 296.15 |
| **Crystal system** | monoclinic |
| **Space group** | P2₁/c |
| **a/Å** | 7.7321(4) |
| **b/Å** | 21.1258(12) |
| **c/Å** | 8.6805(4) |
| **α/°** | 90 |
| **β/°** | 96.614(3) |
| **γ/°** | 90 |
| **Volume/Å³** | 1408.49(13) |
| **Z** | 4 |
| **ρ calc/g/cm³** | 2.287 |
| **μ/mm⁻¹** | 11.186 |
| **F(000)** | 912.0 |
| **Crystal size/mm³** | 0.04 × 0.04 × 0.04 |
| **Radiation** | MoKα (λ = 0.71073) |
| **2Θ range for data collection/°** | 6.958 to 65.576 |
| **Index ranges** | -11 ≤ h ≤ 11, -31 ≤ k ≤ 31, -11 ≤ l ≤ 12 |
| **Reflections collected** | 17266 |
| **Independent reflections** | 4646 [Rint = 0.0463, Rσ = 0.0507] |
| **Data/restraints/parameters** | 4646/0/140 |
| **Goodness-of-fit on F²** | 0.999 |
| **Final R indexes [I>=2σ (I)]** | R₁ = 0.0281, wR₂ = 0.0430 |
| **Final R indexes [all data]** | R₁ = 0.0443, wR₂ = 0.0464 |
| **Largest diff. peak/hole / e Å⁻³** | 0.87/-1.20 |
| **CCDC Number** | 2075038 |
Table S.8. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\AA^2 \times 10^3$) for 2. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{ij}$ tensor.

| Atom  | $x$     | $y$     | $z$     | $U_{eq}$ |
|-------|---------|---------|---------|----------|
| Au$^{[1]}$ | 3366.2(2) | 3364.8(2) | 4165.4(2) | 11.15(4) |
| Cl$^{[2]}$ | 3352.6(12) | 4154.5(4) | 2379.0(10) | 19.84(19) |
| Cl$^{[3]}$ | 2738(5) | 5025.2(17) | 6070(4) | 21.7(8) |
| Cl$^{[4]}$ | 3342.5(13) | 2551.7(4) | 5896.3(11) | 22.8(2) |
| Cl$^{[1]}$ | 469.4(12) | 3520.9(4) | 4272.7(11) | 20.13(19) |
| Cl$^{[2]}$ | 6298.6(12) | 3249.0(4) | 4128.1(12) | 20.35(19) |
| Cl$^{[3]}$ | 3342.5(13) | 2551.7(4) | 5896.3(11) | 22.8(2) |
| Cl$^{[4]}$ | 469.4(12) | 3520.9(4) | 4272.7(11) | 20.13(19) |
| Cl$^{[1]}$ | 6298.6(12) | 3249.0(4) | 4128.1(12) | 20.35(19) |
| C$^{[2]}$ | 9415(5) | 3157.4(19) | 8223(5) | 29.3(10) |
| C$^{[3]}$ | 8817(6) | 3734(2) | 10505(5) | 49.4(14) |
| C$^{[4]}$ | 8489(6) | 4262.8(19) | 7978(6) | 42.0(13) |
| C$^{[2]}$ | 9415(5) | 3157.4(19) | 8223(5) | 29.3(10) |
| Cl$^{[3]}$ | 3342.5(13) | 2551.7(4) | 5896.3(11) | 22.8(2) |
| Cl$^{[4]}$ | 469.4(12) | 3520.9(4) | 4272.7(11) | 20.13(19) |
| Cl$^{[1]}$ | 6298.6(12) | 3249.0(4) | 4128.1(12) | 20.35(19) |

