

**Elucidating the Structural Features of Aryl-BIAN Bismuth Complexes: A
Combined Single-Crystal X-Ray Diffraction and Hirschfeld Analysis
Approach**

Beatriz P. Machado ^{1,†}, Maria Celador-Garcia ^{1,†}, Vitor Rosa ^{1,*} and Clara S. B. Gomes ^{1,*}

¹ LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology,
NOVA University of Lisbon, 2829-516 Caparica, Portugal;

* Correspondence: clara.gomes@fct.unl.pt (C.S.B.G.); vitor.rosa@fct.unl.pt (V.R.)

† These authors contributed equally to this work

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Infrared spectra

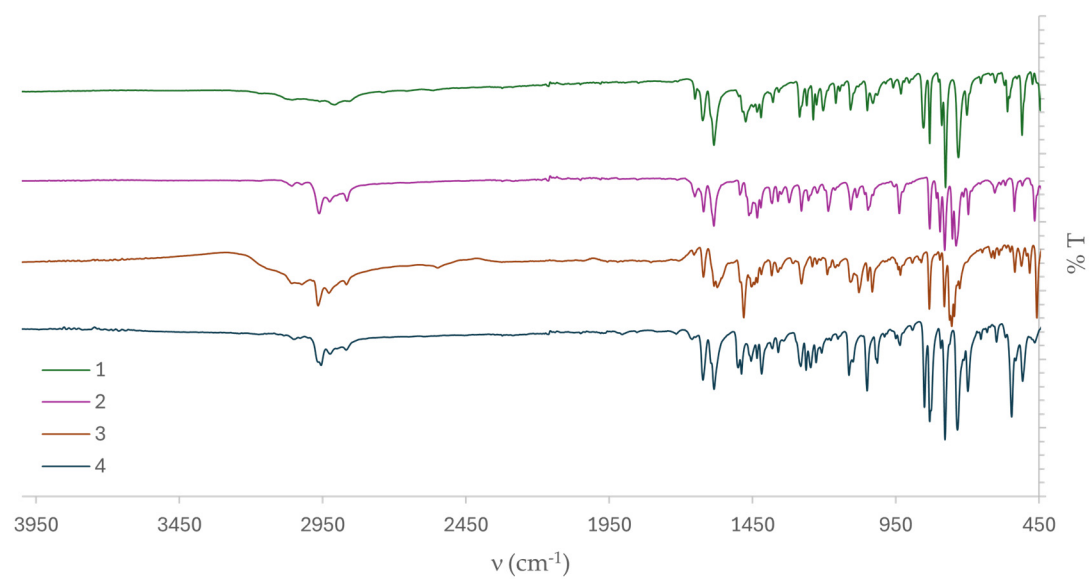


Figure S1. Stack of all FT ATR-IR spectra of complexes **1-4**.

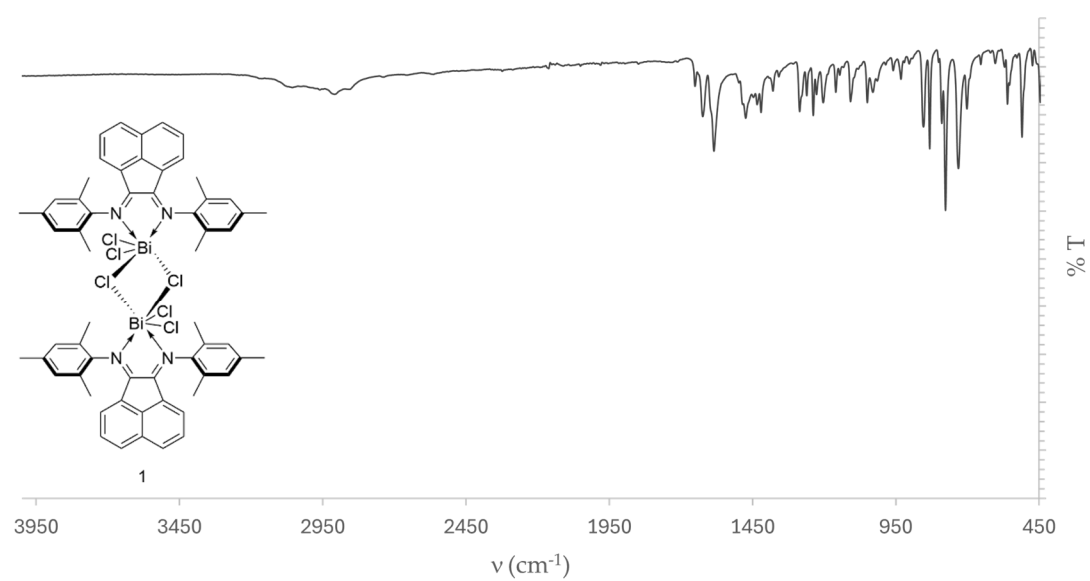


Figure S2. FT ATR-IR spectrum of complex **1**.

