Supporting Information

Cation- and Anion-Mediated Supramolecular Assembly of Bismuth and Antimony Tris(3-pyridyl) Complexes

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Contents

NMR studies and NMR spectra ........................................................................................................ 4

Figure S1. Compound 1, Sb(3-py)₃ .......................................................................................... 4
Figure S2. ¹H NMR spectrum of 1 .......................................................................................... 4
Figure S3. ¹³C(¹H) NMR spectrum of 1 .................................................................................. 4
Figure S4. ¹H–¹³C HSQC spectrum of 1 .................................................................................. 5
Figure S5. Selected region of the ¹H–¹³C HMBC spectrum of 1 ............................................... 5
Figure S6. Compound 2, Bi(3-py)₃ .......................................................................................... 6
Figure S7. ¹H NMR spectrum of 2 .......................................................................................... 6
Figure S8. ¹³C(¹H) NMR spectrum of 2 .................................................................................. 6
Figure S9. Stacked ¹H NMR spectra of 1 with THTAuCl ......................................................... 7
Figure S10. Stacked ¹H NMR spectra of 2 with THTAuCl ....................................................... 7

High resolution mass data ......................................................................................................... 8

Figure S11. HR-MS (MALDI-TOF) of 1 .................................................................................. 8
Figure S12. HR-MS (ESI-TOF) of 2 .......................................................................................... 8
Figure S13. HR-MS (ESI-TOF) of (1•AgBF₄) .......................................................................... 9
Figure S14. HR-MS (ESI-TOF) of 3,3'-bipyridine ................................................................... 9

X-ray Crystallographic Studies .................................................................................................. 10

Figure S15. Three-layer synthesis method to obtain crystals for X-ray diffraction studies ....... 10
Details of the refinement methods of the structures ..................................................................... 10

Figure S16. Compounds 1•CuBF₄ and 1•CuPF₆ .................................................................... 11
Figure S17. Compounds 1•AgBF₄, 1•AgPF₆, 1•AgSbF₆ and 1•AgOTf .................................... 12
Figure S18. Compounds 2•CuPF₆ and 2•AgSbF₆ ................................................................. 13
Figure S19. Values for the angle N–M–Sb for the Sb and Bi MOFs ........................................ 14
Figure S20. Values of ΣMα for the Sb and Bi MOFs ............................................................... 14
Table S1. Void volumes of the cage units .................................................................................. 15
Figure S21. Representation of the of the void volumes the Sb MOFs ....................................... 15
Figure S22. Linear relationship observed between the cage volume and anion volume .......... 16
Table S2. Crystallographic data ............................................................................................... 17
Table S3. Selected bond length and angles ............................................................................. 20

Powder X-ray studies ................................................................................................................. 21

Figure S23. Comparison of the experimental and the predicted XRPD patterns for 1•CuBF₄ ... 21
Figure S24. Comparison of the experimental and the predicted XRPD patterns for 1•CuPF₆ ... 21
Figure S25. Comparison of the experimental and the predicted XRPD patterns for 1•AgBF₄ ... 22
Figure S26. Comparison of the experimental and the predicted XRPD patterns for 1•AgPF₆ ... 22
Figure S27. Comparison of the experimental and the predicted XRPD patterns for 1•AgSbF₆ ... 23
Figure S28. Comparison of the experimental and the predicted XRPD patterns for 1•AgOTf.

Figure S29. Comparison of the experimental and the predicted XRPD patterns for 2•CuPF₆.

Figure S30. Comparison of the experimental and the predicted XRPD patterns for 2•AgSbF₆.

Figure S31. Comparison of the experimental and the predicted XRPD patterns for 2•CuBF₄.

Figure S32. Comparison of the experimental and the predicted XRPD patterns for 2•LiBr.

Figure S33. Experimental XRPD pattern for the yellow insoluble solid obtained from the reaction of equimolar amounts of 2 and CuBr.

Emission studies for selected copper complexes .................................................................27

Figure S34. Emission spectra of 1•CuPF₆ and 2•CuPF₆ ............................................................27

Figure S35. Emission spectra of 1•CuPF₆, 1•CuBF₄ and 2•CuPF₆ ...........................................27

Table S4. Excitation and emission data (nm) for crystal powders of 1•CuPF₆ and 2•CuPF₆ ...28

Figure S36. Exponential components analysis for 1•CuPF₆ ....................................................28

Figure S37. Exponential components analysis for 2•CuPF₆ .....................................................28

Computational details ..........................................................................................................29

Table S5. Bi-Ag distance for various functionals .................................................................29

Table S6. Energy of the E-M interaction and composition of the orbital involved ..........29

Figure S38. Simple model of the Bi MOF 2•AgSbF₆ .................................................................30

References ...........................................................................................................................37
NMR studies and NMR spectra

Figure S1. Compound 1, Sb(3-py)₃, with the atom labelling used in the NMR studies.

Figure S2. ¹H NMR (298 K, CDCl₃, 500 MHz) spectrum of 1.

Figure S3. ¹³C(¹H) NMR (298 K, CDCl₃, 100.5 MHz) spectrum of 1.
Figure S4. $^1$H–$^{13}$C HSQC (298 K, CDCl$_3$) spectrum of 1.

Figure S5. Selected region of the $^1$H–$^{13}$C HMBC (298 K, CDCl$_3$) spectrum of 1 used for the identification of the Sb–C bonded carbon ($C_3$) (signal at 131.95 ppm).
Figure S6. Compound 2, Bi(3-py)$_3$, with the atom labelling used in the NMR studies.

Figure S7. $^1$H NMR (298 K, CDCl$_3$, 500 MHz) spectrum of 2.

Figure S8. $^{13}$C($^1$H) NMR (298 K, CDCl$_3$, 100.5 MHz) spectrum of 2.
Figure S9. Stacked $^1$H NMR spectra of the evolution of a sample of an equimolar amount of 1 and THTAuCl in DMSO-$d_6$ over 2 hours, 1 day and 2 weeks at r.t. After 2 weeks the appearance of 3,3-bipyridine (in blue), along with other unidentified species, was observed.

