

Supporting Information

Controlling the formation of two concomitant polymorphs in Hg(II) coordination polymers

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Furnace conditions

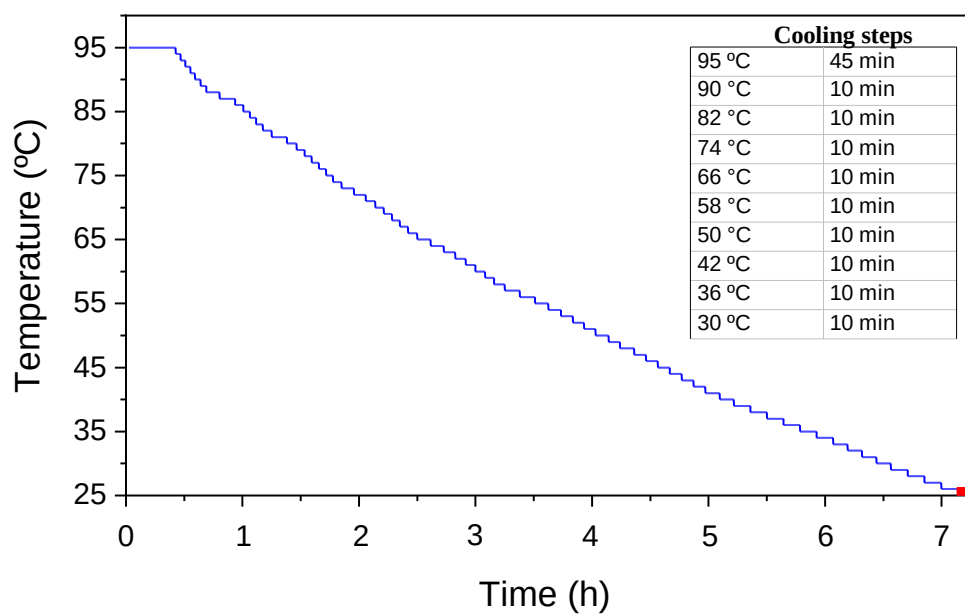


Figure S1. Cooling ramp used in the synthesis of isolated **P1A** and **P1B**.

PXRD patterns

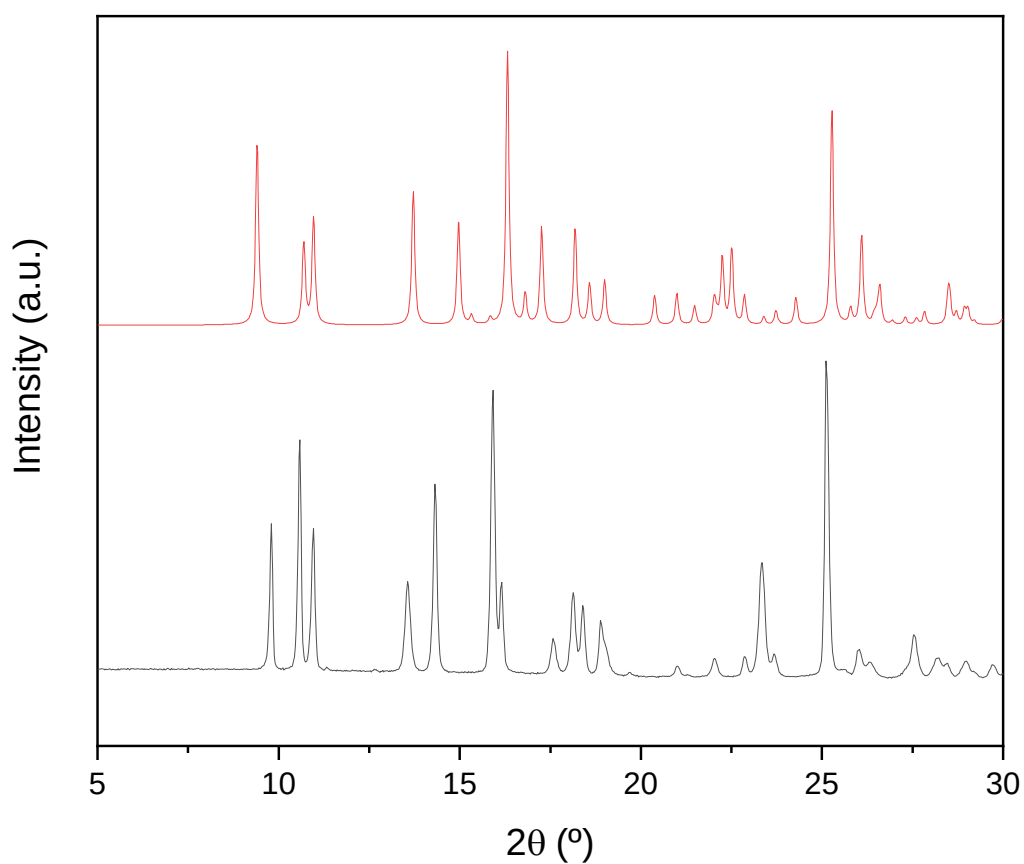


Figure S2. SC-XRD (top) and PXRD (bottom) patterns of **2**.

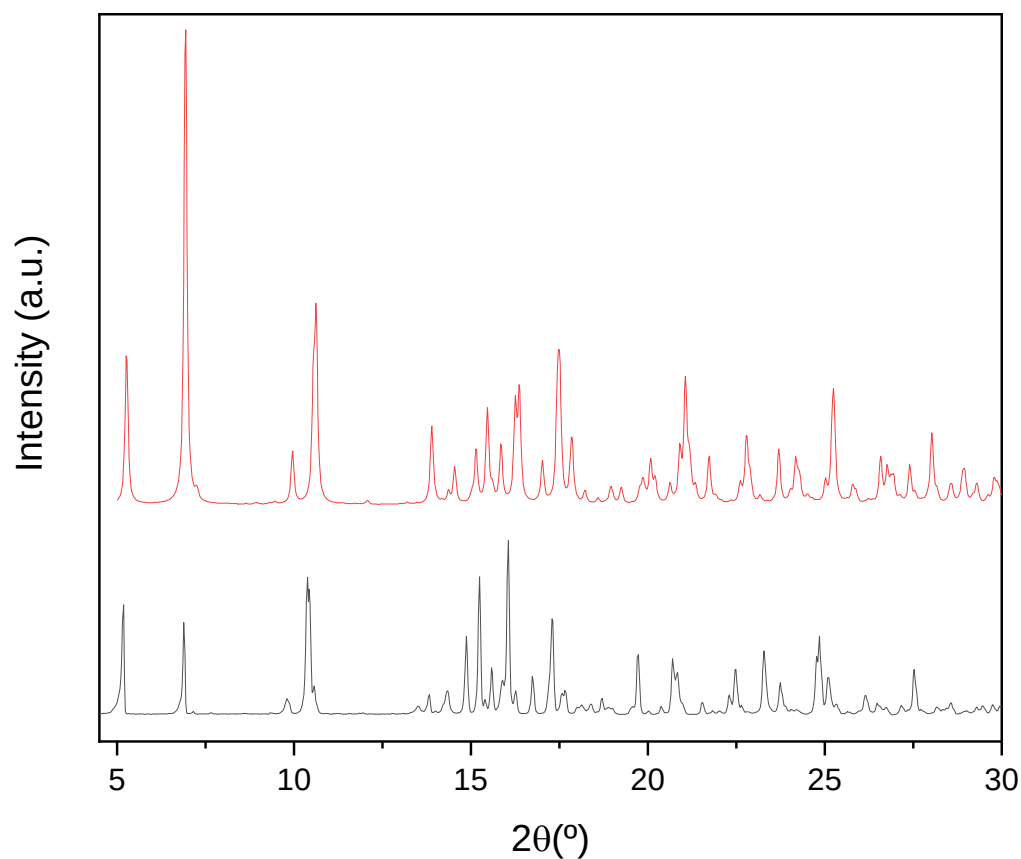


Figure S3. SC-XRD (top) and PXRD (bottom) patterns of **P1B**.