Table S.9. Anisotropic Displacement Parameters ($\AA^2 \times 10^3$) for 2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^2U_{11}+2hka*b*U_{12}+\ldots].$

| Atom  | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|-------|----------|----------|----------|----------|----------|----------|
| Au$^{[1]}$ | 10.38(7) | 11.57(6) | 11.21(6) | 0.16(5) | -0.04(4) | -0.33(6) |
| Cl$^{[2]}$ | 24.3(5) | 17.9(4) | 17.4(4) | 5.2(3) | 2.6(4) | 0.2(4) |
| Cl$^{[3]}$ | 25(2) | 22(2) | 17.7(19) | -0.9(15) | -0.6(16) | 2.6(16) |
| Cl$^{[4]}$ | 11.6(4) | 24.8(5) | 24.0(5) | -0.9(4) | 2.4(4) | 0.5(3) |
| Cl$^{[1]}$ | 12.3(4) | 17.7(5) | 31.1(5) | -1.7(4) | 2.9(4) | 1.0(3) |
| C$^{[2]}$ | 27(2) | 35(2) | 26(2) | 6.0(18) | 5.5(19) | 16.5(19) |
| C$^{[3]}$ | 23(2) | 13.8(18) | 33(2) | 1.8(16) | -0.9(17) | -2.8(16) |
| C$^{[4]}$ | 49(3) | 65(4) | 29(3) | -23(2) | -22(2) | 25(3) |
| C$^{[1]}$ | 19(2) | 23(2) | 85(4) | 24(2) | 10(2) | -2.6(18) |
| N$^{[1]}$ | 15.7(17) | 19.9(16) | 16.8(17) | -1.8(12) | -0.7(13) | 1.1(13) |
| C$^{[5]}$ | 19(2) | 31(2) | 30(2) | 10.5(18) | 4.3(18) | 0.0(17) |
| O$^{[1]}$ | 15.0(14) | 18.5(13) | 18.3(13) | 0.8(10) | -0.1(11) | 4.8(10) |
| O$^{[2]}$ | 25.3(17) | 41.2(18) | 26.2(16) | 6.0(13) | 9.9(13) | 11.3(14) |
| C$^{[6]}$ | 13.0(19) | 15.6(18) | 26(2) | -1.8(15) | -0.6(16) | -2.7(14) |
### Table S.10. Bond Lengths for 2.

| Atom | Atom | Length/Å |
|------|------|----------|
| Au(1) | Cl(2) | 2.2768(8) |
| Au(1) | Cl(4) | 2.2837(9) |
| Au(1) | Cl(1) | 2.2765(9) |
| Au(1) | Cl(3) | 2.2844(9) |
| Cl(1) | Au(1) | 2.2765(8) |
| Cl(1) | Au(1) | 2.2837(9) |
| Cl(1) | Au(1) | 2.2765(9) |
| Cl(2) | Au(1) | 2.2844(9) |

### Table S.11. Bond Angles for 2.

| Atom | Atom | Atom | Angle/˚ |
|------|------|------|---------|
| Cl(2) | Au(1) | C(3) | 178.18(3) |
| Cl(2) | Au(1) | C(1) | 89.74(3) |
| Cl(3) | Au(1) | C(1) | 110.3(3) |
| Cl(4) | Au(1) | C(1) | 111.3(4) |
| Cl(4) | Au(1) | C(3) | 109.1(3) |
| Cl(4) | Au(1) | C(1) | 114.5(3) |
| Cl(4) | C(3) | N(1) | 115.7(3) |
| Cl(4) | C(3) | N(1) | 112.4(3) |
| Cl(4) | C(3) | N(1) | 125.4(3) |
| Cl(4) | N(1) | C(2) | 107.6(3) |

