

Supporting Information

Dynamic Mechanochemistry: Accelerated self-sorting of two imine-based metal complexes under solvent-free mechanochemical conditions

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General Methods: All reactions were carried out under air, at ambient temperature (20-22 °C, 40-52% relative humidity). 4-methylaniline (**1**), aminoquinoline (**2**), 5-methylpyridine-2-carboxaldehyde (**3**), 6-methylpyridine-2-carboxaldehyde (**4**), $\text{Cu}(\text{CH}_3\text{CN})_4(\text{BF}_4)$ and $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ were purchased from Sigma Aldrich/Millipore Sigma and used as received. CD_3CN was purchased from TCI America and used as received. High resolution mass spectra were acquired using an Agilent 6230B Time-of-Flight mass spectrometer to perform flow injection mass spectrometry. Mobile phase flow was provided by an Agilent 1260 quaternary pump delivering 0.300 mL/min of 50% water with 0.1% formic acid (Fisher)/50% acetonitrile (Fisher). Analyte solution was infused at 10 $\mu\text{L}/\text{min}$ using a syringe pump (New Era Pump Systems). Scan data was collected over 3 minutes at a sampling rate of 2 scan/sec.

Vibratory ball milling experiments: All experiments were conducted with a SPEX® 8000 M mill (18 Hz) in 5 mL stainless steel (ss) Smartsnap™ grinding jars from Form-Tech Scientific. An aluminum holder was manufactured in house to allow for three concurrent trials per run. Individual complexes were synthesized using a 1:2:2 molar ratio of metal salts to ligand components. The total reagent mass in each vial was approximately 200 mg, excluding the mass of four 3.175 mm ss (440c) balls, to prevent any imbalances during each trial. Self-sorting trials without additives were conducted in a similar fashion, with a bulk reagent mass of approximately 250 mg with components present in a 1:1:2:2:2:2 molar ratio of metal salts to ligand precursors. Self-sorting trials with celite additive were conducted in a similar manner to their non-additive counterparts but had the reagent mass halved. The other half of the mass was then comprised of the celite. A similar process was undertaken with MgSO_4 . After each trial, 0.7 mL of CD_3CN were introduced to the Smartsnap™ jar and passed through a .22 μm nylon filter, with a syringe, directly into an NMR tube. NMR samples were run on a Bruker Avance III 400 MHz and a Bruker Avance III 500 MHz and processed with Mestrelab's MestReNova 10.0 software. Spectra were referenced to residual CD_3CN (^1H δ 1.94).