FTIR-ATR and ^1H , $^{13}\text{C}\{^1\text{H}\}$ and DEPT-135 NMR spectroscopies

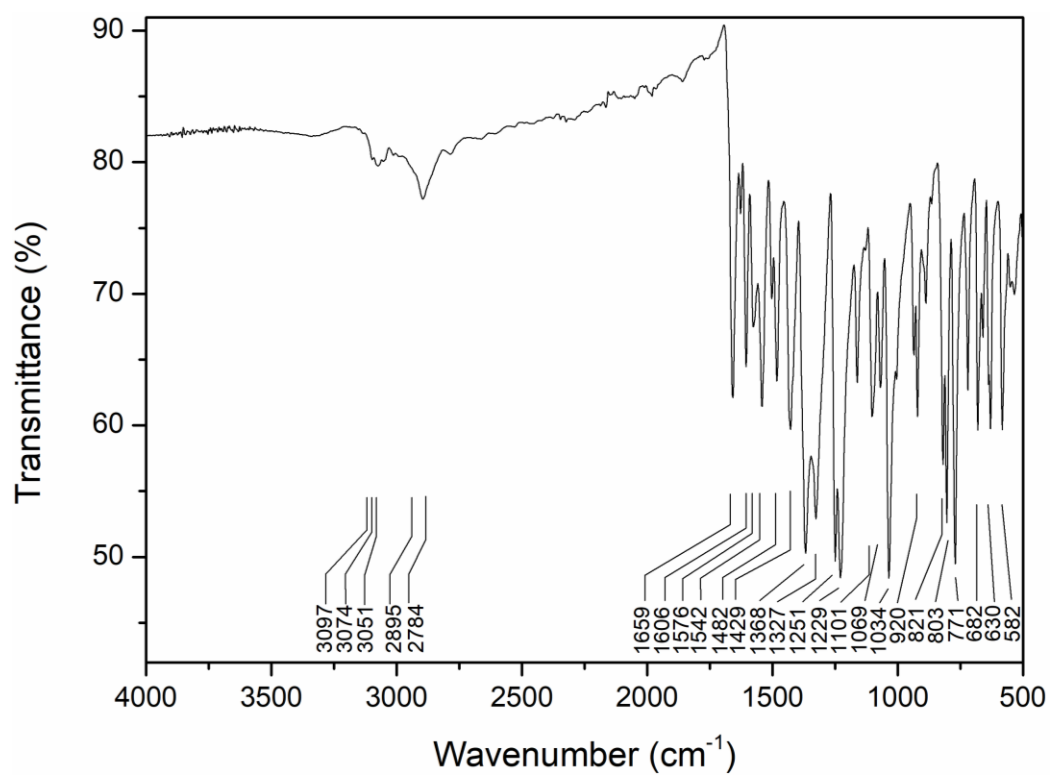


Figure S4. FTIR-ATR spectrum of **P1A** and **P1B** crystals mixture.

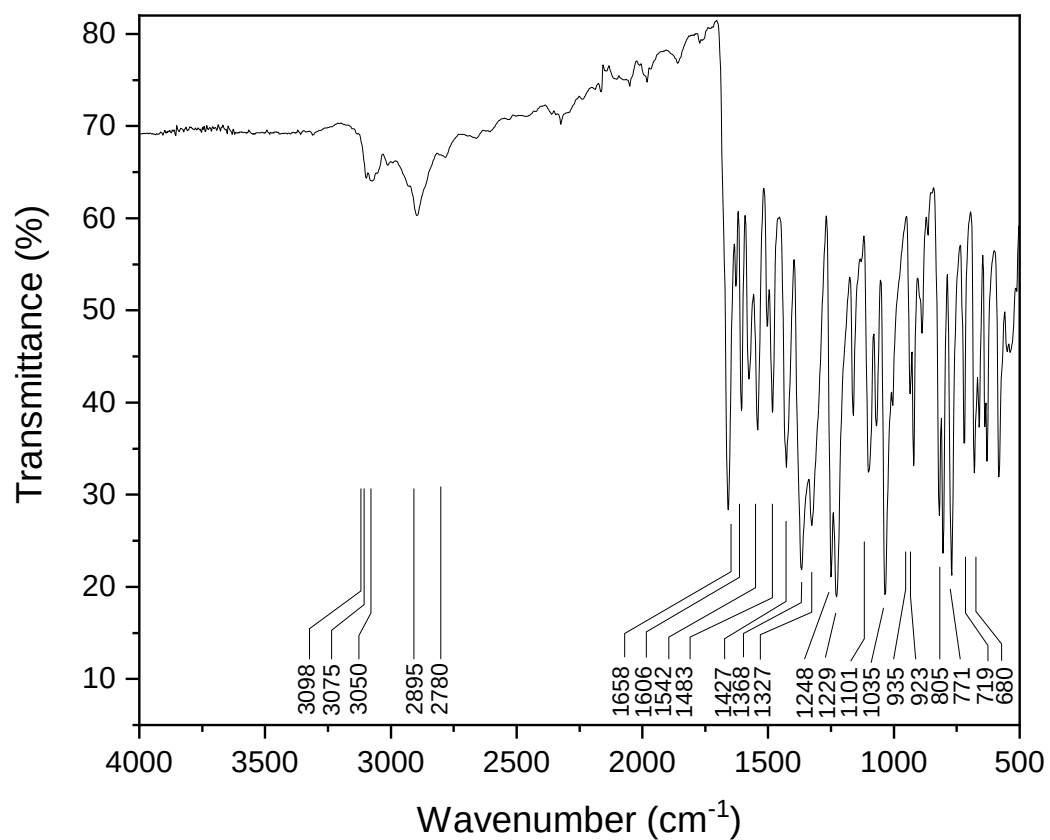


Figure S5. FTIR-ATR spectrum of isolated **P1A** crystals.