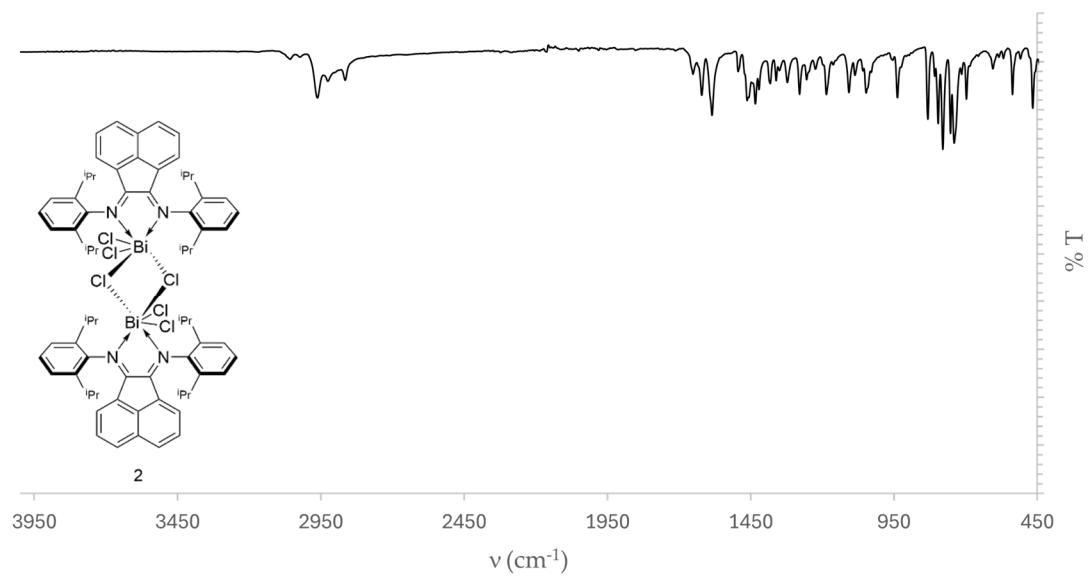


Figure S3. FT ATR-IR spectrum of complex **2**.

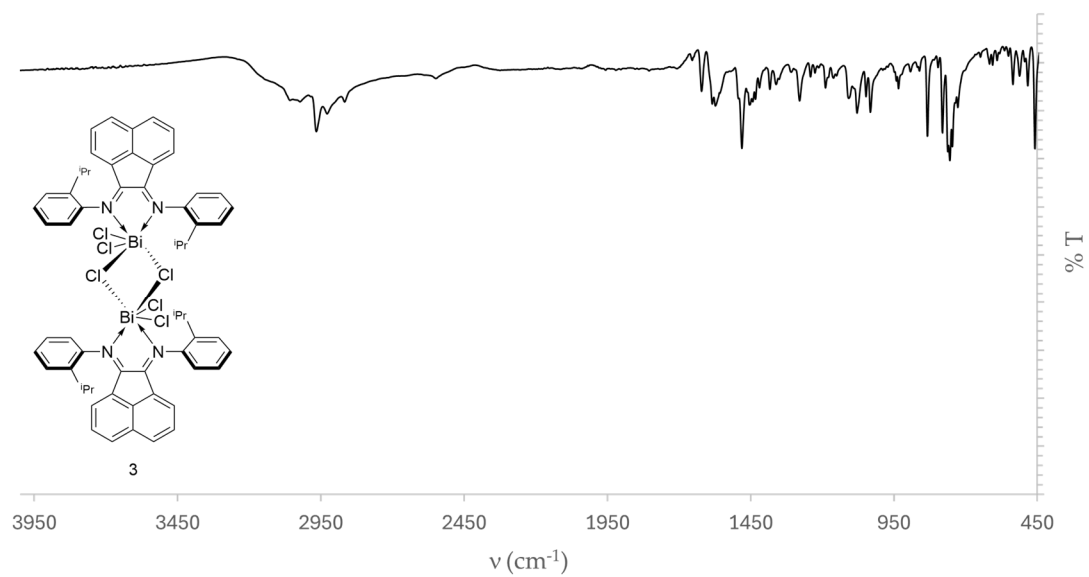


Figure S4. FT ATR-IR spectrum of complex **3**.

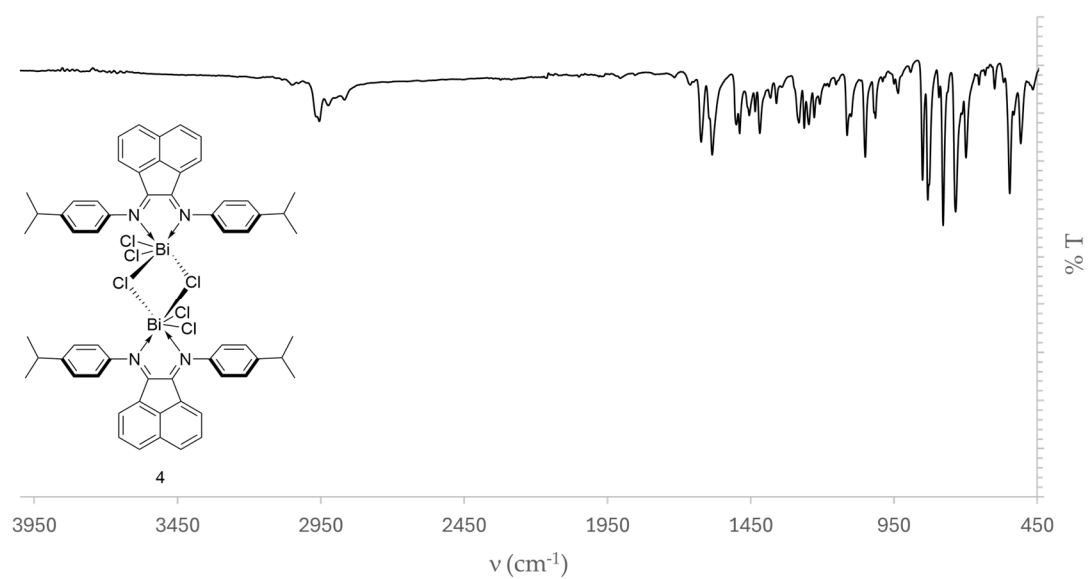


Figure S5. FT ATR-IR spectrum of complex 4.