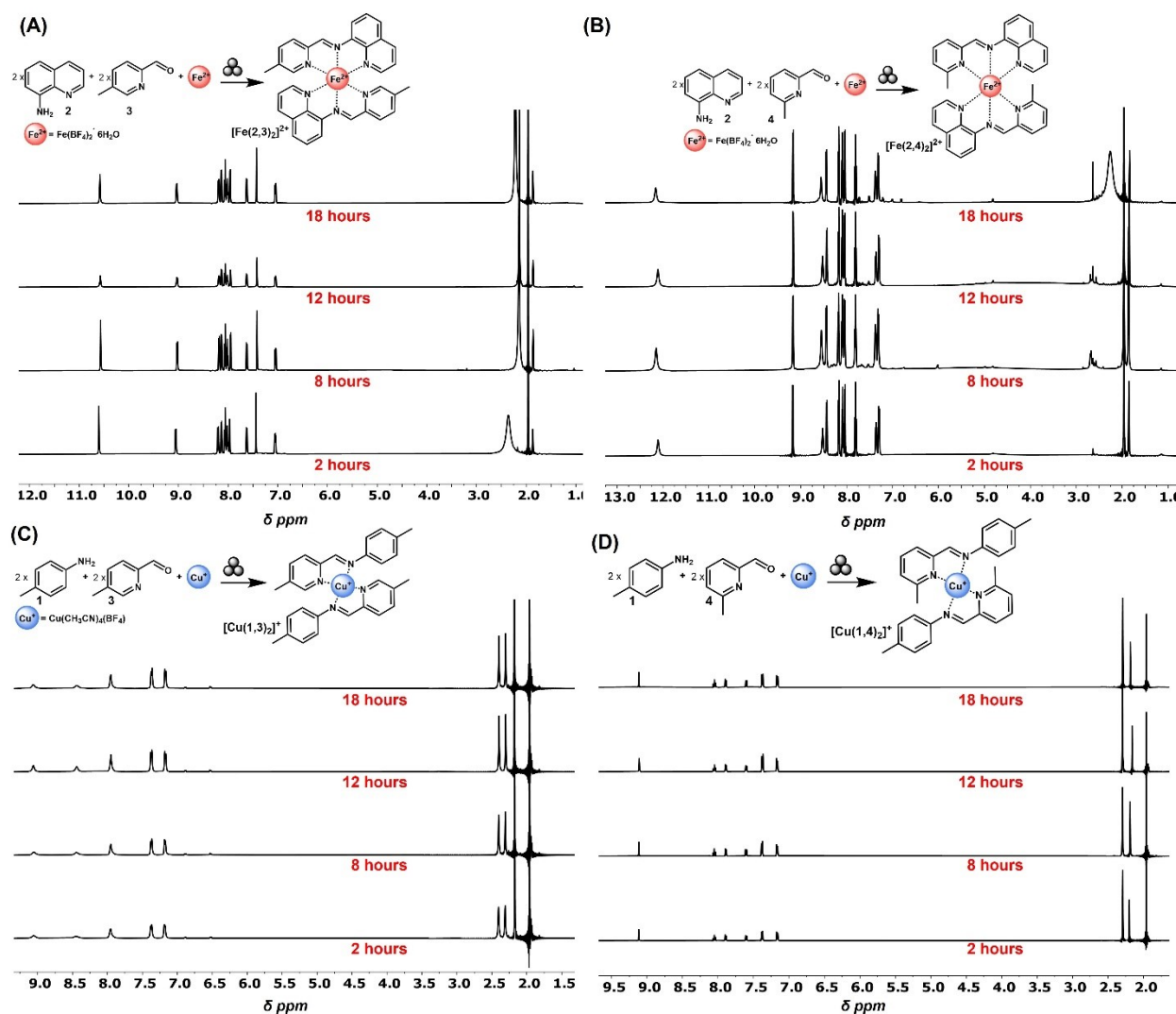


Figure S1. ^1H NMR (CD_3CN) for the one-pot formation of complexes (A) $[\text{Fe}(\mathbf{2},\mathbf{3})_2]^{2+}$, (B) $[\text{Fe}(\mathbf{2},\mathbf{4})_2]^{2+}$, (C) $[\text{Cu}(\mathbf{1},\mathbf{3})_2]^+$, and (D) $[\text{Cu}(\mathbf{1},\mathbf{4})_2]^+$, through vibratory ball-milling. Each timepoint represents a separate reaction.

Scale-up synthesis of $[\text{Cu}(\mathbf{1},\mathbf{3})_2][\text{BF}_4]$: Experiments were conducted on the same mill, SPEX® 8000 M (18 Hz), in a 65 mL SPEX® 8007 stainless steel grinding jar with two 12.7 mm ss balls. 550 mg of $\text{Cu}(\text{CH}_3\text{CN})_4(\text{BF}_4)$ was mixed with 2 equiv. of 4-methylaniline (**1**) (370 mg), and , 5-methylpyridine-2-carboxaldehyde (**3**) (424 mg). The reaction vessel was sealed, and allowed to react under continuous milling for 1 h. When complete, the powder was washed with minimal hexanes then dried under vacuum to afford dark burgundy solid $[\text{Cu}(\mathbf{1},\mathbf{3})_2][\text{BF}_4]$ in 96% yield (960 mg). The was confirmed by ESI-MS of $[\text{Cu}(\mathbf{1},\mathbf{3})_2]^+$, $m/z = 483.1644$. The powder was further characterized by ^1H (500 MHz) and ^{13}C (150 MHz) in CD_3CN ; the ^{13}C measurement was conducted on a Bruker Avance III HD 600 MHz spectrometer at 308.15 K to enhance solubility and lower signal to noise.

Single crystals of $[\text{Cu}(\mathbf{1},\mathbf{3})_2][\text{BF}_4]$ were obtained by dissolving a small amount of the complex in fresh dichloromethane and using pentane as a counter solvent. X-ray Diffraction studies of $[\text{Cu}(\mathbf{1},\mathbf{3})_2][\text{BF}_4]$ were conducted on a Rigaku XTA-Lab Mini II diffractometer using a

Mo K α ($\lambda = 0.7103$ Å) source and a CCD plate detector at 298.0(9) K. Data collection, cell parameter determinations, data reduction, and absorption corrections were performed via CrysAlis Pro.¹ Structure solution, refinement, and publication materials were generated *via* SHELXL, SHELXLT, and Olex2.²⁻⁴