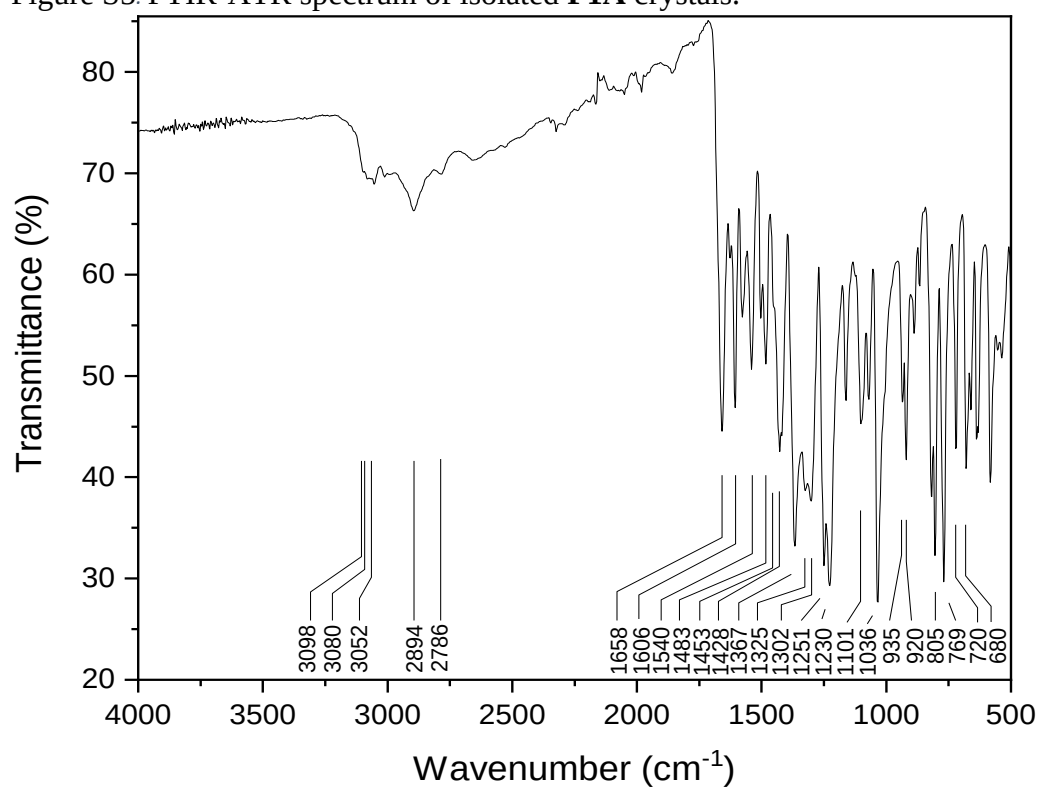


Figure S6. FTIR-ATR spectrum of isolated **P1B** crystals.

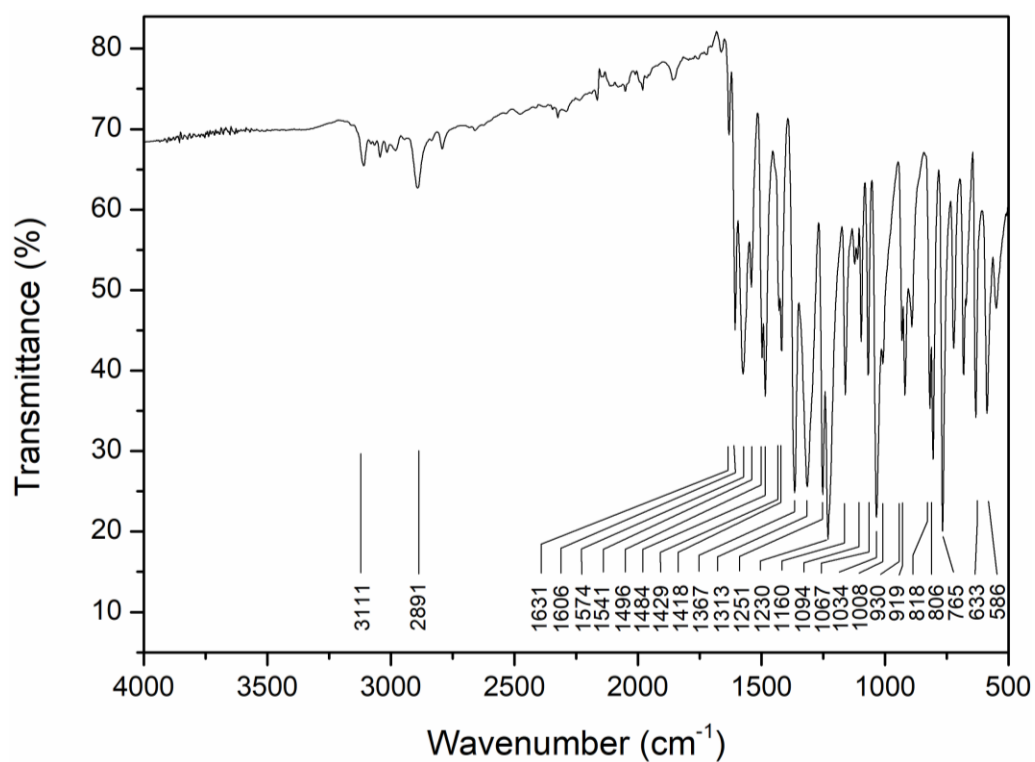


Figure S7. FTIR-ATR spectrum of compound **2** synthesized in DMF as solvent.

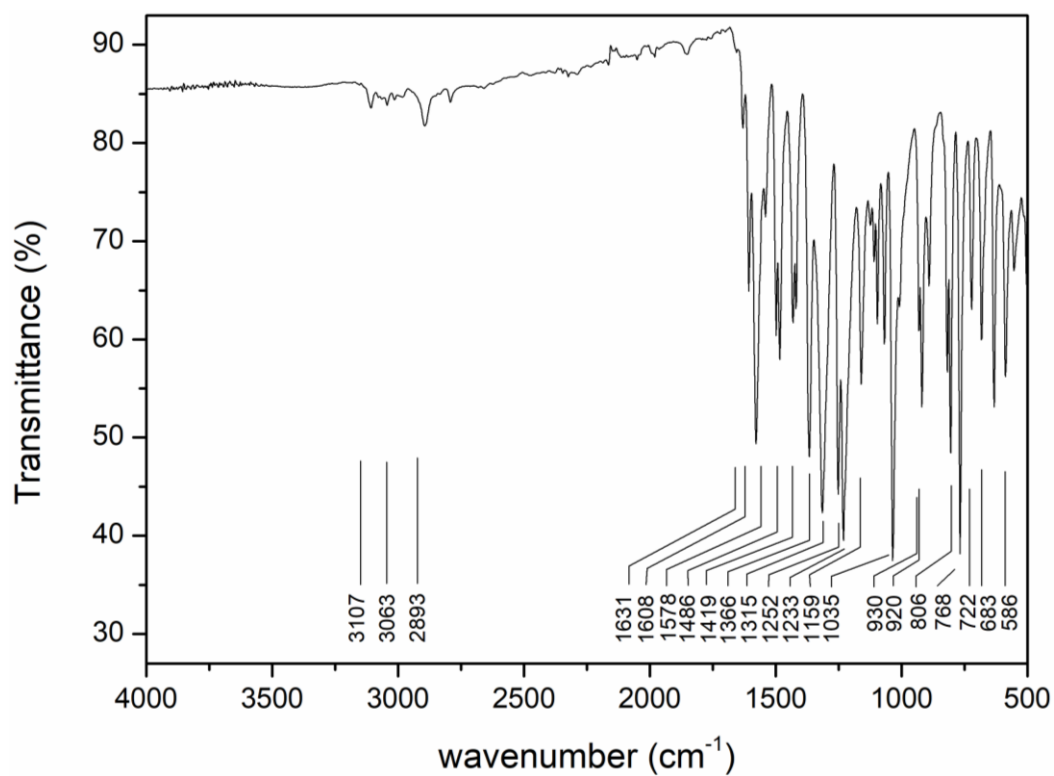


Figure S8. FTIR-ATR spectrum of compound **2** synthesized in milliQ as solvent.