NMR spectra

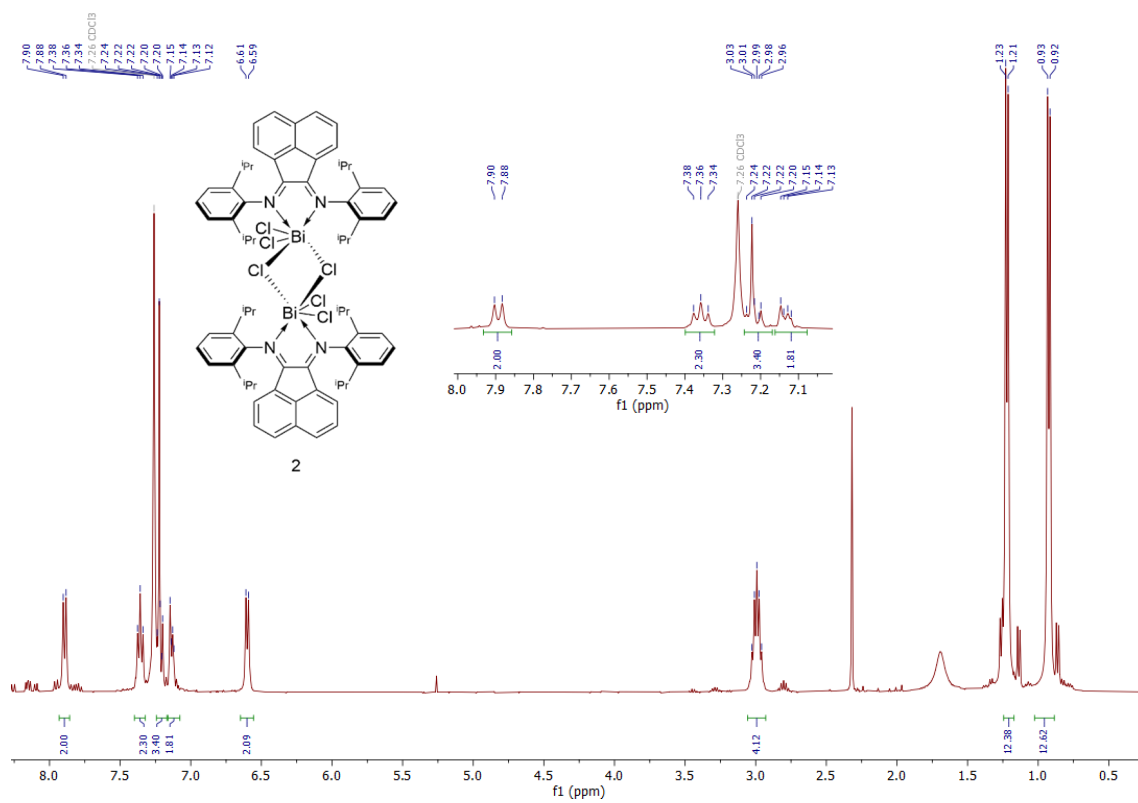


Figure S6. ^1H NMR spectrum of complex 2 in CDCl_3 .

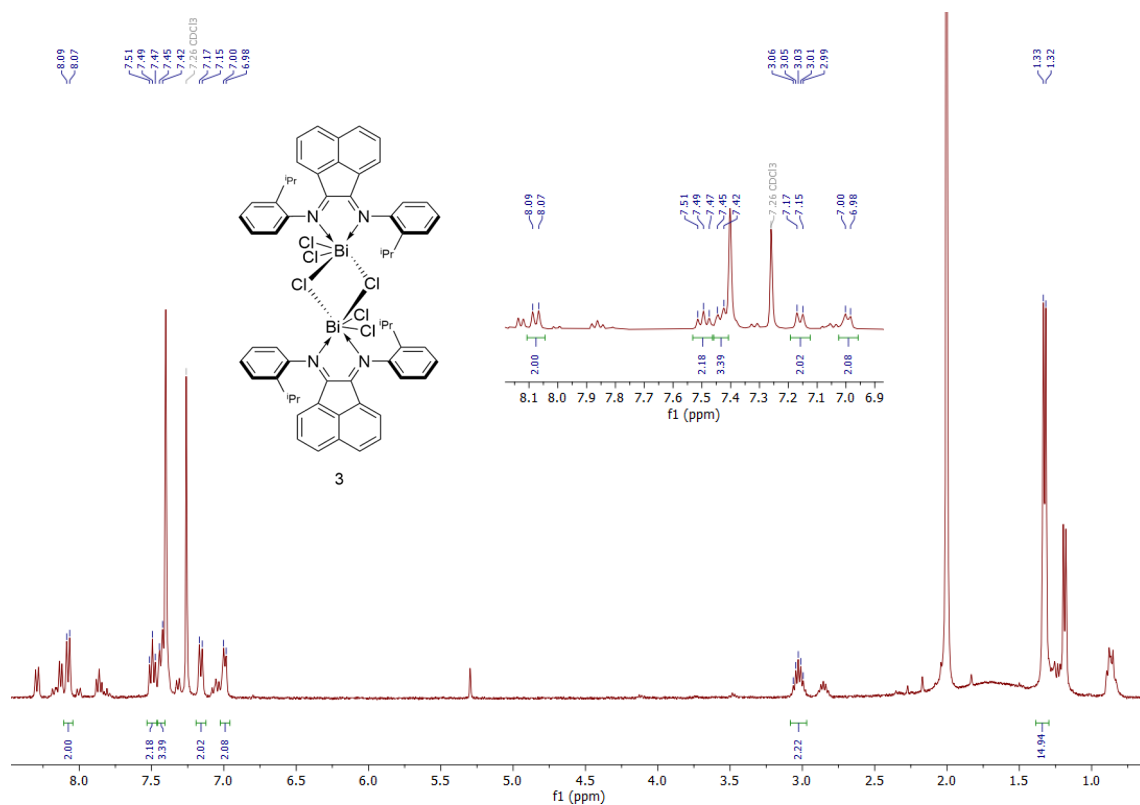


Figure S7. ¹H NMR spectra of complex **3** in CDCl₃.