Figure S10. Stacked $^1$H NMR spectra of the evolution of a sample of an equimolar amount of 2 and THTAuCl in DMSO-$d_6$ over 2 hours, 1 day and 2 weeks at r.t. After 2 weeks the appearance of 3,3-bipyridine and free pyridine, along with small amounts of other unidentified species, was observed.
High resolution mass data

Figure S11. HR-MS (MALDI-TOF) of 1.

Figure S12. HR-MS (ESI-TOF) of 2.
The study of the extended supramolecular complexes by mass spectrometry proved challenging and not very informative. An illustrative example is given below only for the case of 1•AgBF₄⁺, for which the fragment [1+Ag]⁺ was identified.

**Figure S13. HR-MS (ESI-TOF) of (1•AgBF₄).**

**Figure S14. HR-MS (ESI-TOF) indicating the formation of 3,3'-bipyridine from the reaction crude of 1 with AuCl(THT). The identification of the formation of 3,3'-bipyridine in the reaction mixture was also done by ¹H NMR (see Fig S9).**
As a general procedure, X-ray quality crystals were obtained by slow diffusion of a solution of the corresponding metal precursor (1 equivalent in 5 mL MeCN) into a DCM solution of 1 or 2 (typically 25–50 mg). In order to increase the quality of the crystals, the process can be slowed by placing an intermediate layer of MeCN (ca. 3 mL) between the other two to obtain a more controlled diffusion (Fig. S15). This leads to better quality crystals.

Figure S15. Three-layer synthesis method to obtain high-quality crystals for single-crystal X-ray diffraction studies.
Details of the data collections and structural refinements are given in Table S2. Further details of the methods of refinement of the structures are as follows.

1•CuBF₄ and 1•AgBF₄: The BF₄⁻ anions were disordered and very poorly resolved (disordered by symmetry, on special positions) and they were treated as a rigid body with their site occupancies in the asymmetric unit constrained to 1/4 (for the BF₄⁻ in the void) and 1/12 (for the BF₄⁻ in the cage), to produce a total of 8 BF₄⁻ anions in the unit cell (2 in the cage and 6 in the exo voids, as in the related structures with PF₆⁻ and SbF₆⁻ anions discussed in the main text). The structure is charge balanced, with 8 Cu⁺ and 8 BF₄⁻ in the unit cell. Restraints were applied to maintain sensible bond distances and geometry, and the BF₄⁻ anions were treated as a rigid body for the final refinement cycles. Rigor restraints were applied to keep the ADPS of the disordered BF₄⁻ anions to a reasonable value. The presence of BF₄⁻ in the crystal was also assigned on the basis of the additional characterization information, as described in the main text, including ¹⁹F NMR and elemental analysis.

1•AgOTf: The framework structure is clear; however, the OTf⁻ anions are not clearly resolved and therefore SQUEEZE¹ was applied (i.e., removing the disordered OTf anions). SQUEEZE was applied accounting for 566 electrons in a total solvent accessible volume of 1054 cubic angstroms per unit cell. This is consistent with the presence of 8 triflates (CF₃SO₃⁻) per unit cell (i.e., 1 CF₃SO₃ per formula unit), located in 8 voids (2 cages and 6 exo voids), which account for 592 electrons per unit cell. This is also consistent with the expected stoichiometry (i.e., one CF₃SO₃⁻ per Ag⁺ cation), as well as with the elemental analysis. The presence of OTf⁻ in the crystal was also determined by ¹⁹F NMR.

X-ray diffraction structures

Figure S16. Compounds 1•CuBF₄ and 1•CuPF₆: (left) Schematic representation of the formation of the monomeric cubane unit. (center) Crystal structure showing the heterocubane monomeric unit [Cu(1)([Cu]X)][X= BF₄⁻ or PF₆⁻] of the 3D-MOF. In the case of 1•CuBF₄, disordered BF₄⁻ anions are omitted for clarity. (right) Wireframe X-ray structure along the a, b or c axis of the 3D structure of the compound MOFs. Displacement ellipsoids at 50% probability. H atoms are omitted for clarity. Colour key: C (gray), Cu (orange), P (light orange), Sb (light purple), N (blue) and F (yellow).
Figure S17. Compounds 1•AgBF₄, 1•AgPF₆, 1•AgSbF₆ and 1•AgOTf: (left) Schematic representation of the formation of the monomeric cubane unit. (center) Crystal structure showing the heterocubane monomeric unit [Ag(1)(X)]³⁺ (X = BF₄, PF₆, SbF₆ or OTf) of the 3D-MOF. In the cases of 1•AgBF₄ and 1•AgOTf, disordered BF₄⁻ and OTf⁻ anions, respectively, are omitted for clarity. In the case of 1•AgOTf, the OTf⁻ anions were not clearly resolved and therefore SQUEEZE was applied (see details above). Wireframe X-ray structure along the a, b or c axis of the 3D structure of the compound MOFs. Displacement ellipsoids at 50% probability. H atoms are omitted for clarity. Colour key: C (gray), Ag (light gray), P (light orange), Sb (light purple), N (blue) and F (yellow).
Figure S18. Compounds 2•CuPF$_6$ and 2•AgSbF$_6$: (left) Schematic representation of the formation of the monomeric cubane unit. (center) Crystal structure showing the heterocubane monomeric unit [M(1)(⊂X)]$^{3+}$ (M = Cu or Ag) (X = PF$_6$ or SbF$_6$) of the 3D-MOF. (right) Wireframe X-ray structure along the a, b or c axis of the 3D structure of the compound MOFs. Displacement ellipsoids at 50% probability. H atoms are omitted for clarity. Colour key: C (gray), Ag (light gray), Cu (orange), P (light orange), Sb (light purple), N (blue), Bi (purple) and F (yellow).
Analysing the X-ray structures of the MOFs, we found that in those containing the Sb ligand, the pyramidalization of the metal atom (Cu or Ag) was much greater than that in those containing the Bi ligand. The N–M–Sb (M = Cu, Ag) angle varies between 108.3 and 112.6° (Fig. S19 left), while the N–M–Bi (M = Cu, Ag) angle takes the values 93.7 and 96.0° (Fig. S19 right). The rather unusual, almost planar coordination of the pyridyl-N atoms of the Bi-ligand to the Cu(I) and Ag(I) centers can be seen from the sums of the N–M–N bond angles ($\sum M\alpha$, $M = Cu, Ag$), which are very close to 360 (Fig S20, right).