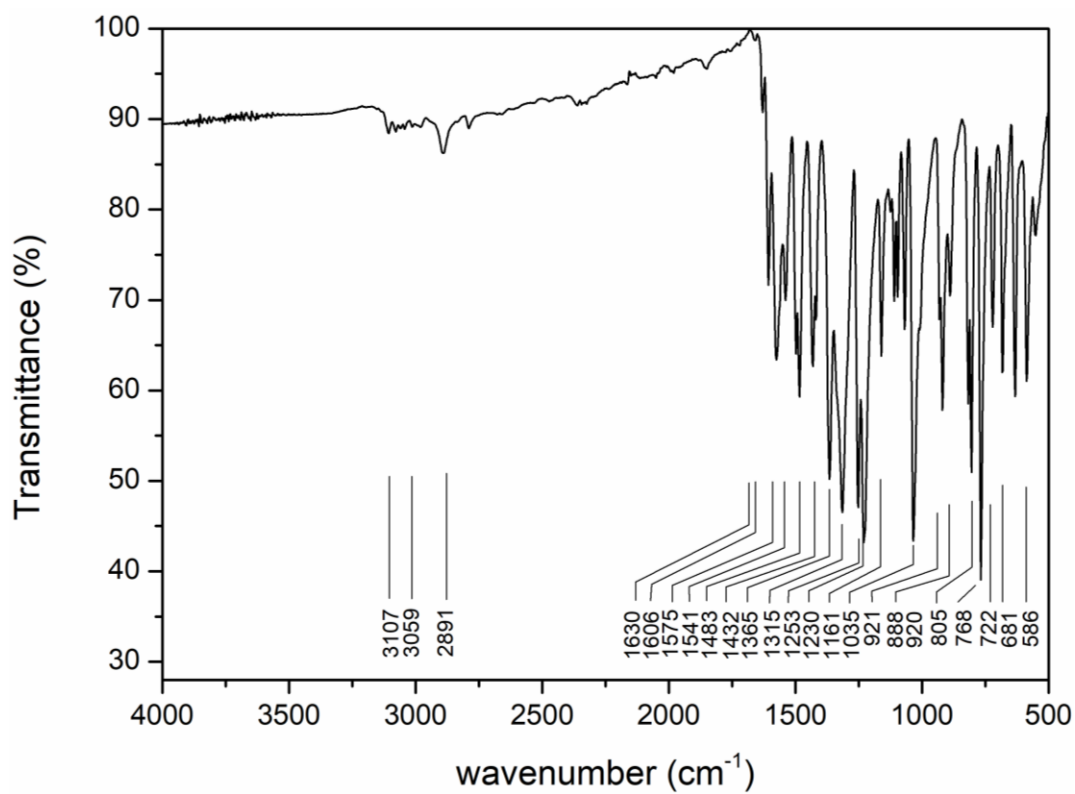


Figure S9. FTIR-ATR spectrum of compound **2** synthesized in MeOH as solvent.

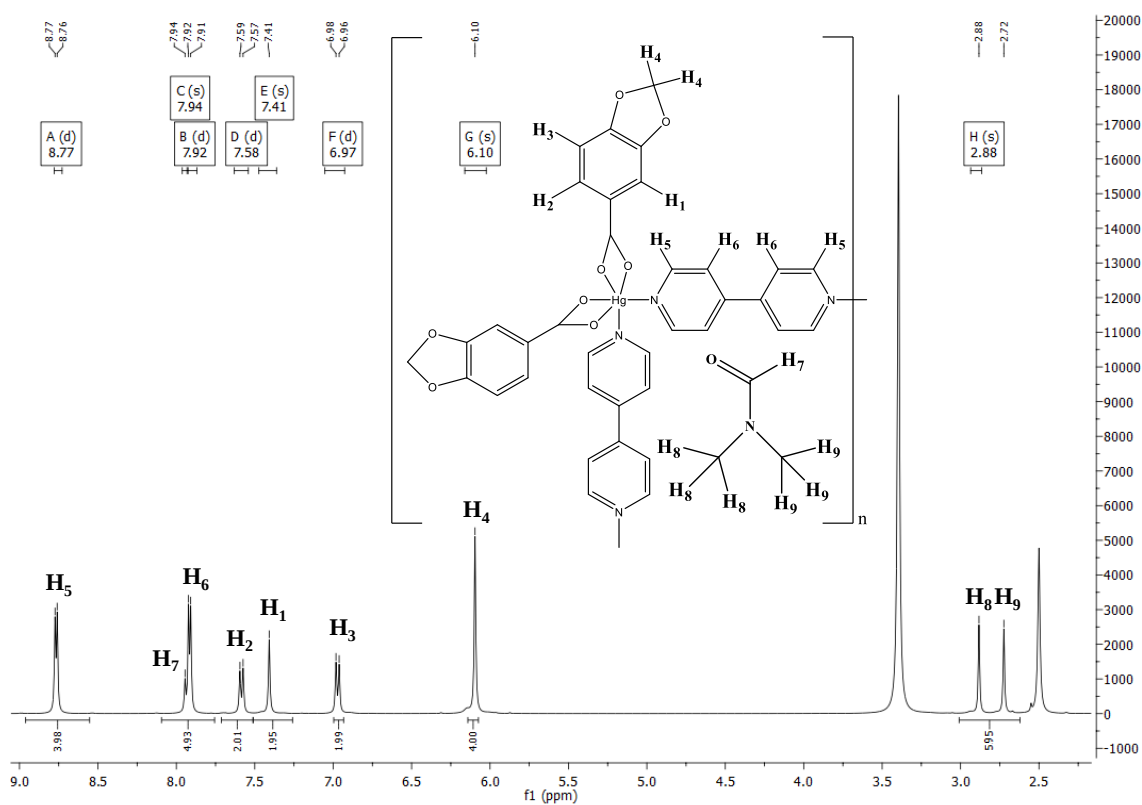


Figure S10. ^1H NMR spectrum of **P1A** and **P1B** mixture recorded at 298K in $\text{DMSO-}d_6$.