### Table S.12. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2.

| Atom | x | y | z | U(eq) |
|------|---|---|---|-------|
| H(7A) | 2093.13 | 5399.71 | 6263.14 | 33 |
| H(7B) | 2011.88 | 4744.91 | 5408.14 | 33 |
| H(7C) | 3740.54 | 5139.44 | 5574.5 | 33 |
| H(7D) | 6196.99 | 3298.17 | 7441.45 | 28 |
| H(7E) | 6299.74 | 3061.85 | 9156.88 | 28 |
| H(7F) | 8706.96 | 3334.52 | 11010.19 | 74 |
| H(7G) | 8079.87 | 4040.63 | 10921.66 | 74 |
| H(7H) | 1004.68 | 3874.08 | 10675.66 | 74 |
| H(7I) | 9687.7 | 4390.87 | 8122.65 | 63 |
| H(7J) | 7784.22 | 4583.84 | 8379.42 | 63 |
| H(7K) | 8125.68 | 4204.31 | 6892.25 | 63 |
| H(7L) | 4047.21 | 3684.47 | 9142.46 | 32 |
| H(7M) | 5505.39 | 4184.71 | 9658.35 | 32 |
Figure S.2. Unit cell content and thermal ellipsoid for structure 2 along the three crystallographic axis $a$ (top), $b$ (middle) and $c$ (bottom). Color code: gray, carbon; whitish, hydrogen; ocher, gold; red, oxygen; blue, nitrogen; yellow, sulfur.
Figure S.3. Representation (Mercury 4.3.1) of the network of hydrogen bonds (black dotted lines) involving AuCl₄⁻ anions in the crystal packing of 1 (left) and 2 (right). The S···Cl ChB in 1 is also depicted (brown dotted line) and the respective separation (pm) and angle (°) are reported.
**S3. Cambridge Structural Database (CSD) Survey.**

**Table S.13.** Number of structures in the CSD containing gold(III) anions.

| Anion         | Structures in CSD\(^a\) | Hits displaying close contact (percentage)\(^b\) |
|---------------|-------------------------|-----------------------------------------------|
| AuCl\(_4^\text{−}\) | 354                     | 103 (29%)                                     |
| AuBr\(_4^\text{−}\) | 71                      | 12 (17%)                                      |
| AuCN\(_4^\text{−}\) | 56                      | 19 (34%)                                      |

\(^a\) Total number of structures in the CSD containing the respective anion.  
\(^b\) Number of structures displaying a π-hole CIB, namely an Au···Nu close contact between the gold atom and a nucleophile (Nu = N, P, O, S, Se, F, Cl, Br, I; Cl/Br/C···Au···Nu angles spanning the range 80-100\(^\circ\)). The van der Waals radius for Gold(III) used for this survey is assumed 210 pm\(^4\). The percentage of total structures displaying a close contact is indicated in brackets.

**Table S.14.** REFCODEs of CSD structure containing the AuCl\(_4^\text{−}\) anion. In bold, the structures displaying an Au···Nu CIB (Nu=N, P, O, S, Se, F, Cl, Br, I; Cl···Au···Nu angles in the range 80-100\(^\circ\)).

| REFCODE     | Structure Refcode |
|-------------|-------------------|
| AZOREO01    | BICHIC18          |
| KOVVOJ      | BIBRUU            |
| ROQQAR01    | BOFSEV            |
| ROQQEV01    | BOGBIJ            |
| ZUKTEH      | BOKFIS            |
| ZUKTIL      | BOKQOK            |
| AFOAWAV     | BONFEQ            |
| AHIWEV      | BTURAN            |
| AHIYEX      | BUHZUB            |
| AHODUY      | BUVEU             |
| AHOFOU      | BUXDAA            |
| AHOGEL      | BUYMUD            |
| AHOGOU      | CAVVON            |
| AHOGOV      | CEMVEY            |
| AHOGB       | CERMOD            |
| ALEMUA      | CEMJUG            |
| ALIPIV      | CESNAQ            |
| ASABAX      | CETWUT            |
| ASABEB      | CEWREC            |
| ASABIF      | CICBIZ            |
| ASABOL      | CISZAF            |
| ASACAY      | CITKIA            |
| ASACEC      | CITKOG            |
| ASACIG      | CITKUM            |
| ASACOM      | COQBII            |
| AVAVAV      | CUZSOF            |
| AVEPEZ      | DEDKUS            |
| AYATEB      | DILJIR            |