**Figure S19.** (Left) Values for the angle N–M–Sb ($M = Cu, Ag$) for the Sb MOFs obtained from the corresponding X-ray structures. (Right) Values for the angle N–M–Bi ($M = Cu, Ag$) for the Bi MOFs obtained from the corresponding X-ray structures.

| Compound | N-M-Sb  |
|----------|---------|
| 1•CuBF$_4$ | 108.3(2) |
| 1•CuPF$_6$ | 108.9(2) |
| 1•AgBF$_4$ | 111.4(2) |
| 1•AgPF$_6$ | 112.3(2) |
| 1•AgSbF$_6$ | 112.6(2) |
| 1•AgOTf | 111.6(2) |

| Compound | N-M-Bi  |
|----------|---------|
| 2•CuPF$_6$ | 96.0(2) |
| 2•AgSbF$_6$ | 93.7(5) |

**Figure S20.** (Left) Values of the summation of the three angles N–M–N ($\sum M\alpha$) ($M = Cu, Ag$) for the Sb MOFs obtained from the corresponding X-ray structures. (Right) Values for the summation of the three angles N–M–N ($\sum M\alpha$) ($M = Cu, Ag$) for the Bi MOFs obtained from the corresponding X-ray structures.

| Compound | $\sum M\alpha$ |
|----------|----------------|
| 1•CuBF$_4$ | 331.8 |
| 1•CuPF$_6$ | 330.0 |
| 1•AgBF$_4$ | 322.5 |
| 1•AgPF$_6$ | 319.5 |
| 1•AgSbF$_6$ | 318.6 |
| 1•AgOTf | 321.9 |

| Compound | $\sum M\alpha$ |
|----------|----------------|
| 2•CuPF$_6$ | 356.7 |
| 2•AgSbF$_6$ | 358.8 |
**Void analysis**

| Compound     | Cage void volume [Å³] | Anion volume [Å³] |
|--------------|------------------------|-------------------|
| 1•CuBF₄     | 125.5                  | 53.4              |
| 1•CuPF₆     | 138.4                  | 73.0              |
| 1•AgBF₄     | 102.8                  | 53.4              |
| 1•AgPF₆     | 113.0                  | 73.0              |
| 1•AgSbF₆    | 116.1                  | 88.7              |
| 1•AgOTf     | 123.5                  | 86.9              |

Table S1. Void volumes of the cage units for the Sb MOFs and anion volume for the corresponding anion (as determined using quantum-chemical calculations according to ref. 45 in the main manuscript).

*Figure S21. Representation of the void volumes of the cage units for the Sb MOFs depending on the encapsulated anion.*
Figure S22. Linear relationship observed between the cage volume and anion volume (ref. 45 in the main manuscript) for $1\cdot$AgBF$_4$, $1\cdot$AgPF$_6$ and $1\cdot$AgSbF$_6$ (according to this correlation, $1\cdot$AgOTf would have an anion volume closer to 105 Å$^3$).
Table S2. Crystallographic data

| Identification code | 1             | 2             | 1•CuBF₄        | 1•CuPF₆        | 1•AgBF₄        |
|---------------------|---------------|---------------|----------------|----------------|----------------|
| CCDC Number         | 2110784       | 2110788       | 2110793        | 2110786        | 2110792        |
| Empirical formula   | C₁₅H₁₂N₁Sb   | C₁₅H₁₂BiN₃   | C₁₅H₁₂CuF₄N₁Sb| C₁₅H₁₂CuF₆N₁PSb| C₁₅H₁₂AgBF₄N₁Sb|
| Formula weight      | 356.03        | 443.26        | 506.38         | 564.54         | 550.71         |
| Temperature [K]     | 180(2)        | 293(2)        | 293(2)         | 293(2)         | 293(2)         |
| Crystal system      | monoclinic    | monoclinic    | cubic          | cubic          | cubic          |
| Space group         | P2₁/c         | I2/a          | P-43n          | P-43n          | P-43n          |
| a [Å]               | 28.1372(11)   | 12.2816(5)    | 15.08330(11)   | 15.2117(2)     | 15.3710(2)     |
| b [Å]               | 8.0071(3)     | 8.1825(4)     | 15.08330(11)   | 15.2117(2)     | 15.3710(2)     |
| c [Å]               | 12.2521(5)    | 28.5136(14)   | 15.08330(11)   | 15.2117(2)     | 15.3710(2)     |
| α [°]               | 90            | 90            | 90             | 90             | 90             |
| β [°]               | 96.259(4)     | 98.764(4)     | 90             | 90             | 90             |
| γ [°]               | 90            | 90            | 90             | 90             | 90             |
| V [Å³]              | 2743.91(18)   | 2832.0(2)     | 3431.54(8)     | 3519.92(14)    | 3631.69(14)    |
| Z                   | 8             | 8             | 8              | 8              | 8              |
| ρcalc [g/cm³]       | 1.724         | 2.079         | 1.960          | 2.131          | 2.014          |
| μ [mm⁻¹]            | 2.000         | 12.440        | 2.856          | 2.900          | 2.606          |
| F(000)              | 1392.0        | 1648.0        | 1952.0         | 2176.0         | 2096.0         |
| Crystal size [mm³]  | 0.30 × 0.23 × 0.07 | 0.34 × 0.22 × 0.08 | 0.19 × 0.16 × 0.09 | 0.18 × 0.16 × 0.08 | 0.23 × 0.19 × 0.11 |
| Radiation           | MoKα          | MoKα          | MoKα           | MoKα           | MoKα           |
| 2θ range for data collection [°] | 6.69 to 52.758 | 6.604 to 59.108 | 6.616 to 58.864 | 6.56 to 53.484 | 6.492 to 59.166 |
| Reflections collected | 13954        | 11651         | 36007          | 23475          | 30433          |
| Independent reflections | 5586 [Rint = 0.0299, Rsigma = 0.0431] | 3524 [Rint = 0.0397, Rsigma = 0.0394] | 1586 [Rint = 0.0363, Rsigma = 0.0143] | 1255 [Rint = 0.0402, Rsigma = 0.0143] | 1671 [Rint = 0.0388, Rsigma = 0.0182] |
| Data/restraints/parameters | 5586/0/343 | 3524/0/172 | 1586/60/133 | 1255/3/83 | 1671/60/133 |
| GOF on F²           | 1.009         | 1.035         | 1.112          | 1.063          | 1.032          |
| Final R indexes [I > 2σ (I)] | R₁ = 0.0374, wR₂ = 0.0845 | R₁ = 0.0280, wR₂ = 0.0494 | R₁ = 0.0405, wR₂ = 0.1093 | R₁ = 0.0383, wR₂ = 0.1197 | R₁ = 0.0421, wR₂ = 0.1181 |
| Final R indexes [all data] | R₁ = 0.0544, wR₂ = 0.0952 | R₁ = 0.0391, wR₂ = 0.0546 | R₁ = 0.0562, wR₂ = 0.1185 | R₁ = 0.0471, wR₂ = 0.1297 | R₁ = 0.0847, wR₂ = 0.1470 |
| Max/min Δρ [eÅ⁻³]  | 2.32/-0.63 | 0.95/-1.25 | 0.45/-1.14 | 0.57/-1.40 | 0.32/-0.82 |
| Flack parameter     | -             | -             | 0.005(12)      | -0.027(16)     | 0.01(2)        |