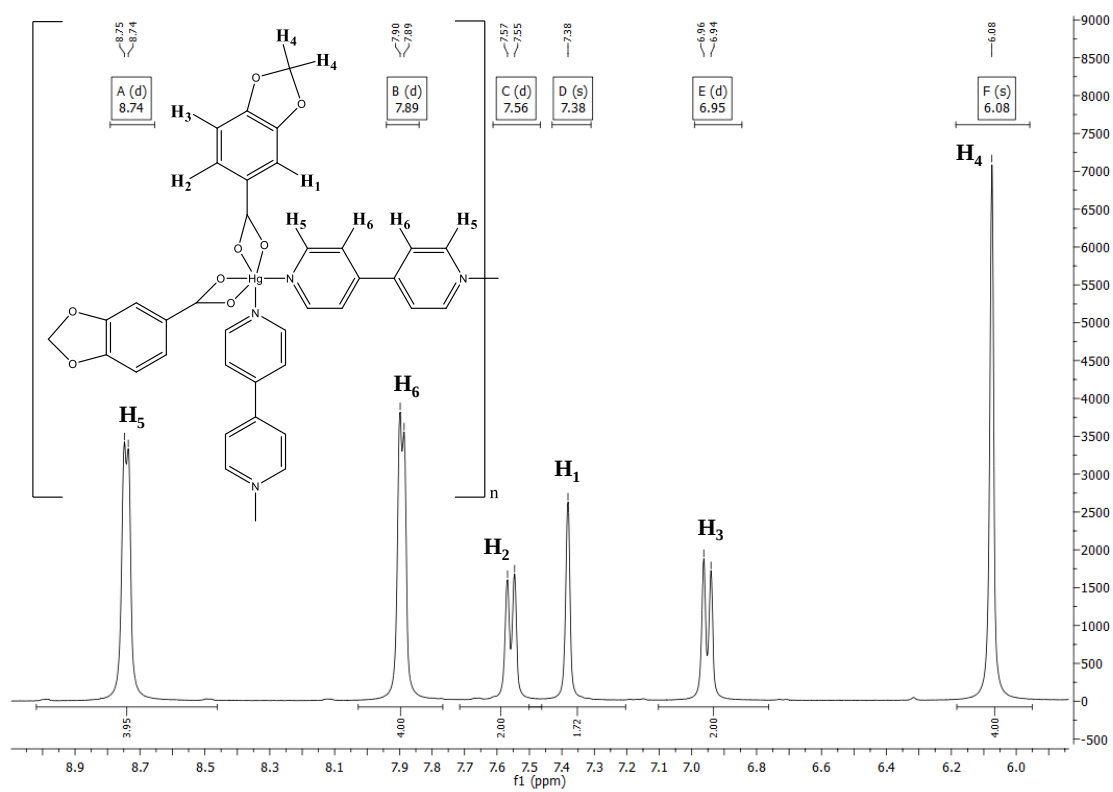


Figure S11. ^1H NMR spectrum of compound **2** recorded at 298K in $\text{DMSO-}d_6$.

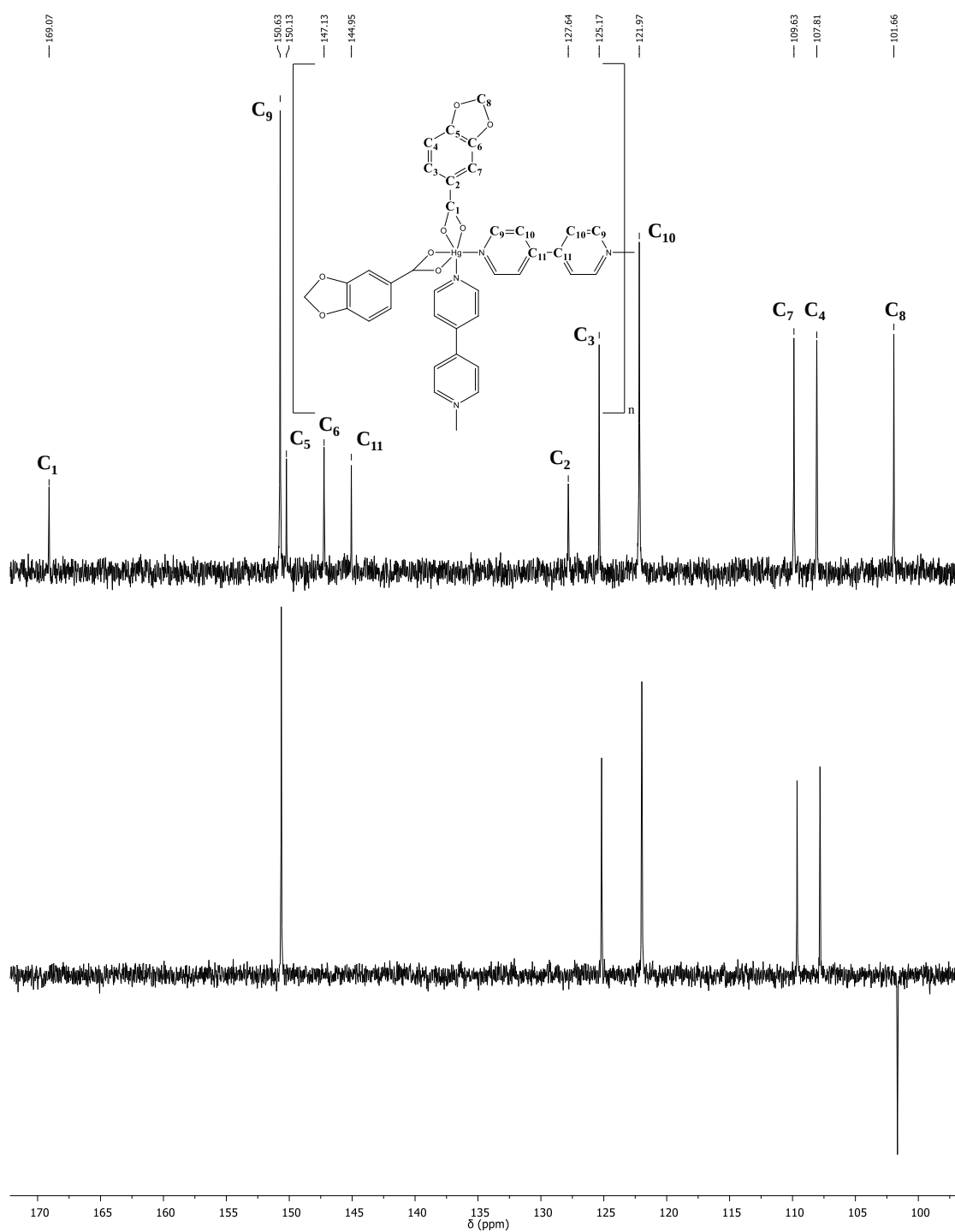


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR (top) and DEPT-135 NMR (bottom) spectra of compound 2 recorded at 298K in $\text{DMSO}-d_6$.

Thermogravimetric analysis

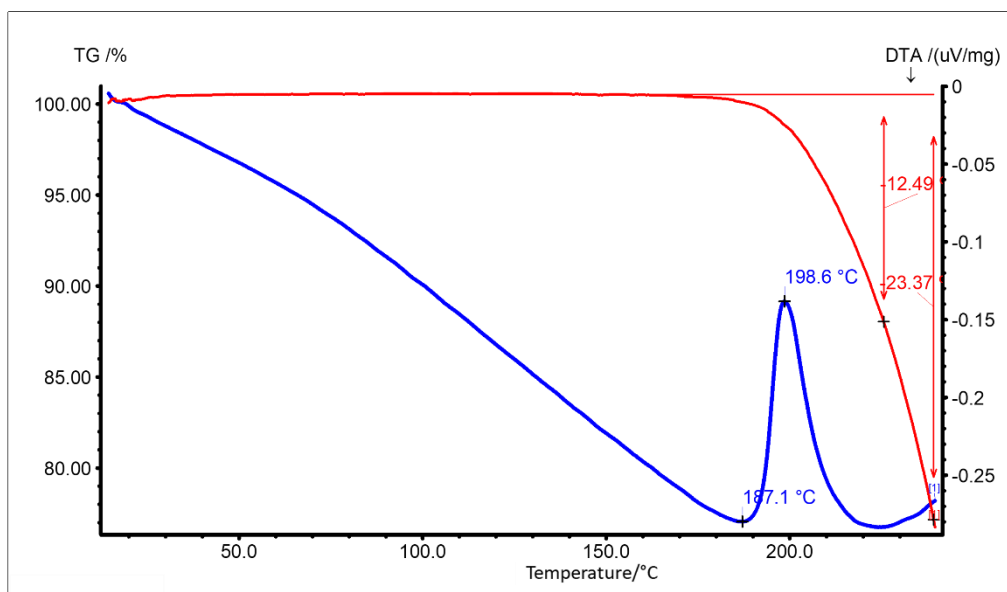


Figure S13. TG-DTA of **2**.