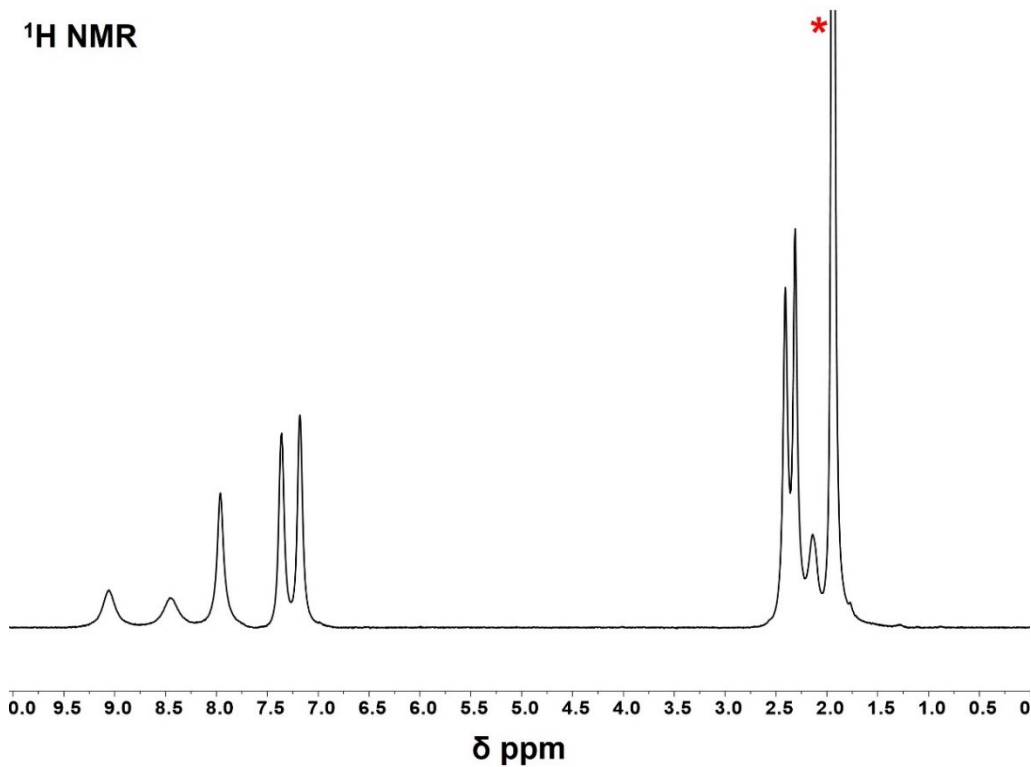


Figure S2. ¹H NMR spectrum of [Cu(1,3)₂][BF₄] in CD₃CN (*).

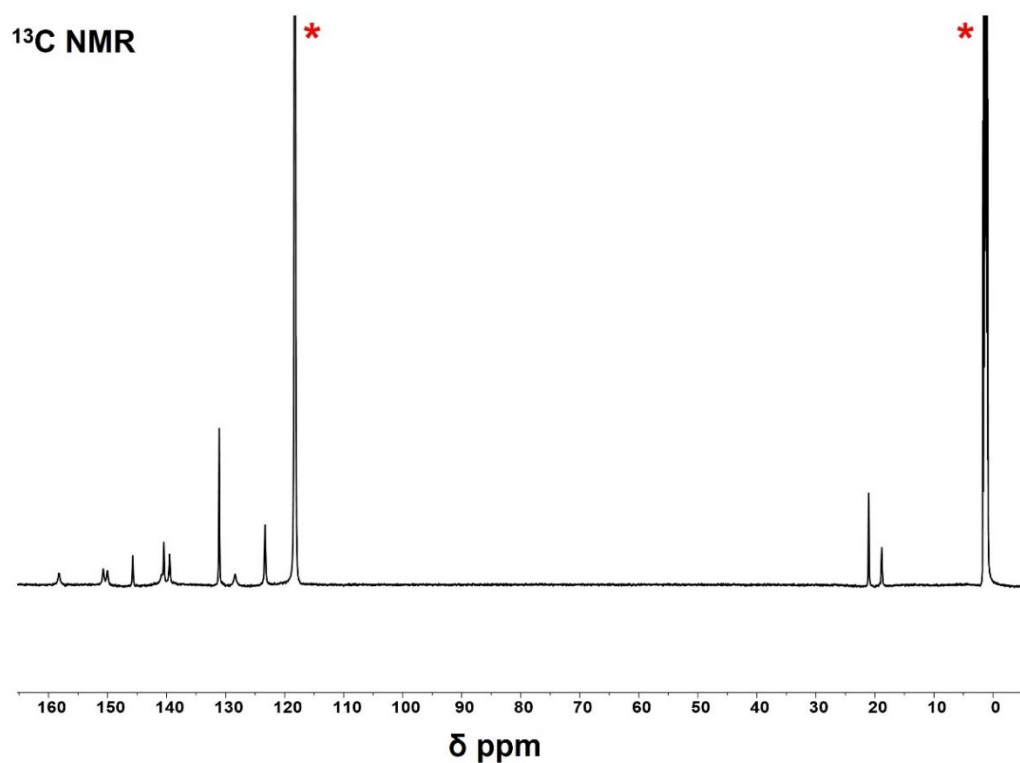
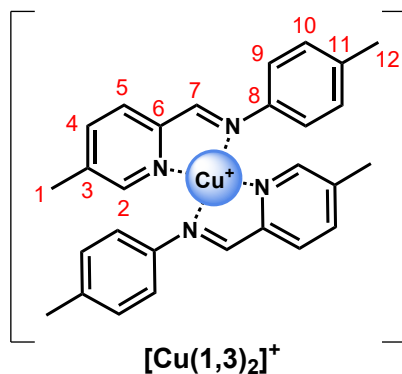


Figure S3. ^{13}C NMR spectrum of $[\text{Cu}(\mathbf{1},\mathbf{3})_2][\text{BF}_4]$ in CD_3CN (*), measured at 308.15 K to aid solubility and enhance signal to noise.