S17
| Identification code | 1•AgPF₆ | 1•AgSbF₆ | 1•AgOTf | 2•CuPF₆ | 2•AgSbF₆ |
|---------------------|--------|--------|--------|--------|--------|
| CCDC Number         | 2110782| 2110787| 2110783| 2110791| 2110785|
| Empirical formula   | C₁₃H₁₂AgF₆N₆P₂Sb | C₁₃H₁₂AgF₆N₆Sb₂ | AgCuS₆F₁₂H₂N₂O₄S₆S₆ | C₁₃H₁₂BiCuF₆N₆P | C₁₃H₁₂N₆F₆AgSbBi |
| Formula weight      | 608.87 | 699.65 | 612.97 | 651.77 | 786.88 |
| Temperature [K]     | 293(2) | 293(2) | 293(2) | 220(2) | 220(2) |
| Crystal system      | cubic  | cubic  | cubic  | cubic  | cubic  |
| Space group         | P-43n  | P-43n  | P-43n  | P-43n  | P-43n  |
| a [Å]               | 15.5531(3) | 15.7019(3) | 15.72180(15) | 15.30475(19) | 15.7606(6) |
| b [Å]               | 15.5531(3) | 15.7019(3) | 15.72180(15) | 15.30475(19) | 15.7606(6) |
| c [Å]               | 15.5531(3) | 15.7019(3) | 15.72180(15) | 15.30475(19) | 15.7606(6) |
| α [°]               | 90      | 90      | 90      | 90      | 90      |
| β [°]               | 90      | 90      | 90      | 90      | 90      |
| γ [°]               | 90      | 90      | 90      | 90      | 90      |
| V [Å³]              | 3762.3(2) | 3871.3(2) | 3886.03(11) | 3584.92(13) | 3914.9(4) |
| Z                   | 8       | 8       | 8       | 8       | 8       |
| pcalc[g/cm³]        | 2.150   | 2.401   | 2.095   | 2.415   | 2.670   |
| μ [mm⁻¹]            | 2.623   | 3.833   | 2.556   | 11.144  | 11.388  |
| F(000)              | 2320.0 | 2608.0 | 2352.0 | 2432.0 | 2864.0 |
| Crystal size [mm³]  | 0.29 × 0.22 × 0.12 | 0.37 × 0.26 × 0.24 | 0.34 × 0.27 × 0.22 | 0.20 × 0.16 × 0.08 | 0.12 × 0.10 × 0.08 |
| Radiation           | MoKα   | MoKα   | MoKα   | MoKα   | MoKα   |
| 2θ range for data   | 7.41 to 59.384 | 7.34 to 58.422 | 7.332 to 59.504 | 6.52 to 59.09 | 7.312 to 51.332 |
| collection [°]      | 3730   | 4105   | 27599  | 25132  | 3273   |
| Reflections collected| 1443 | 1502 | 1753 | 1641 | 1181 |
| Independent reflections | Rint = 0.0294, Rsigma = 0.0397 | Rint = 0.0296, Rsigma = 0.0368 | Rint = 0.0347, Rsigma = 0.0156 | Rint = 0.0445, Rsigma = 0.0228 | Rint = 0.0581, Rsigma = 0.0711 |
| Data/restraint s/parameters | 1443/0/83 | 1502/0/83 | 1753/0/61 | 1641/0/83 | 1181/0/83 |
| GOF on F²            | 1.043  | 1.076  | 1.067  | 1.064  | 1.064  |
| Final R indexes [l=2θ (ii)] | R₁ = 0.0375, wR₂ = 0.0835 | R₁ = 0.0344, wR₂ = 0.0729 | R₁ = 0.0436, wR₂ = 0.1092 | R₁ = 0.0291, wR₂ = 0.0677 | R₁ = 0.0497, wR₂ = 0.0951 |
| Final R indexes [all data] | R₁ = 0.0657, wR₂ = 0.1009 | R₁ = 0.0529, wR₂ = 0.0822 | R₁ = 0.0633, wR₂ = 0.1200 | R₁ = 0.0512, wR₂ = 0.0764 | R₁ = 0.0992, wR₂ = 0.1195 |
| Max/min Δρ [eÅ⁻³]   | 0.34/-0.93 | 0.57/-1.51 | 1.10/-1.01 | 0.64/-1.12 | 0.66/-1.95 |
| Flack parameter      | -0.10(5) | -0.01(4) | 0.00(2) | -0.006(7) | -0.032(12) |
| Identification code | 2•CuBF₄ | 2•LiBr•MeCN |
|---------------------|---------|------------|
| CCDC Number         | 2110789 | 2110790    |
| Empirical formula   | C₃₀H₂₄Bi₂CuF₄N₆ | C₁₇H₁₅BiBrLIN₄ |
| Formula weight      | 1036.86 | 571.16     |
| Temperature [K]     | 180(2)  | 180(2)     |
| Crystal system      | triclinic | triclinic |
| Space group         | P-1     | P-1        |
| a [Å]               | 9.3481(9) | 9.2995(4) |
| b [Å]               | 13.8529(13) | 9.6180(4) |
| c [Å]               | 14.0214(13) | 11.2939(5) |
| α [°]               | 113.223(4) | 99.809(2) |
| β [°]               | 105.177(3) | 97.8330(10) |
| γ [°]               | 99.420(4) | 108.493(2) |
| V [Å³]              | 1535.8(3) | 924.20(7) |
| Z                   | 2       | 2          |
| ρcalc[g/cm³]        | 2.242   | 2.052      |
| μ [mm⁻¹]            | 12.172  | 11.704     |
| F(000)              | 964.0   | 532.0      |
| Crystal size [mm³]  | 0.15 × 0.03 × 0.02 | 0.1 × 0.1 × 0.08 |
| Radiation           | MoKα    | MoKα       |
| 2θ range for data collection [°] | 4.728 to 48.944 | 6.448 to 55.028 |
| Refractions collected | 29918   | 28433      |
| Independent reflections | 5064 [Rint = 0.0673, Rsigma = 0.0439] | 4181 [Rint = 0.0636, Rsigma = 0.0377] |
| Data/restraints/parameters | 5064/0/397 | 4181/0/219 |
| GOF on F²           | 1.069   | 1.049      |
| Final R indexes [I>=2σ (I)] | R₁ = 0.0392, wR₂ = 0.0873 | R₁ = 0.0200, wR₂ = 0.0463 |
| Final R indexes [all data] | R₁ = 0.0539, wR₂ = 0.0960 | R₁ = 0.0229, wR₂ = 0.0472 |
| Max/min Δρ [eÅ⁻³]   | 4.14/−2.13 | 0.99/−1.06 |
| Flack parameter     | -       | -          |
Table S3. Selected bond length and angles.