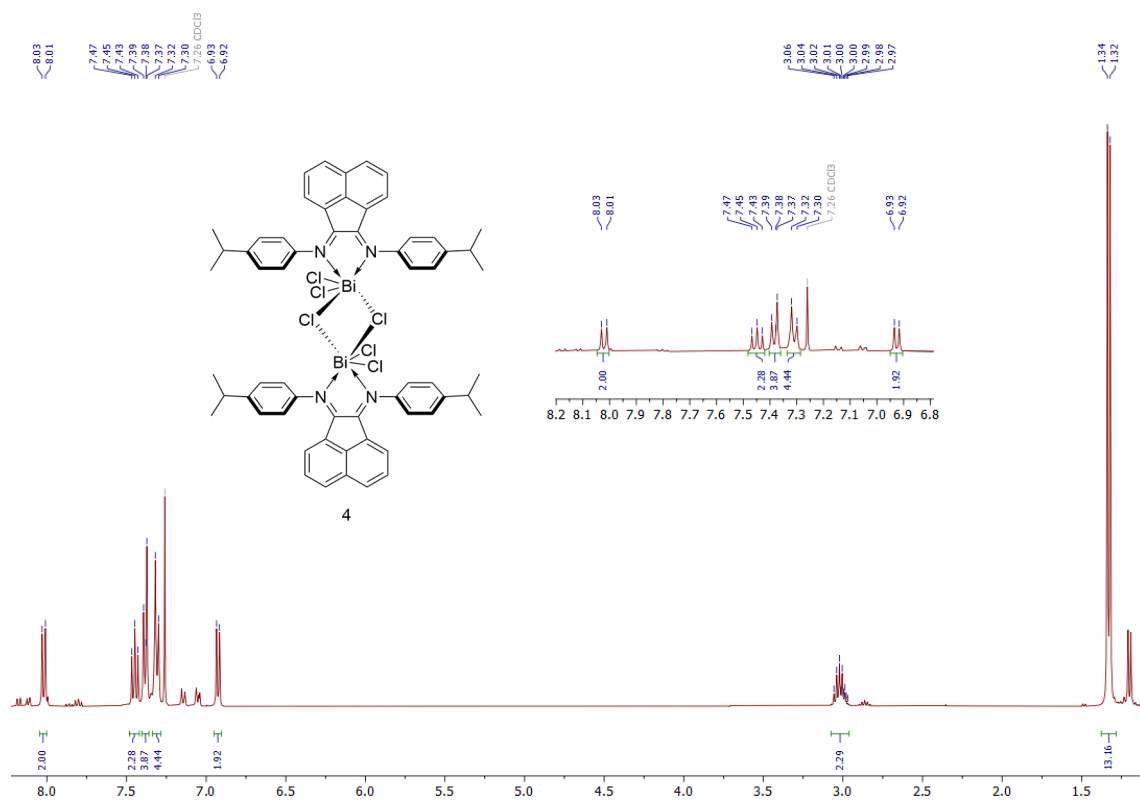


Figure S8. ¹H NMR spectrum of the complex **4** in CDCl₃.

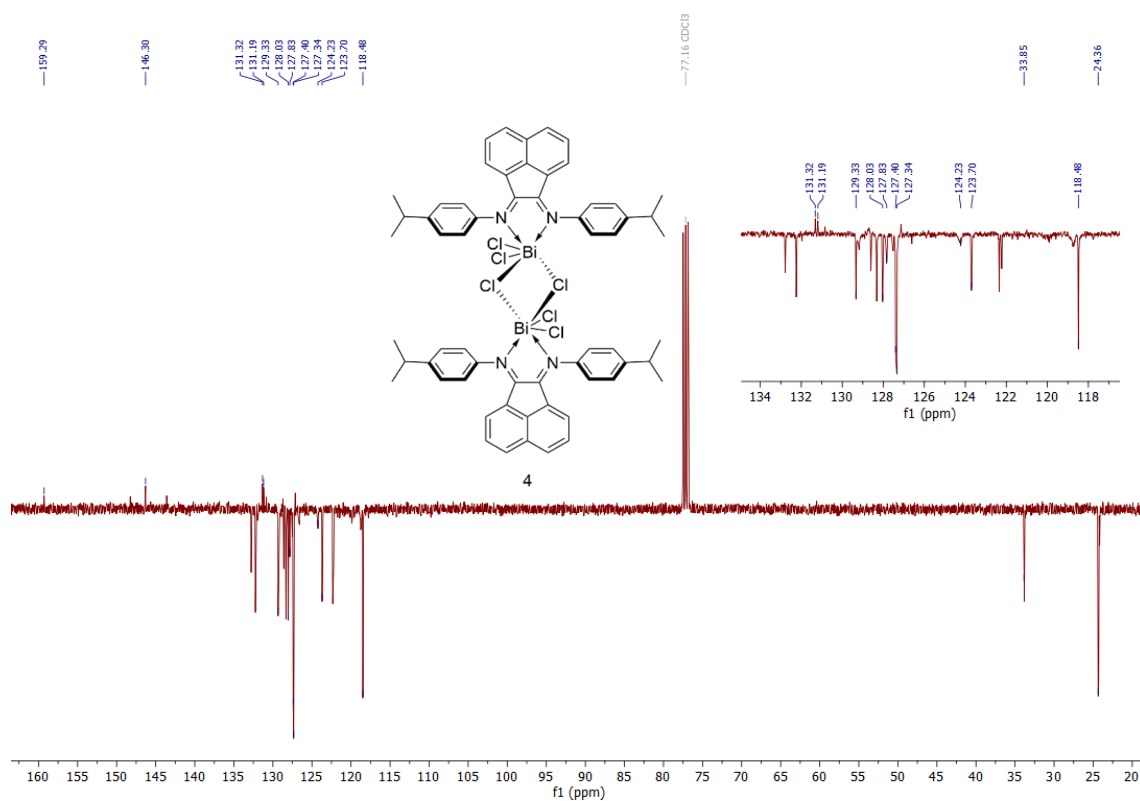


Figure S9. ^{13}C NMR spectrum of the complex **4** in CDCl_3 .