BF_4^- **^1H -NMR (500 MHz, CD_3CN):** δ (ppm) 9.06 (s, 2H, H_7), 8.46 (bs, 2H, H_2), 7.96 (bs, 4H, H_4 , H_5), 7.36 (bs, 2H, H_9), 7.18 (bs, 2H, H_{10}), 2.41 (s, 6H, H_1), 2.31 (s, 6H, H_{12}).

^{13}C -NMR (150 MHz, CD_3CN): δ (ppm) 158.26 (C_2 , C_7), 151.75 (C_6), 150.02 (C_4), 145.73 (C_8), 140.47 (C_{11}), 139.49 (C_{10}), 131.09 (C_3), 128.38 (C_5), 123.31 (C_9), 21.05 (C_1), 18.85 (C_{12}).

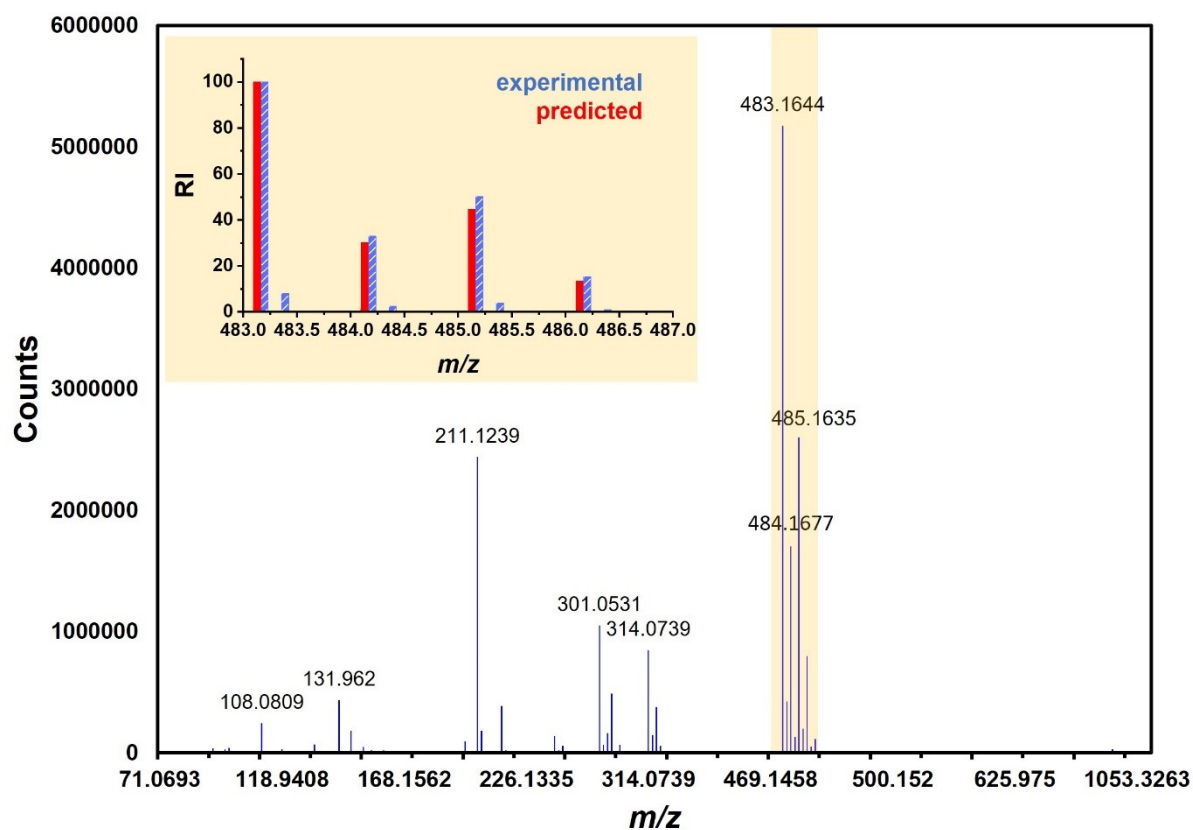


Figure S4. ESI-MS of $[\text{Cu}(\mathbf{1},\mathbf{3})_2]^+$, $m/z = 483.1644$. *Inset:* close up plot with predicted vs experimental data.