|       | 1•AgSbF₆  | 1•AgOTf | 2•AgSbF₆  | 2•CuBF₄  | 2•LiBr•MeCN |
|-------|-----------|---------|-----------|----------|-------------|
| **Epy-E** | 2126(8)   | 2115(8) | 2239(8)   | 226(2)   | 2261(4)-2.26(1) |
| **Epy-Epy** | 100.4(3)  | 100.8(3) | 94.3(3)   | 93.9(8)  | 91.5(5)-95.3(5) |
| **M--E** | 2684(9)   | 27092(9) | 3041(2)   | 3178(2)  | -            |
| **N-M** | 2305(8)   | 2310(8)  | 1987(6)   | 221(2)   | 203(1)-2.07(1) |
| **Npy-M-Npy** | 106.2(3)  | 107.3(3) | 118.9(3)  | 119.6(7) | 105.7(4)-114.9(4) |

(E=Sb,Bi; M=Cu,Ag,Li)
Powder X-ray studies

Figure S23. Comparison of the experimental (above, red) and the predicted (below, blue) XRPD patterns for compound $1\cdot\text{CuBF}_4$.

Figure S24. Comparison of the experimental (above, red) and the predicted (below, blue) XRPD patterns for compound $1\cdot\text{CuPF}_6$. 

Figure S25. Comparison of the experimental (above, red) and the predicted (below, blue) XRPD patterns for compound 1•AgBF₄.

Figure S26. Comparison of the experimental (above, red) and the predicted (below, blue) XRPD patterns for compound 1•AgPF₆.
Figure S27. Comparison of the experimental (above, red) and the predicted (below, blue) XRPD patterns for compound 1•Ag$_2$SbF$_6$.

Figure S28. Comparison of the experimental (above, red) and the predicted (below, blue) XRPD patterns for compound 1•AgOTf.
Figure S29. Comparison of the experimental (above, red) and the predicted (below, blue) XRPD patterns for compound $2\cdot\text{CuPF}_6$.

Figure S30. Comparison of the experimental (above, red) and the predicted (below, blue) XRPD patterns for compound $2\cdot\text{AgSbF}_6$. 
Figure S31. Comparison of the experimental (above, red) and the predicted (below, blue) XRPD patterns for compound 2•CuBF₄.

Figure S32. Comparison of the experimental (above, red) and the predicted (below, blue) XRPD patterns for compound 2•LiBr•MeCN.
Figure S33. Experimental XRPD pattern for the yellow insoluble solid obtained from the reaction of equimolar amounts of 2 and CuBr, indicating a different outcome from the 3D-MOFs (see XRPD patterns for 3D MOFs shown previously).
Emission studies for selected copper complexes

Figure S34. (Left) Emission spectra (room temperature) of antimony MOF $\text{1}_\text{CuPF}_6$ and bismuth MOF $\text{2}_\text{CuPF}_6$ as crystal powders at room temperature. The samples were excited at $\lambda_{\text{exc}} = 375$ nm. (Right) Pictures of $\text{1}_\text{CuPF}_6$ and $\text{2}_\text{CuPF}_6$ after grinding the samples under natural light (above) and under UV lamp light at 365 nm (below). Note: In both cases, no changes were observed in the emission upon grinding the samples.