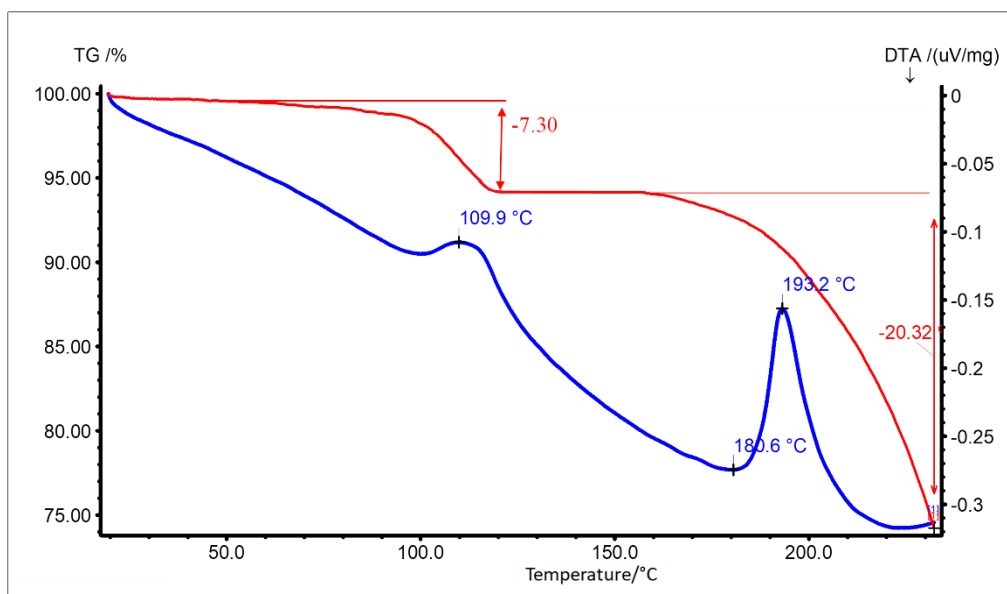


Figure S14. TG-DTA of **P1A**.

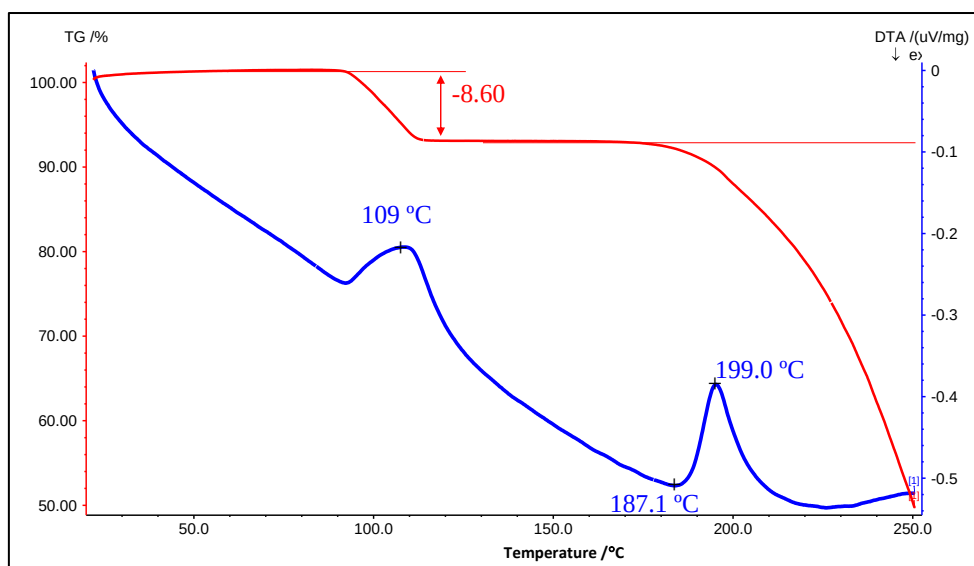


Figure S15. TG-DTA of **P1B**

Hirshfeld Surfaces and 2D fingerprint plot analyses

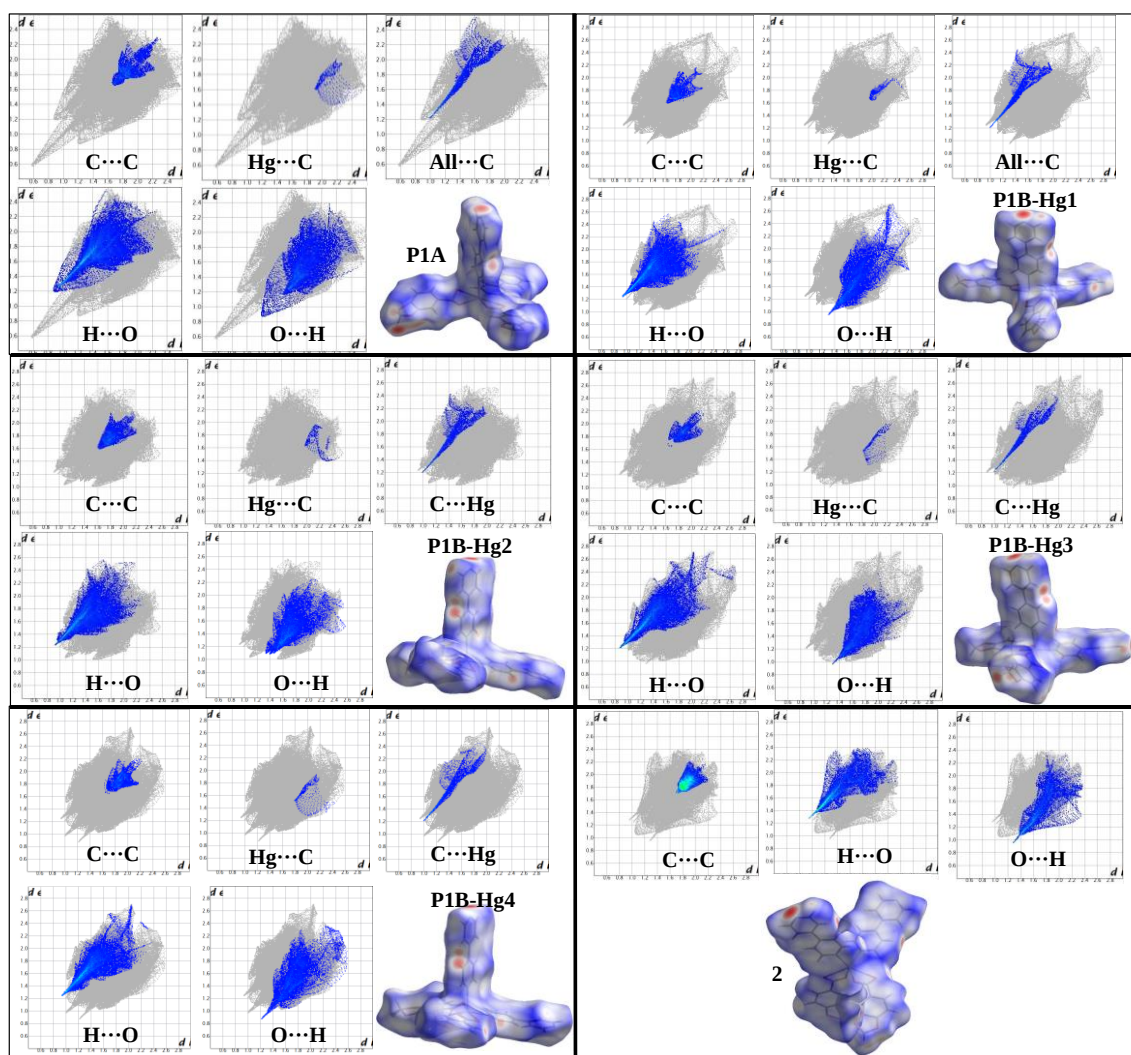


Figure S16. Hirshfeld surfaces and 2D fingerprint plots of complexes **P1A**, **P1B** and **2**.