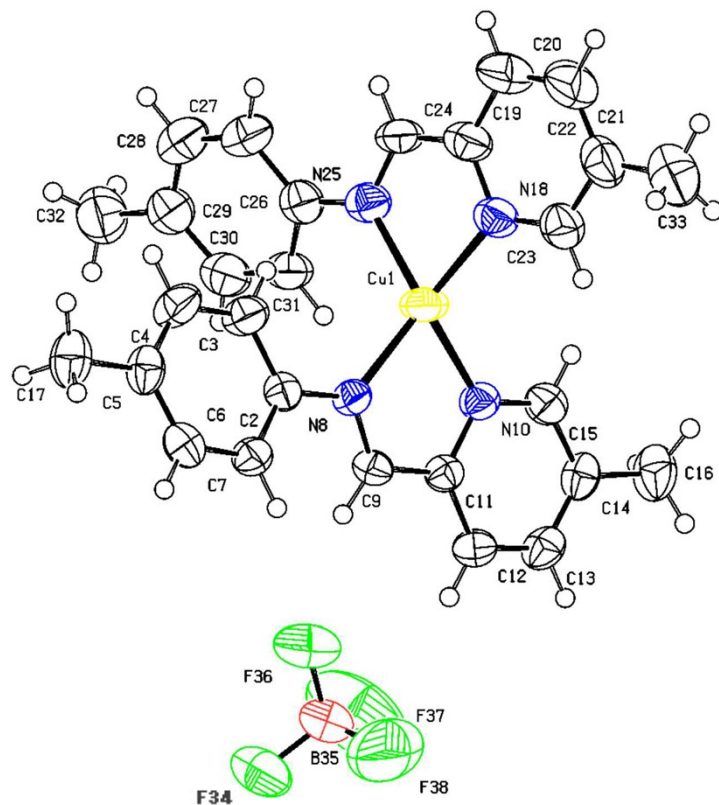


Figure S5. Thermal ellipsoid plot of $[\text{Cu}(\text{1,3})_2][\text{BF}_4]$ with thermal ellipsoids at 50% probability.

Table 1 Crystal data and structure refinement for [Cu(1,3)₂][BF₄].

Empirical formula	C ₂₈ H ₂₈ BCuF ₄ N ₄
Formula weight	570.89
Temperature/K	298.0(9)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	8.4782(2)
b/Å	15.1109(5)
c/Å	21.1155(6)
α/°	90
β/°	97.371(3)
γ/°	90
Volume/Å ³	2682.84(14)
Z	4
ρ _{calc} /g/cm ³	1.413
μ/mm ⁻¹	0.866
F(000)	1176.0
Crystal size/mm ³	0.254 × 0.171 × 0.166
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	3.324 to 54.966
Index ranges	-10 ≤ h ≤ 11, -19 ≤ k ≤ 18, -27 ≤ l ≤ 27
Reflections collected	26642
Independent reflections	6151 [R _{int} = 0.0311, R _{sigma} = 0.0379]
Data/restraints/parameters	6151/0/347
Goodness-of-fit on F ²	1.058
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0674, wR ₂ = 0.1508
Final R indexes [all data]	R ₁ = 0.0994, wR ₂ = 0.1658
Largest diff. peak/hole / e Å ⁻³	0.93/-0.45

Table 2 Bond Lengths for [Cu(1,3)₂][BF₄].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
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Table 2 Bond Lengths for [Cu(1,3)₂][BF₄].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	N10	2.027(3)	C7	C6	1.389(5)
Cu1	N8	2.068(3)	C26	C31	1.375(5)
Cu1	N25	2.043(3)	C26	C27	1.412(5)
Cu1	N18	2.050(3)	C13	C12	1.377(5)
N10	C11	1.354(4)	C5	C6	1.378(5)
N10	C15	1.331(4)	C5	C4	1.374(5)
N8	C9	1.284(4)	C5	C17	1.516(5)
N8	C2	1.434(4)	C24	C19	1.448(6)
N25	C26	1.419(5)	C31	C30	1.369(6)
N25	C24	1.281(4)	C3	C4	1.385(5)
N18	C19	1.343(5)	C19	C20	1.394(6)
N18	C23	1.331(5)	C30	C29	1.380(6)
F34	B35	1.343(6)	C29	C28	1.396(6)
C11	C9	1.457(4)	C29	C32	1.502(6)
C11	C12	1.384(4)	C27	C28	1.380(6)
F36	B35	1.344(6)	C23	C22	1.391(6)
C2	C7	1.386(4)	C22	C21	1.380(6)
C2	C3	1.381(5)	C22	C33	1.482(7)
C14	C13	1.365(5)	C20	C21	1.377(7)
C14	C15	1.394(5)	F38	B35	1.327(7)
C14	C16	1.514(5)	F37	B35	1.320(7)

Table 3 Bond Angles for [Cu(1,3)₂][BF₄].