Figure S35. Emission spectra (room temperature, crystal powders) of antimony $\text{1}_\text{CuPF}_6$ and $\text{1}_\text{CuBF}_4$ MOFs and bismuth MOF $\text{2}_\text{CuPF}_6$. While changing the anion does not substantially change the emission spectra (cf. $\text{1}_\text{CuPF}_6$ and $\text{1}_\text{CuBF}_4$), changing the bridgehead has a larger impact on the luminescence properties of the MOF (cf. $\text{1}_\text{CuX}$ ($X = BF_4, PF_6$) and $\text{2}_\text{CuPF}_6$).
Table S4. Excitation and emission data (nm) (solid state, room temperature) for crystal powders of 1•CuPF₆ and 2•CuPF₆. Average lifetime \( \tau_{av} = \frac{A_1\tau_1 + A_2\tau_2}{A_1A_2} \). \( \tau_n \) = Natural lifetime. \( A_n \) = Intensity coefficient.

| Compound | \( \lambda_{exc} \) | \( \lambda_{emis} \) | \( \Phi \) (%) | \( \tau_{av} \) (ns) | \( \tau_n \); \( A_n \) |
|----------|----------------|---------------|--------------|----------------|----------------|
| 1•CuPF₆   | 375            | 570           | 8.0          | 7.58           | \( \tau_1 = 1.63; A_1 = 0.45 \) |
|           |                |               |              |                | \( \tau_2 = 8.52; A_2 = 0.55 \) |
| 2•CuPF₆   | 375            | 530           | 0.31         | 6.16           | \( \tau_1 = 1.50; A_1 = 0.33 \) |
|           |                |               |              |                | \( \tau_2 = 6.68; A_2 = 0.67 \) |

Figure S36. Exponential components analysis for 1•CuPF₆.

Figure S37. Exponential components analysis for 2•CuPF₆.
Computational details

All computations were carried out using the Gaussian16 package,\(^2\) in which the hybrid method of Austin, Petersson and Frisch with spherical atom dispersion terms (APFD) was applied.\(^3\) The triple zeta cc-pVTZ-PP basis set with effective core potentials was used for the heavy atoms (Sb, Bi, Cu, Ag),\(^4\)\(^–\)\(^7\) as found in the basis set exchange library,\(^8\) and 6-31G(d’) was used for the rest of the atoms. Geometry optimizations were performed without symmetry restrictions using the initial coordinates derived from X-ray data when available, and frequency analyses were performed to ensure that a minimum structure with no imaginary frequencies was achieved in each case. Energy Decomposition Analysis (EDA) was performed on the geometry optimized models and on the X-ray geometry models with the AOMix program.\(^9\),\(^10\) NBO analysis was performed with the NBO 7.0 program.\(^11\) The visualization of the calculation results was performed with GaussView 6.1.\(^12\)

Optimization of the model structure
The X-ray derived model structure of the compound 2•AgSbF\(_6\) was optimized without symmetry restrictions using various functionals, and, in all cases, the Bi-Ag distance was found to be shorter than in the X-ray structure.

| Functional | Bi-Ag distance (Å) |
|------------|--------------------|
| APFD       | 2.655              |
| B3LYP      | 2.869              |
| M06        | 2.962              |
| TPSSh      | 2.794              |
| X-ray      | 3.180              |

*Table S5. Bi-Ag distance (for compound 2•AgSbF\(_6\)) for various functionals.*

Study of the E \(\rightarrow\) M interaction
The energy of the E-M interaction was calculated using an Energy Decomposition Analysis (EDA) that was carried out on both the optimized structures and the X-ray derived structures. The composition of the orbitals involved in the interaction was studied using a NBO analysis.

| Compound     | M-E Distance (Å) | Sum of angles N-M-N | Energy E-M (kcal/mol) | Composition Lp(E) \(\rightarrow\) Lv(M) |
|--------------|------------------|---------------------|-----------------------|----------------------------------------|
| 1•CuPF\(_6\) (xray) | 2.596            | 324.6               | -34.2                 | 69% s + 31% p \(\rightarrow\) 100% s    |
| 1•CuPF\(_6\) (opt)  | 2.399            | 324.6               | -39.3                 | 67% s + 33% p \(\rightarrow\) 100% s    |
| 2•CuPF\(_6\) (xray) | 2.501            | 339.3               | -15.0                 | 79% s + 21% p \(\rightarrow\) 98% s     |
| 2•CuPF\(_6\) (opt)  | 2.501            | 339.3               | -39.3                 | 79% s + 21% p \(\rightarrow\) 99% s     |
| 1•AgSbF\(_6\) (xray) | 2.661            | 318.6               | -35.2                 | 66% s + 34% p \(\rightarrow\) 100% s    |
| 1•AgSbF\(_6\) (opt)  | 2.517            | 305.1               | -39.5                 | 67% s + 33% p \(\rightarrow\) 100% s    |
| 2•AgSbF\(_6\) (xray) | 3.178            | 358.8               | -14.1                 | 80% s + 20% p \(\rightarrow\) 98% s     |
| 2•AgSbF\(_6\) (opt)  | 2.655            | 341.4               | -27.0                 | 80% s + 20% p \(\rightarrow\) 98% s     |

*Table S6. Energy of the E-M interaction and composition of the orbital involved*
Figure S38. Simple model of the Bi MOF $\text{Bi}_2\text{AgSbF}_6$ by taking a fragment of the extended X-ray structure consisting of a $[\text{Ag(py)}]_3^+$ moiety attached to a $\text{Bi(3-py)}_3$ ligand.
### 1•CuPF$_6$ optimized structure coordinates