X-Ray data

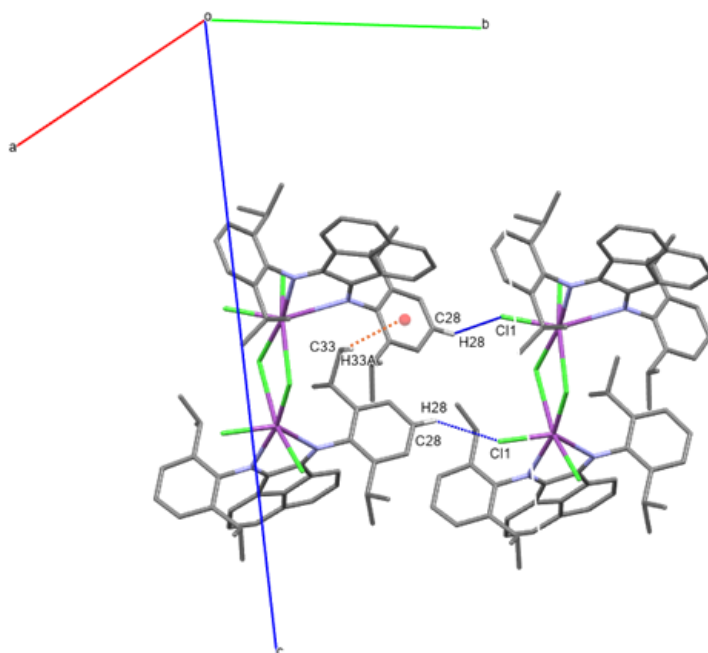


Figure S10. Intermolecular interactions of complex **2** shown as blue or orange dashed lines for $\text{C-H}\cdots\text{Cl}$ and $\text{C-H}\cdots\pi$ interactions, respectively.

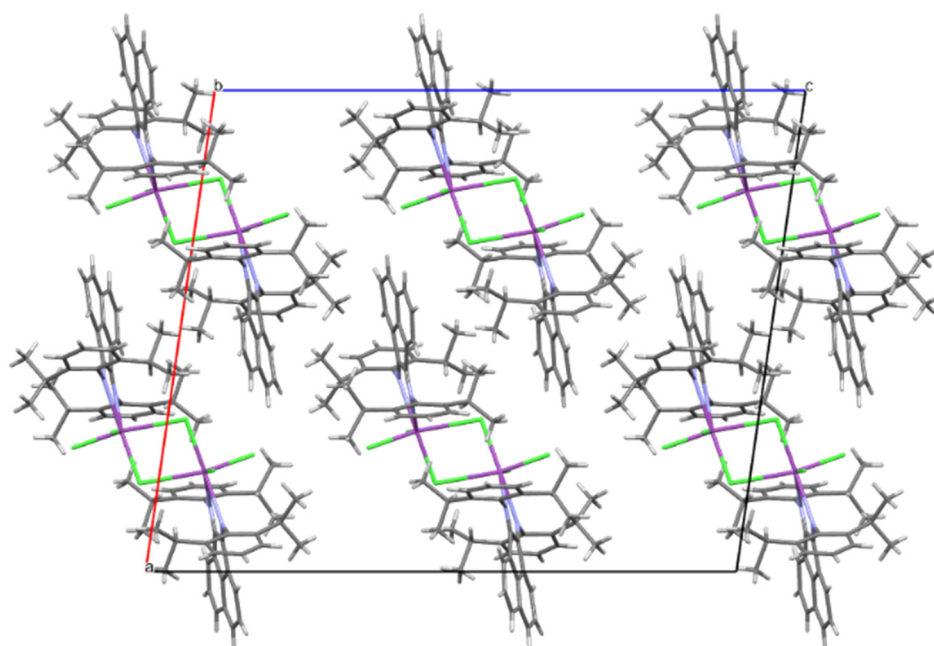


Figure S11. Packing of complex **2** viewed along *b* axis.

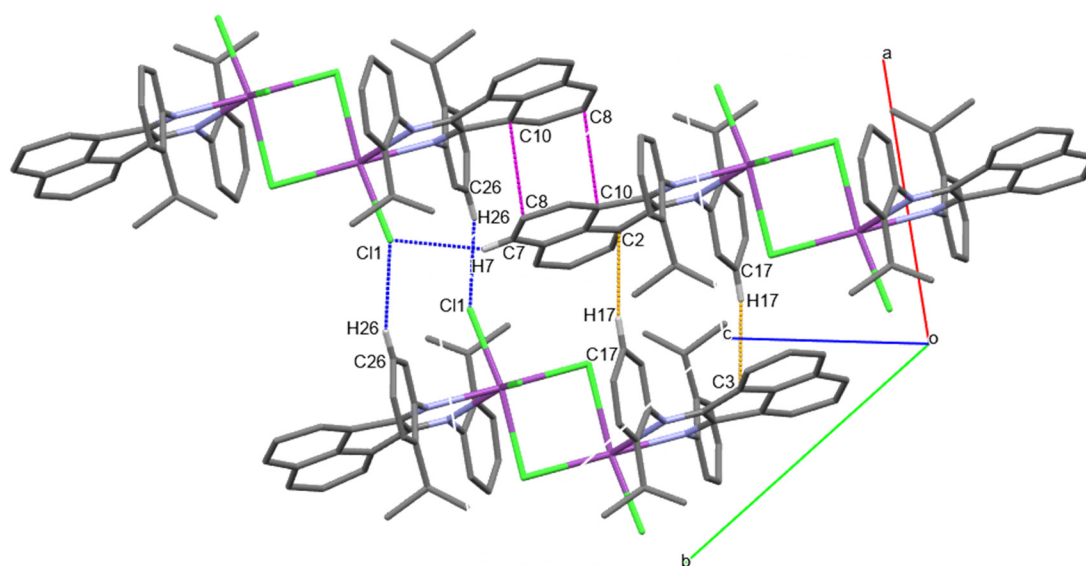


Figure S12. Intermolecular interactions of complex **3** shown as blue dashed lines for C – H...Cl interactions, orange dashed bonds for C-H... π interactions and magenta for π ... π interactions.