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N10	Cu1	N8	81.86(10)	C14	C13	C12	120.9(3)
N10	Cu1	N25	131.63(11)	C13	C12	C11	118.5(3)
N10	Cu1	N18	118.70(12)	C6	C5	C17	121.1(4)
N25	Cu1	N8	119.01(11)	C4	C5	C6	117.5(3)
N25	Cu1	N18	81.50(13)	C4	C5	C17	121.5(3)
N18	Cu1	N8	131.28(11)	C5	C6	C7	121.9(3)
C11	N10	Cu1	111.7(2)	N25	C24	C19	119.3(3)
C15	N10	Cu1	130.5(2)	C30	C31	C26	121.7(4)
C15	N10	C11	117.7(3)	N10	C15	C14	123.9(3)
C9	N8	Cu1	110.9(2)	C2	C3	C4	120.5(3)
C9	N8	C2	119.7(3)	N18	C19	C24	116.3(3)
C2	N8	Cu1	129.2(2)	N18	C19	C20	120.5(4)
C26	N25	Cu1	125.8(2)	C20	C19	C24	123.2(4)
C24	N25	Cu1	111.9(3)	C31	C30	C29	121.6(4)
C24	N25	C26	122.4(3)	C30	C29	C28	117.3(4)
C19	N18	Cu1	110.8(3)	C30	C29	C32	121.3(4)
C23	N18	Cu1	130.0(3)	C28	C29	C32	121.4(4)
C23	N18	C19	119.2(3)	C28	C27	C26	119.6(4)
N10	C11	C9	115.9(3)	C5	C4	C3	121.7(3)
N10	C11	C12	122.0(3)	C27	C28	C29	121.8(4)
C12	C11	C9	122.1(3)	N18	C23	C22	124.4(4)
N8	C9	C11	119.4(3)	C23	C22	C33	122.1(4)
C7	C2	N8	123.9(3)	C21	C22	C23	115.3(4)
C3	C2	N8	117.6(3)	C21	C22	C33	122.6(4)
C3	C2	C7	118.5(3)	C21	C20	C19	118.8(5)
C13	C14	C15	117.0(3)	C20	C21	C22	121.7(4)
C13	C14	C16	123.2(3)	F34	B35	F36	112.2(5)
C15	C14	C16	119.7(3)	F38	B35	F34	110.7(5)
C2	C7	C6	119.9(3)	F38	B35	F36	106.5(5)
C31	C26	N25	118.5(3)	F37	B35	F34	109.3(5)
C31	C26	C27	117.9(4)	F37	B35	F36	110.5(5)
C27	C26	N25	123.6(3)	F37	B35	F38	107.5(6)

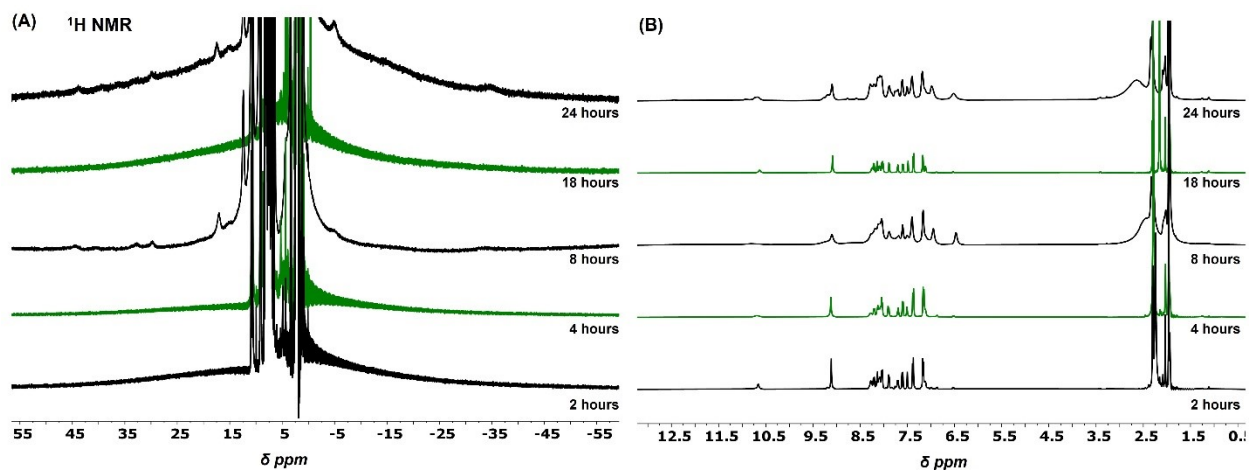


Figure S6. (A) Expanded and (B) standard range ^1H NMR (CD_3CN) for the one-pot formation of complexes $[\text{Cu}(\mathbf{1},\mathbf{4})_2]^+$, $[\text{Fe}(\mathbf{2},\mathbf{3})_2]^{2+}$ and trace $[\text{Fe}(\mathbf{2},\mathbf{3})(\mathbf{2},\mathbf{4})]^{2+}$ through solvent-free vibratory ball-milling of the 6-reagent library (Figure 3 in the manuscript). Each timepoint represents a separate reaction. *Expanded range highlights the formation of low intensity broad peaks at 8 and 24 h commensurate with paramagnetic species (proposed in Figure S6).*