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| AHOHAI | GEVAR | LONBUO | OWOBAF | WIMFUW | YIHIJJK |
|--------|-------|--------|--------|--------|----------|
| AHOFIA | EPAXOJ | LEYNOS | OWIQUI | VUWKEF | YIHIJAC  |
| ALAMOR | ECUXAB | JARLEW | OWIQIW | VAYZEA | YEYCOX   |
| ALAZIY | EPAXOJ | LEYNOS | OWIQUI | VUWKEF | YIHIJAC  |
| ALENOW | GEVAR | LONBUO | OWOBAF | WIMFUW | YIHIJJK  |
| AXECOX | HEDJEF | NOKRUC | OYOJOD | WOQMEU | YIHIJUW  |

Table S.15. REFCODEs of CSD structure containing the AuBr$_4^-$ anion. In bold, the structures displaying an Au···Nu ClB (Nu=N, P, O, S, Se, F, Cl, Br, I; Cl–Au···Nu angles in the range 80-100°).
Table S.16. REFCODEs of CSD structure containing the Au(CN)$_4$\(^{-}\) anion. In bold, the structures displaying an Au···Nu C\(_{\text{B}}\) (Nu=N, P, O, S, Se, F, Cl, Br, I; Cl–Au···Nu angles in the range 80-100°).

| CIKYUR  | GOXCOL | OBUTEN | OVAMII | VIKSIS01 | YEBZAI |
|---------|--------|--------|--------|----------|--------|
| CIKYUR01| IHOPOK | OTEVUF | OVAMOO | VIKSIS02 | YINXUP |
| CIKZAY  | IHOPUQ | OTEWAM | OVAMUU | VIKSOY   | YINYAW |
| CIKZAY01| IHOQAX | OTEWEQ | OVANAB | VIKSOY01 | YINYE  |
| DONYUA  | IHOQEB | OTEWII | OVANEF | VIKSUE   | YINYIE |
| EVIMED  | IHOQIF | OTEWOA | SEGKIZ | VIKSUE01 | YIRZIJ |
| GASBAG  | LIRZUI | OTEWUG | SEGKOF | VIKTAL   |        |
| GEFROZ  | LISBAR | OTEXAN | TUKHOX | VIKTAL01 |        |
| GEFROZ01| MUXXOS | OTEXER | VAZWOJ | VUZDEZ   |        |
| GOXCIF  | OBUTAJ | OTEXIV | VIKSIS | XIZCOY   |        |
S4. Theoretical Methods.

S.4.1. General Remarks.
The energetic features of the adducts analyzed in this work were calculated at the PBE0\(^{[5]}\)-D3\(^{[6]}\)/def2-TZVP\(^{[7]}\) level of theory using the crystallographic coordinates. The GAUSSIAN-16 program has been used for the energetic calculations and NBO analysis.\(^{[8]}\) The basis set superposition error for the calculation of interaction energies has been corrected using the counterpoise method.\(^{[9]}\) Molecular electrostatic potential (MEP) surfaces have been computed at the same level of theory and represented using several isovalues of electron density to map the electrostatic potential. The QTAIM analysis\(^{[10]}\) has been performed using the AIMAll program at the same level of theory.\(^{[11]}\) The NBOs have been represented using the formatted check point (fchk) files generated with Gaussian-16 and the keyword: pop=saveNBOs. The SAPT\(^{[11]}\) calculations have been performed at the PBE0/def2-TZVP level of theory by using the program MOLPRO.\(^{[12,13]}\) For a comprehensive explanation of SAPT see ref 11.

![MEP surfaces of compound 1 using 0.001 a.u. (a) and 0.008 a.u. (b) isovalues at the PBE0-D3/def2-TZVP level of theory. The values at some points of the surface are given in kcal·mol\(^{-1}\).](image)

**Figure S.4.** MEP surfaces of compound 1 using 0.001 a.u. (a) and 0.008 a.u. (b) isovalues at the PBE0-D3/def2-TZVP level of theory. The values at some points of the surface are given in kcal·mol\(^{-1}\).