| Atom | X             | Y             | Z             |
|------|---------------|---------------|---------------|
| C    | 2.99164500    | -2.18789700   | -3.52081800   |
| N    | 0.69278900    | 1.73450300    | -2.15378600   |
| C    | 0.39895200    | 3.68478900    | -3.52081800   |
| C    | 0.00000000    | 2.43218400    | -3.06660200   |
| H    | -0.90711800   | 1.95643600    | -3.43348000   |
| C    | 1.82148600    | 2.27305800    | -1.66618500   |
| H    | 2.34592000    | 1.67897300    | -0.92109100   |
| C    | 1.57069400    | 4.24043100    | -3.00785600   |
| H    | 1.91102800    | 5.21929600    | -3.33947900   |
| C    | 2.29707400    | 3.51859100    | -2.06208500   |
| H    | 3.21497100    | 3.90952800    | -1.63071000   |
| Cu   | 0.00000000    | 0.00000000    | -1.44716500   |
| N    | -1.84851800   | -0.26727900   | -2.15378600   |
| C    | -3.39059700   | -1.49689200   | -3.52081800   |
| C    | -2.10633300   | -1.21609200   | -3.06660200   |
| H    | -1.24076500   | -1.76380500   | -3.43348000   |
| C    | -2.87926800   | 0.44092400    | -1.66618500   |
| H    | -2.62699300   | 1.19214000    | -0.92109100   |
| C    | -4.45766800   | -0.75995500   | -3.00785600   |
| H    | -5.47555700   | -0.95464900   | -3.33947900   |
| C    | -4.19551800   | 0.23014900    | -2.06208500   |
| H    | -4.99323600   | 0.82948200    | -1.63071000   |
| Sb   | 0.00000000    | 0.00000000    | 0.95150600    |
| N    | 1.15572900    | -1.46722500   | -2.15378600   |
| C    | 2.10633300    | -1.21609200   | -3.06660200   |
| H    | 2.14788200    | -0.19263100   | -3.43348000   |
| C    | 1.05778300    | -2.71398200   | -1.66618500   |
| H    | 0.28107300    | -2.87111200   | -0.92109100   |
| C    | 2.88697400    | -3.48047700   | -3.00785600   |
| H    | 3.56452900    | -4.26464700   | -3.33947900   |
| C    | 1.89844400    | -3.74849900   | -2.06208500   |
| H    | 1.77826500    | -4.73901000   | -1.63071000   |
| N    | 2.30271400    | 2.54575700    | 3.68426700    |
| C    | 0.86914700    | 1.67206300    | 1.94874900    |
| C    | 1.71349300    | 1.52616700    | 3.05781200    |
| H    | 1.92865000    | 0.53660800    | 3.46371100    |
| C    | 2.06103600    | 3.77366100    | 3.22248000    |
| H    | 2.55322400    | 4.58663500    | 3.75726300    |
| C    | 0.63595000    | 2.97040700    | 1.47606700    |
| H    | -0.00838400   | 3.14522900    | 0.61357100    |
| C    | 1.23696300    | 4.04368800    | 2.12732500    |
| H    | 1.07364100    | 5.06770600    | 1.79795500    |
| N    | -3.35604700   | 0.72133000    | 3.68426700    |
| C    | -1.88262300   | -0.0832900    | 1.94874900    |
| C    | -2.17844600   | 0.72084500    | 3.05781200    |
| H    | -1.42904100   | 1.40195500    | 3.46371100    |
| C    | -4.29860500   | -0.10192100   | 3.22248000    |
| H    | -5.24875500   | -0.08216100   | 3.75726300    |
| C    | -2.89042300   | -0.93445500   | 1.47606700    |
| H    | -2.71965600   | -1.57987600   | 0.61357100    |
| Element | X               | Y               | Z               |
|---------|-----------------|-----------------|-----------------|
| C       | -4.12041800     | -0.95060300     | 2.12732500      |
| H       | -4.92558300     | -1.60405300     | 1.79795500      |
| C       | 1.01347600      | -1.58873500     | 1.94874900      |
| N       | 1.05333400      | -3.26708700     | 3.68426700      |
| C       | 0.46495300      | -2.24701200     | 3.05781200      |
| H       | -0.49960800     | -1.93856400     | 3.46371100      |
| C       | 2.23756800      | -3.67174000     | 3.22248000      |
| H       | 2.69553000      | -4.50447500     | 3.75726300      |
| C       | 2.25447300      | -2.03595200     | 1.47606700      |
| H       | 2.72804100      | -1.56535400     | 0.61357100      |
| C       | 2.88345500      | -3.09308500     | 2.12732500      |
| H       | 3.85194200      | -3.46365400     | 1.79795500      |
| H       | -3.54583100     | -2.27808400     | -4.26077200     |
| H       | -0.19996300     | 4.20982200      | -4.26077200     |
| H       | 3.74579400      | -1.93173800     | -4.26077200     |

2•CuPF₆ optimized structure coordinates

| Element | X               | Y               | Z               |
|---------|-----------------|-----------------|-----------------|
| C       | -3.40837200     | -3.43613600     | 1.80523700      |
| Cu      | -1.74064700     | -0.00281400     | -0.00341000     |
| N       | -2.26424300     | 0.59888200      | -1.81843800     |
| C       | -3.36605500     | 0.13957200      | -3.89983100     |
| C       | -1.73580800     | 1.70452100      | -2.36676400     |
| H       | -1.08359700     | 2.28907400      | -1.72163700     |
| C       | -3.06777700     | -0.16426500     | -2.57619000     |
| H       | -3.47441600     | -1.04826200     | -2.08924100     |
| C       | -1.97762100     | 2.08524800      | -3.68191400     |
| H       | -1.51654300     | 2.98652700      | -4.07751200     |
| C       | -2.80833000     | 1.28605100      | -4.46570800     |
| H       | -3.01836300     | 1.55136200      | -5.49983000     |
| N       | -2.28032700     | 1.26896500      | 1.41866800      |
| C       | -3.41040800     | 3.28929300      | 2.05011200      |
| C       | -1.75488500     | 1.20265500      | 2.65242800      |
| H       | -1.09246300     | 0.36093800      | 2.84205200      |
| C       | -3.09612800     | 2.29532700      | 1.12998800      |
| H       | -3.49949500     | 2.30643400      | 0.11950200      |
| C       | -2.01203000     | 2.15209700      | 3.63500800      |
| H       | -1.55276500     | 2.05396000      | 4.61523900      |
| C       | -2.85572900     | 3.21836900      | 3.32793800      |
| H       | -3.07790500     | 3.98146500      | 4.07105900      |
| Bi      | 0.76055100      | -0.00234100     | 0.00418700      |
| N       | -2.27600200     | -1.87229300     | 0.38063500      |
| C       | -1.74314500     | -2.90433600     | -0.29273000     |
| H       | -1.07647400     | -2.64338800     | -1.11171700     |
| C       | -3.09644500     | -2.14040300     | 1.40888100      |
| H       | -3.50528700     | -1.27337900     | 1.92367400      |
| C       | -1.99783500     | -4.23159300     | 0.03372700      |
| H       | -1.53270000     | -5.02859400     | -0.54059800     |
| C       | -2.84653300     | -4.50395900     | 1.10548700      |
| H       | -3.06698200     | -5.53041000     | 1.39132600      |
| N       | 3.53471600      | 2.45106200      | -2.51642300     |
optimized structure coordinates