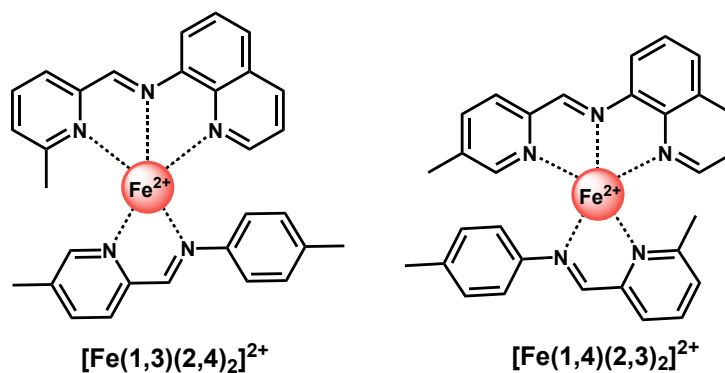


Figure S7. Proposed, transient paramagnetic species observed at 8 h and 24 h for the mechanochemical self-sorting trials (See Figure S5).

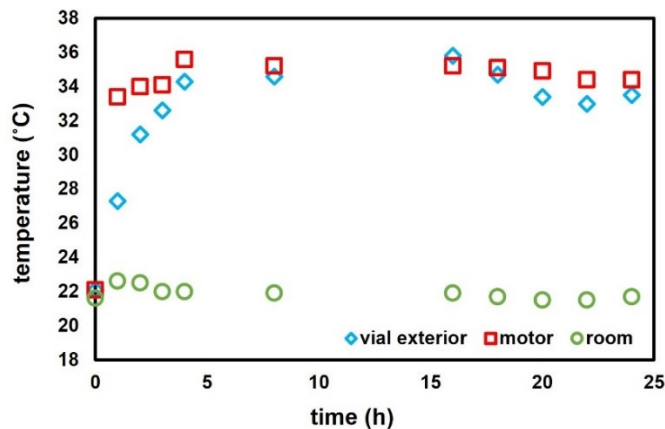


Figure S8. Plot of temperature on the grinding vial exterior, motor, and room (1 m from ball mill enclosure), as a function of time.