S.4.2. SAPT calculations.
To further analyze the energetic features of the trimers of compounds 1 and 2, the interaction energies of the anion···anion and anion···cation dimers were decomposed by means of the symmetry adapted perturbation theory (SAPT). The SAPT terms are grouped into four chemically relevant categories: electrostatics, exchange-repulsion, induction and dispersion. The total SAPT energies of the dimers are similar to the dimerization energies shown in Figure 3 of the main text, thus giving reliability to the partition method. In compound 1 (see Figure S.5), the examination of the individual contributions to the interaction energy of the anion···anion dimer reveals that electrostatic is the largest repulsive term (51.5 kcal/mol, light blue bar) followed by the exchange (17.5 kcal/mol, red bar). The largest attractive term is the induction (−13.5 kcal/mol, dark blue bar).
The dispersion term is smaller (−3.9 kcal/mol, green bar) and similar to that derived from Grimme’s D3 dispersion correction (−4.5 kcal/mol). This contribution is computed as the difference of the binding energies calculated with and without dispersion correction. For the cation···anion dimer, the electrostatic term is the largest contribution (−61.6 kcal/mol) followed by the exchange (+15.9 kcal/mol), that is repulsive. The dispersion and induction terms are smaller and attractive (−6.3 and −8.4 kcal/mol). The contribution of dispersion evaluated using Grimme’s D3 method for the cation···anion dimer is also similar to that predicted by the SAPT. The large contributions of the electrostatic terms in both dimers are quite intuitive, due to the cationic/anionic nature of the monomers. It is important to highlight that the sum of the electrostatic contributions of both dimers is attractive (−10.1 kcal/mol).

![Figure S.5](image)

**Figure S.5.** SAPT decomposition of the interaction energy (in kcal/mol) for the anion···anion and anion···cation dimers of 1. The contribution of exchange (repulsion), electrostatic, induction and dispersion terms are indicated.

The different SAPT contributions computed for compound 2 (see Figure S.6) are parallel to those commented above for compound 1. Moreover, the dispersion terms obtained using SAPT and Grimme’s D3 methods are also similar, giving reliability to the SAPT results. The electrostatic terms are the most important ones in both dimers but of opposite sign, as expected. The sum of both electrostatic contributions is also favorable in this compound.

![Figure S.6](image)

**Figure S.6.** SAPT decomposition of the interaction energy (in kcal/mol) for the anion···anion and anion···cation dimers of 2. The contribution of exchange (repulsion), electrostatic, induction and dispersion terms are indicated.
S.4.3. NBO plots.
Figure S.7 shows the localized NBOs of compound 2 involved in the donor-acceptor interactions described in Figure 3 of the main text. The donor orbitals are p-type atomic orbitals (LPs) localized at the Cl and O atoms above and below the π-hole. The acceptor NBO is an Au p-atomic orbital perpendicular to the AuCl\textsuperscript{−} plane. The localized NBOs of compound 1 involved in the donor-acceptor interactions are the same.

Figure S.7. Plots of the NBOs involved in the donor-acceptor interactions.
Figure S.8. QTAIM distribution of intermolecular bond and ring critical points (red and yellow spheres, respectively) and bond paths for the binding of AuCl₄⁻ anion with the sulfonium moiety in compound 1. The density at the bond CPs that characterize the HBs and the ChB are given in italics (a.u.) The superimposed NCIplot isosurface (RDG isovalue = 0.4 a.u.) is shown. The cut-off $\rho = 0.04$ a.u. has been used. Color range $-0.02 \text{ a.u.} \leq (\text{sign}\lambda_2)\rho \leq 0.02$. Level of theory: PBE0-D3/def2-TZVP. The second order perturbation energies $E^{(2)}$ along with the donor and acceptor orbitals obtained from the NBO analysis are indicated.
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