\[\begin{array}{ccc}
C & 1.85399000 & 0.92005800 \\
C & 3.15813600 & 2.15713800 \\
H & 3.70273700 & 2.67020700 \\
C & 2.89392300 & 1.83799200 \\
H & 3.23149900 & 2.09424700 \\
C & 2.13793700 & 1.25551500 \\
H & 1.87900200 & 1.05008300 \\
C & 1.46977700 & 0.63047400 \\
H & 0.66587700 & -0.07634400 \\
N & 3.55176600 & -3.40312200 \\
C & 1.85728500 & -1.94471000 \\
C & 3.16823000 & -4.33806800 \\
H & 3.71572400 & -5.28017700 \\
C & 2.90758600 & -2.23457200 \\
H & 3.25108500 & -1.48953200 \\
C & 2.13769000 & -4.16172800 \\
H & 1.87338600 & -4.95938900 \\
C & 1.46624500 & -2.94126600 \\
H & 0.65436000 & -2.77368300 \\
C & 1.84869600 & 1.02621500 \\
N & 3.52981900 & 0.97238000 \\
C & 3.14660900 & 2.19644000 \\
H & 3.68886700 & 2.63115500 \\
C & 2.89200400 & 0.40993400 \\
H & 3.23548700 & -0.58735000 \\
C & 2.12253500 & 2.91026200 \\
H & 1.85823100 & 3.90997600 \\
C & 1.45756100 & 2.30778700 \\
H & 0.65079500 & 0.40993400 \\
H & -4.02132200 & -0.51272900 \\
H & -4.07533200 & 4.10096700 \\
H & -4.07710700 & -3.59976400 \\
\end{array}\]
### 2•AgSbF₆ optimized structure coordinates

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| N       | 0.57126500 | 2.07063600 | -2.32792700|
| C       | 0.00000000 | 4.15079700 | -3.37778800|
| C       | -0.18903400| 2.78853900 | -3.16703000|
| H       | -0.97687400| 2.24005300 | -3.68001400|
| C       | 1.81608900 | 4.05647600 | -1.81063200|
| H       | 2.62195300 | 4.51614600 | -1.24417600|
| C       | 1.02238300 | 4.79804400 | -2.68424600|
| H       | 1.19682100 | 5.86316500 | -2.82293000|
| C       | 1.55435400 | 2.69780500 | -1.66639500|
| H       | 2.14092400 | 2.08267400 | -0.98729400|
| Ag      | 0.00000000 | 0.00000000 | -1.76583500|
| C       | 3.59469500 | -2.07539800| -3.37778800|
| N       | -2.07885600| -0.54058800| -2.32792700|
| C       | -3.59469500| -2.07539800| -3.37778800|
| C       | -2.32042900| -1.55797800| -3.16703000|
| H       | -1.45150600| -1.96602400| -3.68001400|
| C       | -4.42105500| -0.45545900| -1.81063200|
| H       | -5.22207400| 0.01260500 | -1.24417600|
| C       | -4.66641900| -1.51361200| -2.68424600|
| H       | -5.67606100| -1.89510500| -2.82293000|
| C       | -3.11354500| -0.00279300| -1.66639500|
| H       | -2.87411100| 0.81275800 | -0.98729400|
| Bi      | 0.00000000 | 0.00000000 | 0.88889800 |
| N       | 1.50759100 | -1.53004800| -2.32792700|
| C       | 2.50946300 | -1.23056200| -3.16703000|
| H       | 2.42837900 | -0.27402900| -3.68001400|
| C       | 2.60496700 | -3.60101700| -1.81063200|
| H       | 2.60012100 | -4.52875100| -1.24417600|
| C       | 3.64403600 | -3.28443200| -2.68424600|
| H       | 4.47923900 | -3.96806000| -2.82293000|
| C       | 1.55919100 | -2.69501300| -1.66639500|
| H       | 0.73318700 | -2.89543200| -0.98729400|
| N       | 2.22839500 | 2.70205200 | 3.67956000 |
| C       | 0.78865000 | 1.77933400 | 1.97841800 |
| C       | 1.69611500 | 1.65993200 | 3.03779900 |
| H       | 2.01255800 | 0.67714400 | 3.39046100 |
| C       | 0.96080500 | 4.16296100 | 2.24323000 |
| H       | 0.69247000 | 5.18132000 | 1.96912300 |
| C       | 0.41961900 | 3.06734600 | 1.57446400 |
| H       | -0.28230400| 3.22191300 | 0.75392200 |
| C       | 1.86037100 | 3.92166300 | 3.28401300 |
| H       | 2.30898200 | 4.75231200 | 3.82996100 |
| N       | -3.45424300| 0.57882000 | 3.67956000 |
| C       | -1.93527400| -0.20667600| 1.97841800 |
| C       | -2.28560100| 0.63891300 | 3.03779900 |
| H       | -1.59270300| 1.40435500 | 3.39046100 |
| C       | -4.08563200| -1.24939900| 2.24323000 |
| H       | -4.83339000| -1.99096400| 1.96912300 |
| C       | -2.86620900| -1.17027200| 1.57446400 |
| H       | -2.64910600| -1.85543900| 0.75392200 |
|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| C | -4.32644500 | -0.34970300 | 3.28401300 |
| H | -5.27011400 | -0.37651900 | 3.82996100 |
| C | 1.14662400  | -1.57265800 | 1.97841800 |
| N | 1.22584900  | -3.28087200 | 3.67956000 |
| C | 0.58948600  | -2.29884500 | 3.03779900 |
| H | -0.41985600 | -2.08149800 | 3.39046100 |
| C | 3.12482800  | -2.91356200 | 2.24323000 |
| H | 4.14092000  | -3.19035600 | 1.96912300 |
| C | 2.44659000  | -1.89707300 | 1.57446400 |
| H | 2.93141100  | -1.36647400 | 0.75392200 |
| C | 2.46607400  | -3.57196000 | 3.28401300 |
| H | 2.96113200  | -4.37579400 | 3.82996100 |
| H | 4.38209200  | -1.78677000 | -4.06957700 |
| H | -0.64365700 | 4.68838800  | -4.06957700 |
| H | -3.73843500 | -2.90161800 | -4.06957700 |
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