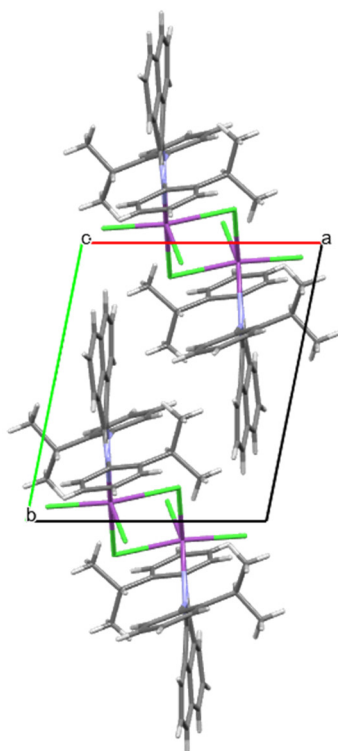


Figure S13. Packing of the complex **3** viewed along the *c* axis.

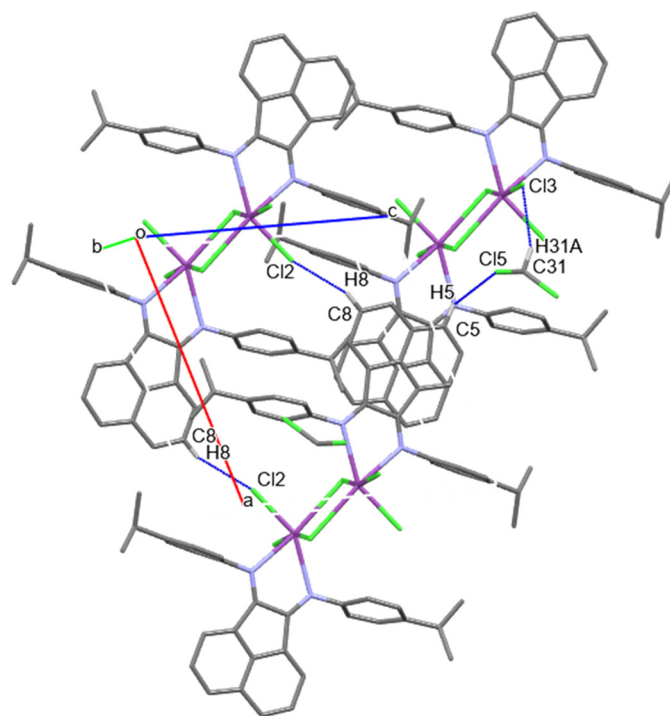


Figure S14. Intermolecular interactions of complex **4** shown as blue dash lines.

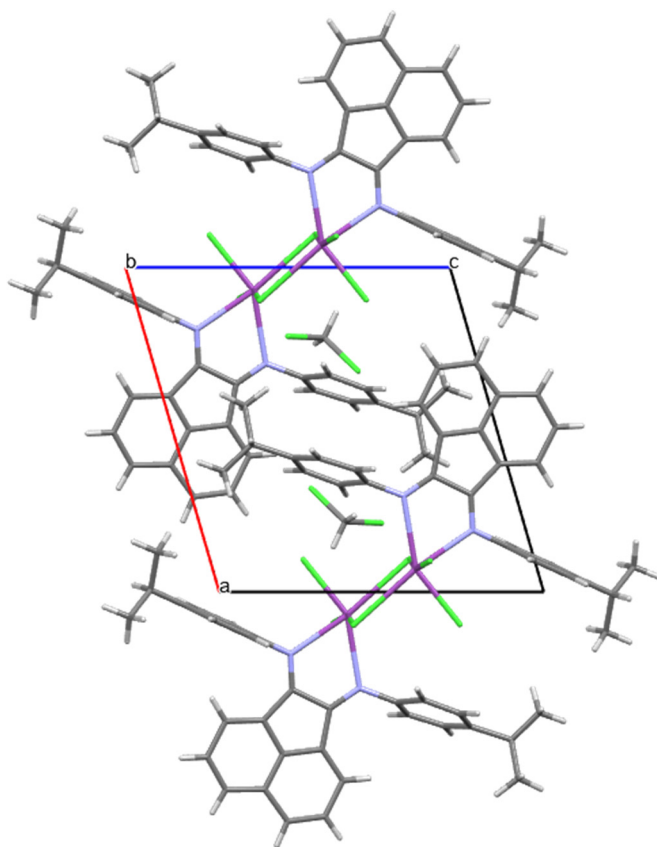


Figure S15. packing of complex **4** viewed along the *b* axis.

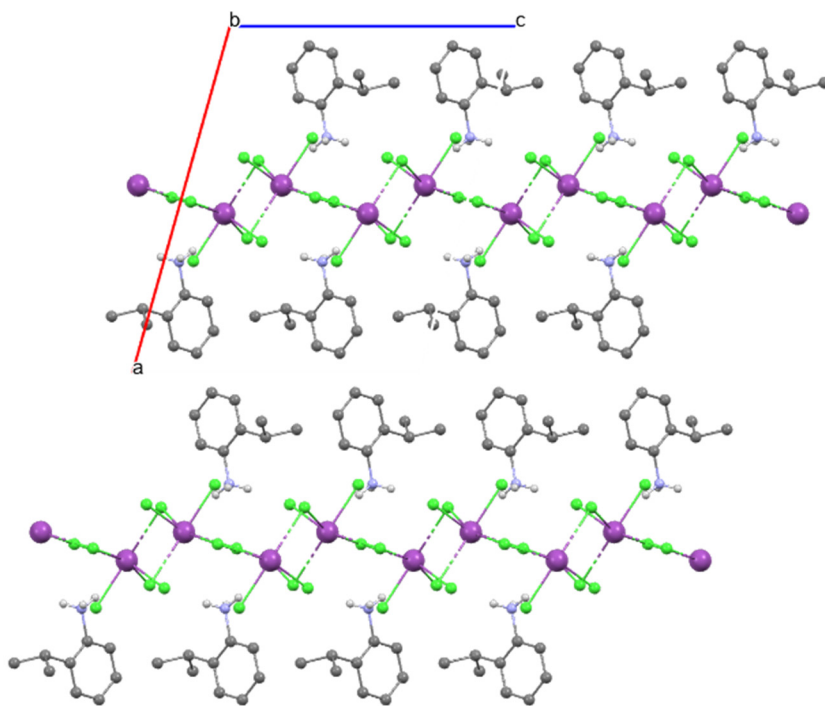


Figure S16. Packing of the compound **3-decomposition** viewed along the *b* axis.