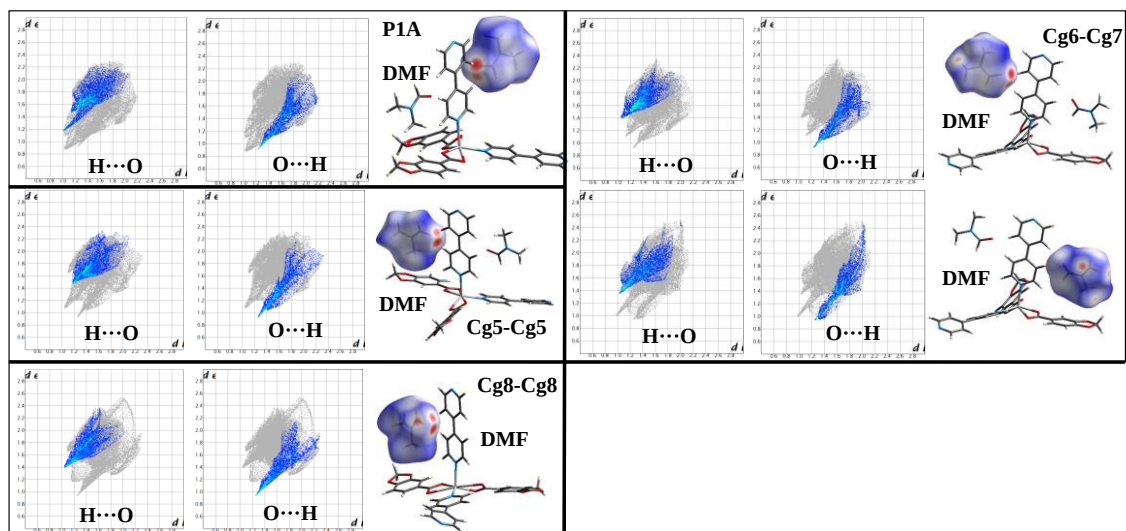


Figure S17. Hirshfeld surfaces and 2D fingerprint plots of DMF molecules in complexes **P1A** and **P1B**.

Energy partitioning scheme

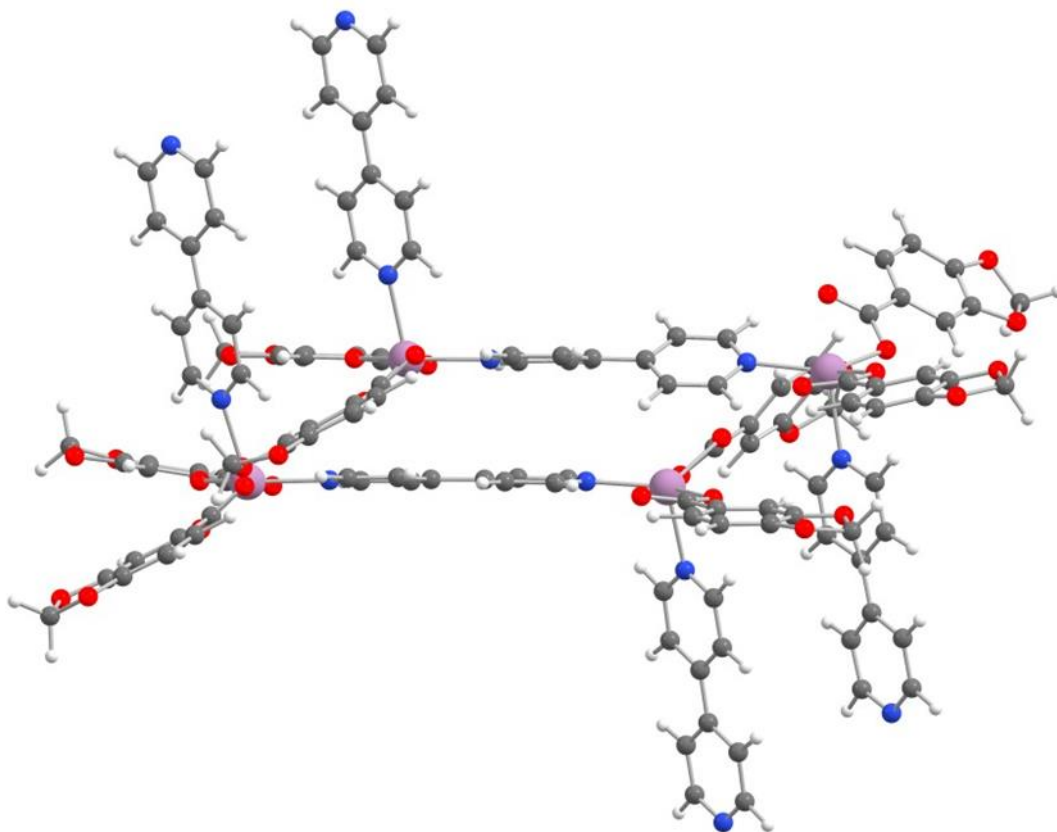


Figure S18. Model used in the energy partitioning scheme. It includes two dimers of vicinal chains in **P1B**.

Solid-state photoluminescence

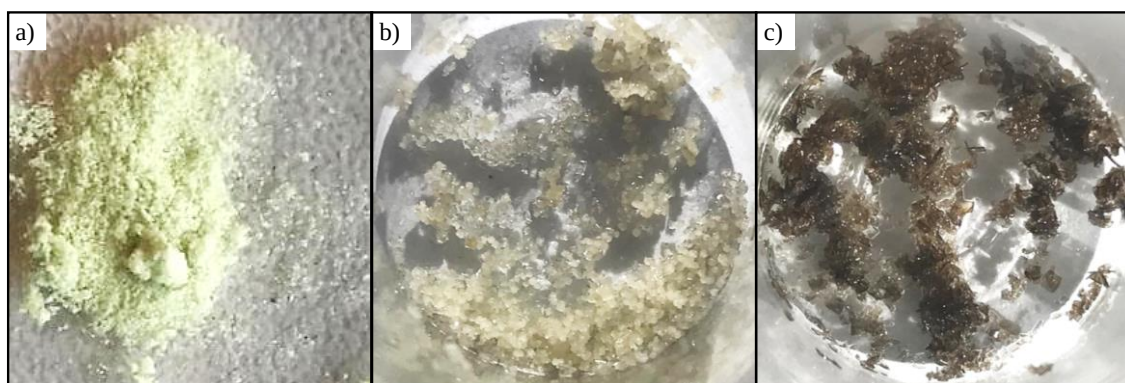


Figure S19. Samples of single crystals of (a) **2**; (b) **P1A** and (c) **P1B** used for the photophysical measurements.