Hirshfeld surface analysis – Fingerprint plots

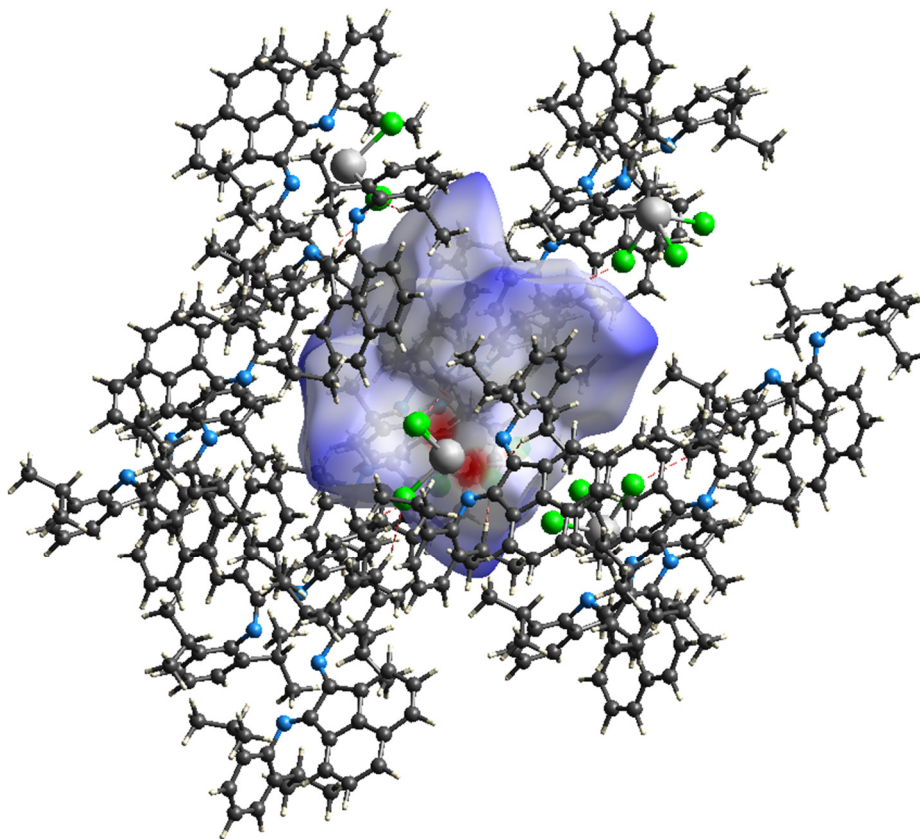


Figure S17. 3D Hirshfeld surface for complex **2**, mapped with d_{norm} property, showing intermolecular short contacts (red-dashed lines).

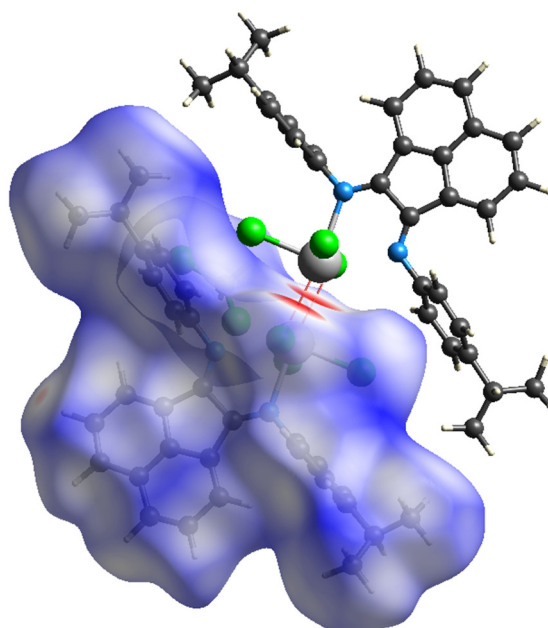


Figure S18. 3D Hirshfeld surface for complex **4**, mapped with d_{norm} property, showing intermolecular short contacts (red-dashed lines).

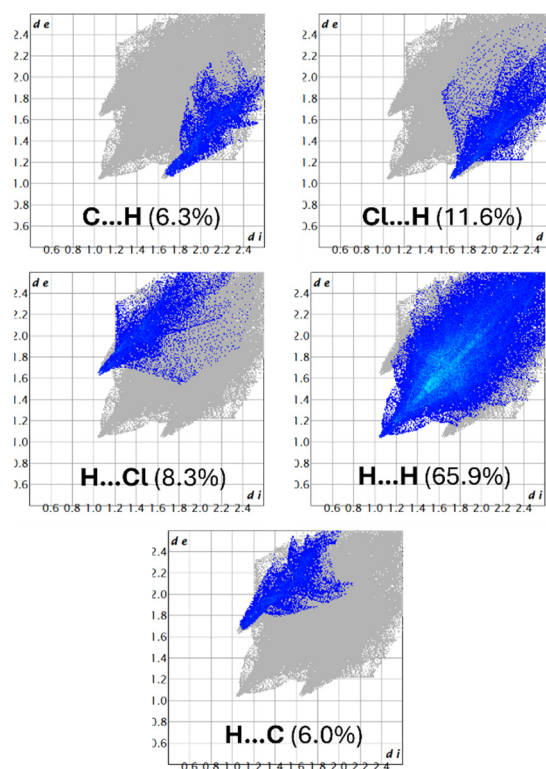


Figure S19. Two-dimensional fingerprint plots for the intermolecular interactions of the metal complex 2.