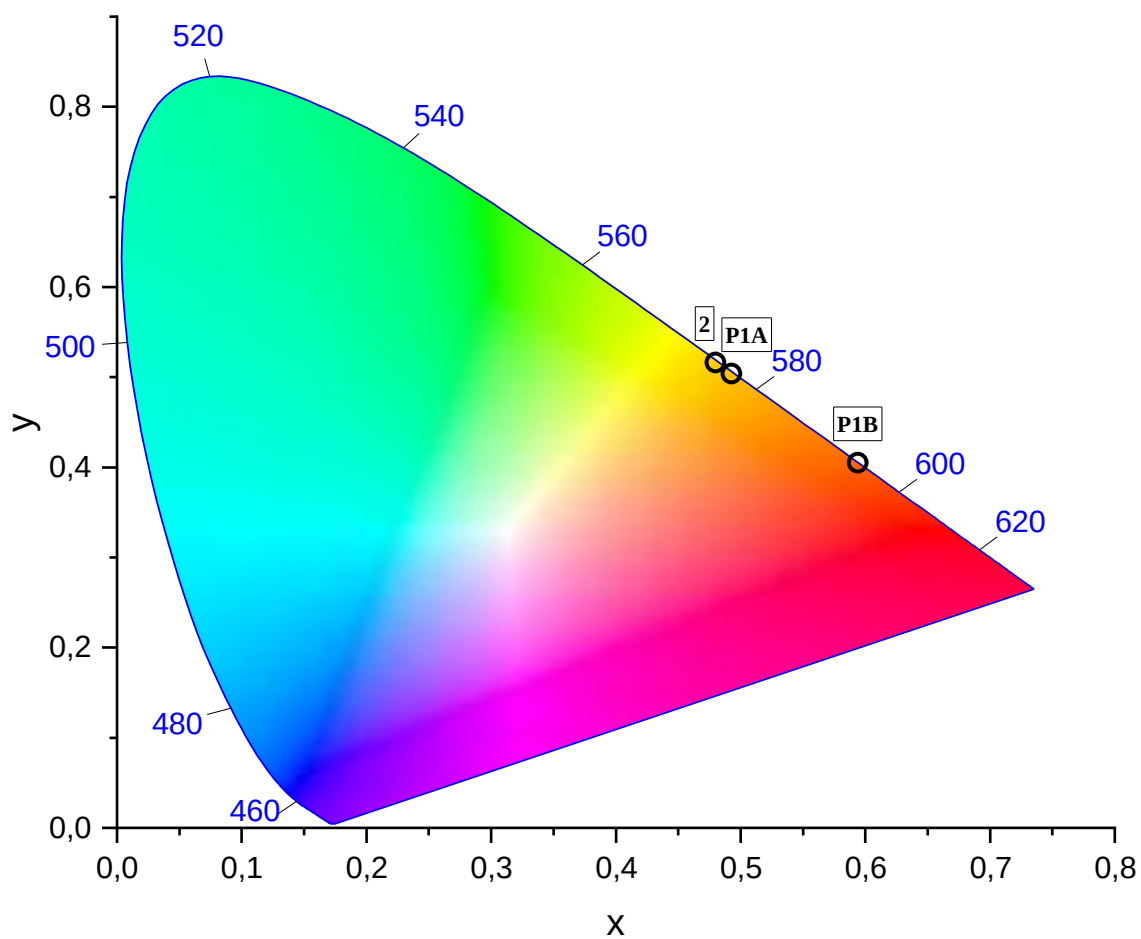


Figure S20. Representation of the emission color of **P1A**, **P1B** and **2** within the CIE 1931 chromaticity diagram.

Table S1. **P1A-P1B** relative energies per [Hg(Pip)₂(4,4'-bipy)]·DMF unit formula in kJ mol⁻¹ as function of the Grimme's dispersion correction term. A positive value indicates that **P1A** is more stable than **P1B**.

Method	ΔE
PBE	8.9
PBE-D2	-13.4
^a PBE-D*	-11.9
PBE-D3	-17.4

^aPBE-D* stands for a modification of the D2 Grimme's empirical term¹

Table S2. Unit cell measurements of **P1A** and **P1B** crystals

P1A (structure elucidation) a = 6.0027(7) α = 71.181(4) b = 13.5859(17) β = 83.249(4) c = 17.769(2) γ = 80.217(4)	P1B (structure elucidation) a = 13.6326(15) α = 105.796(4) b = 20.267(2) β = 105.114(4) c = 21.899(2) γ = 100.923(4)
P1A (unit cell measurement) a = 6.00 α = 71.06 b = 13.60 β = 83.51 c = 17.80 γ = 80.67	P1B (unit cell measurement) a = 13.60 α = 105.75 b = 20.21 β = 105.12 c = 21.80 γ = 100.94
P1A (unit cell measurement) a = 6.16 α = 70.98 b = 13.47 β = 83.12 c = 17.69 γ = 80.10	P1B (unit cell measurement) a = 13.69 α = 105.68 b = 20.33 β = 105.12 c = 21.98 γ = 100.92
P1A (unit cell measurement) a = 6.00 α = 71.65 b = 13.70 β = 83.41 c = 17.80 γ = 80.26	P1B (unit cell measurement) a = 13.60 α = 105.77 b = 20.31 β = 105.20 c = 21.86 γ = 100.90

Table S3. Geometry distortions analysis using *S* parameter calculated with SHAPE^{2,3}

<i>Compound</i>	<i>Geometry</i> ^a	<i>S value</i>
P1A	TPR-6	13.467
	OC-6	23.098
	PPY-6	5.748
P1B (Hg1)	TPR-6	13.187
	OC-6	20.261
	PPY-6	7.550
P1B (Hg2)	TPR-6	12.787
	OC-6	22.941
	PPY-6	6.450
P1B (Hg3)	TPR-6	11.386
	OC-6	20.300
	PPY-6	7.466
P1B (Hg4)	TPR-6	12.540
	OC-6	22.255
	PPY-6	5.863
2	TPR-6	8.452
	OC-6	16.523
	PPY-6	18.028

Closer values have been highlighted in bold. ^aTPR-6 = Trigonal prismatic; OC-6 = Octahedral; PPY-6 = Pentagonal pyramidal.

Table S4. Percentage (%) of Hirshfeld surface implied in each contact for compounds **P1A**, **P1B** and **2**.

Sample		Inter-chain contacts				DMF	
		C...C	Hg ^a	H...O ^b	O...H ^b	H...O	O...H
P1A		4.1	3.4	17.0	10.3	20.4 ^c	15.2 ^c
P1B	Hg1	2.7	3.2	16.6	11.4	18.0 ^d	14.3 ^d
	Hg2	4.1	3.4	16.5	10.7	17.6 ^e	14.2 ^e
	Hg3	2.7	3.0	16.4	11.4	18.9 ^e	15.0 ^e
	Hg4	3.8	3.3	16.0	11.0	16.4 ^f	14.3 ^f
2		14.1	0.0	16.4	11.6	-	-

^aContacts between Hg(II) centers and aromatic rings. ^bContacts belonging from C-H...O interactions. dmf molecules interacting with H atoms from ^cCg1-Cg1; ^dCg5-Cg5; ^eCg6-Cg7; or ^fCg8-Cg8.

References

- (1) Civalleri, B.; Zicovich-Wilson, C. M. ; Valenzano, L.; Ugliengo, P. Analysis of the Compression of Molecular Crystal Structures Using Hirshfeld Surfaces. *CrystEngComm* 2008, 10, 405–410.
- (2) Pinsky, M.; Avnir, D. Continuous Symmetry Measures. 5. The Classical Polyhedra. *Inorg. Chem.* 1998, 37, 5575–5582.
- (3) Llunell, M.; Casanova, D.; Cirera, J.; Bofill, J. M.; Alemany, P.; Alvarez, S.; Pinsky, M.; Avnir, D. SHAPE Version 2.1. Universitat de Barcelona and The Hebrew University of Jerusalem 2013.