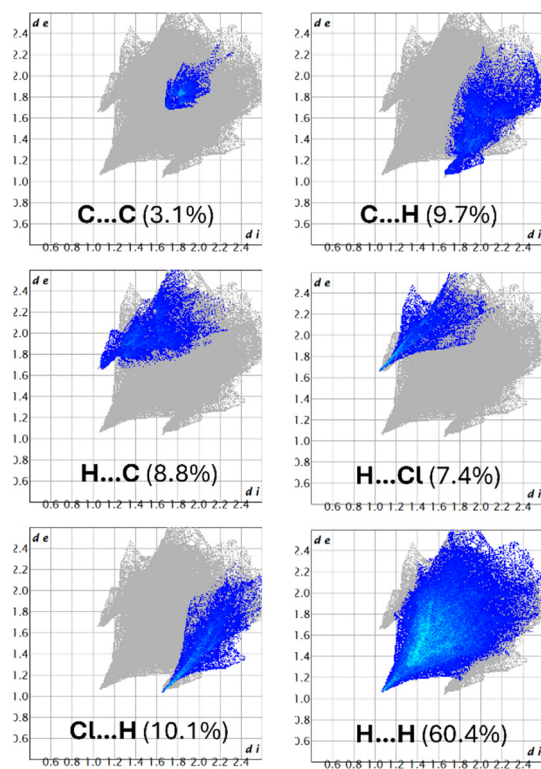


Figure S20. Two-dimensional fingerprint plots for the intermolecular interactions of the metal complex 3.

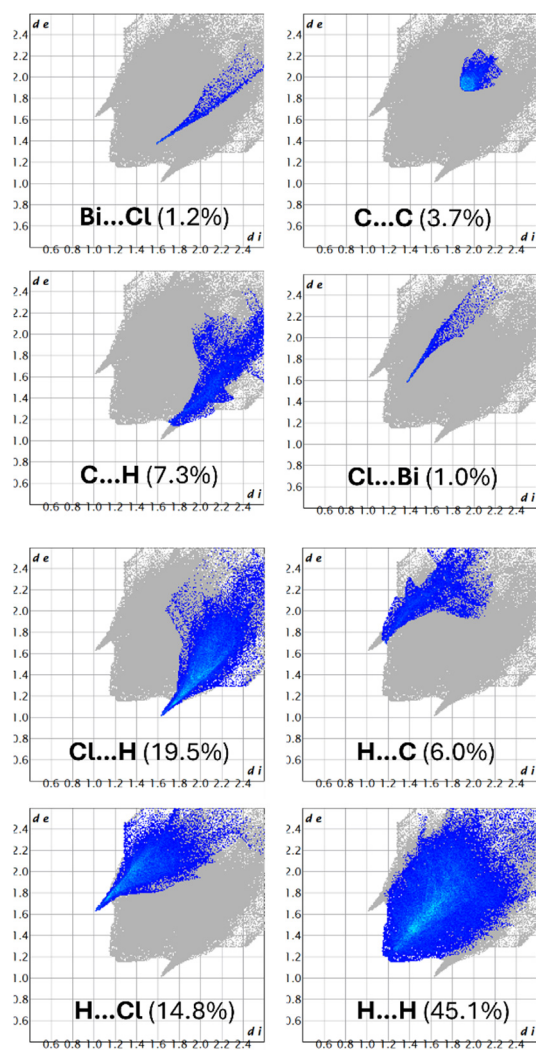


Figure S21. Two-dimensional fingerprint plots for the intermolecular interactions of the metal complex 4.

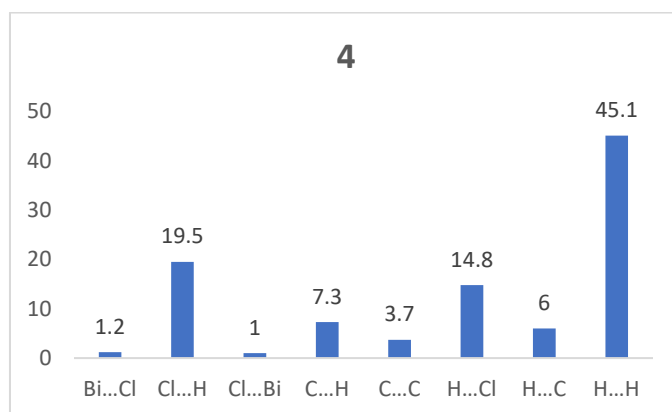
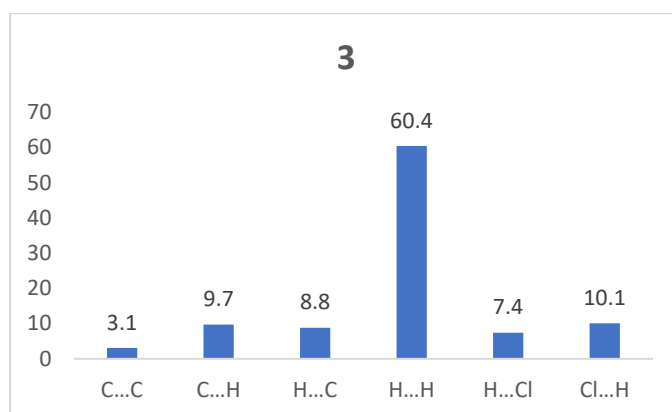
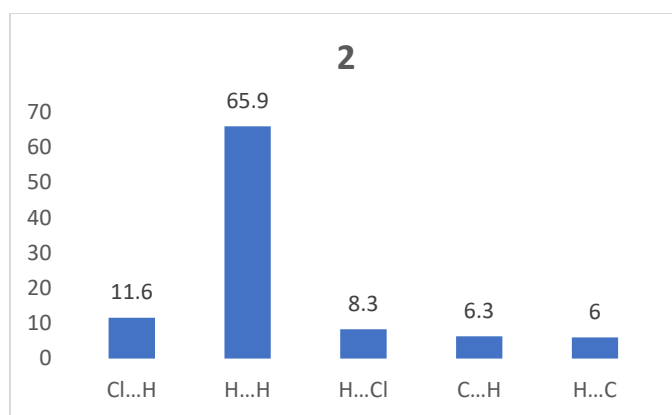


Figure S22. Summary of the percentages contributed by the various noncovalent interactions to the Hirshfeld surface in the crystal structures of complexes **2**, **3** and **4**.