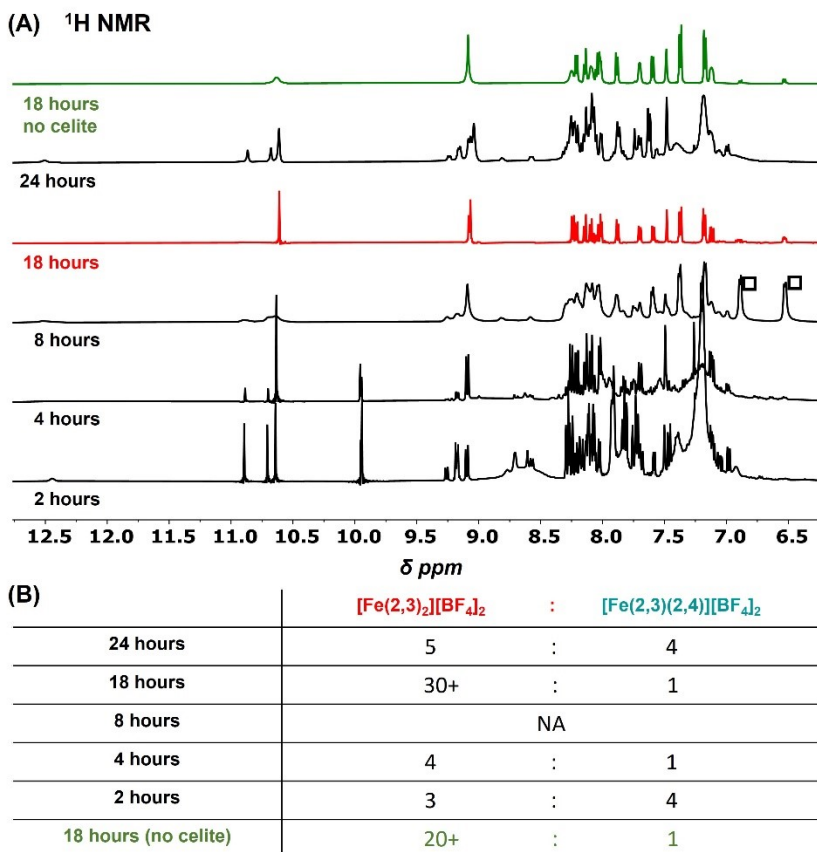


Figure S9. (A) Partial ^1H NMR (CD_3CN) for the one-pot formation of complexes $[\text{Cu}(\mathbf{1},\mathbf{4})_2]^+$, $[\text{Fe}(\mathbf{2},\mathbf{3})_2]^{2+}$ and trace $[\text{Fe}(\mathbf{2},\mathbf{3})(\mathbf{2},\mathbf{4})]^{2+}$ through solvent-free vibratory ball-milling of the 6-reagent library, at $0.5\times$ concentration with celite as additive. Each timepoint represents a separate reaction. Peaks tentatively associated to paramagnetic species are highlighted with hollow squares. (B) Table of observed $[\text{Fe}(\mathbf{2},\mathbf{3})_2][\text{BF}_4]_2$: $[\text{Fe}(\mathbf{2},\mathbf{3})(\mathbf{2},\mathbf{4})][\text{BF}_4]_2$ ratios.

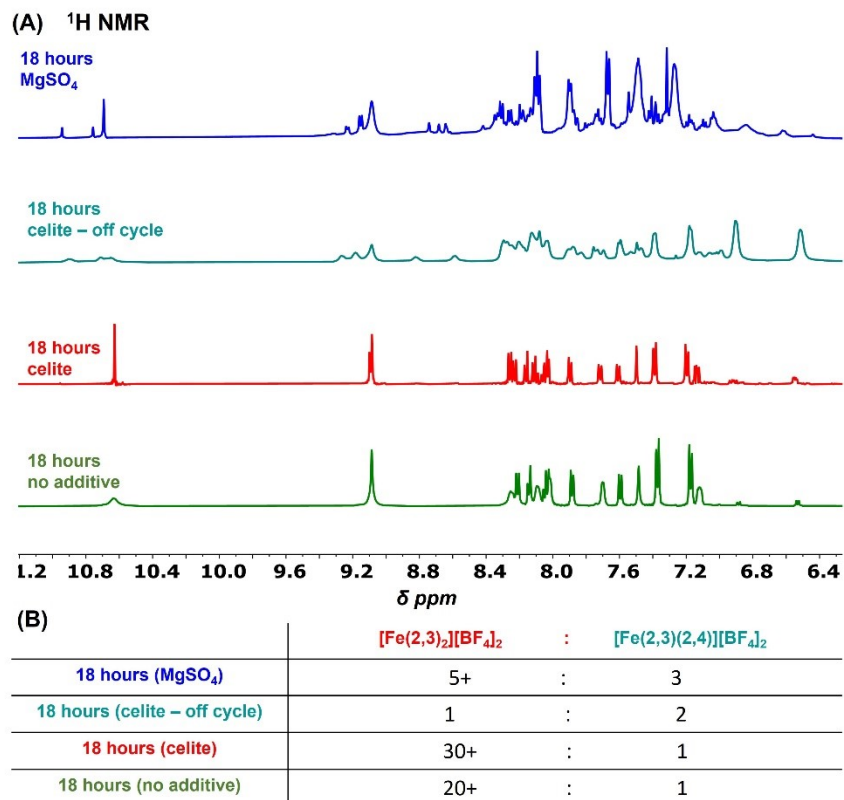


Figure S10. (A) Partial ^1H NMR (CD_3CN) for the one-pot formation of complexes $[\text{Cu}(\mathbf{1},\mathbf{4})_2]^+$, $[\text{Fe}(\mathbf{2},\mathbf{3})_2]^{2+}$ and trace $[\text{Fe}(\mathbf{2},\mathbf{3})(\mathbf{2},\mathbf{4})]^{2+}$ through solvent-free vibratory ball-milling of the 6-reagent library, at $0.5\times$ concentration with celite, or MgSO_4 as additive, at the 18 hour timepoint, with comparison to 18 hour timepoints from additive free, or as reported in Figure S8. (B) Table of observed $[\text{Fe}(\mathbf{2},\mathbf{3})_2][\text{BF}_4]_2$: $[\text{Fe}(\mathbf{2},\mathbf{3})(\mathbf{2},\mathbf{4})][\text{BF}_4]_2$ ratios.

References:

- 1 Rigaku Oxford Diffraction, *CrysAlis PRO.*, Rigaku Oxford Diffraction, Yarnton, Oxfordshire, England. 2020.
- 2 *SHELXTL*, ver. 6.12; Bruker AXS, Inc.: Madison, WI, 2005.
- 3 Olex 2 1.2 (compiled 2014-06-27 svn.r2953 for OlexSys, GUI svn. r4855).
- 4 O. Dolomanov, L. Bourhis, R. Gildea, J. Howard. H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.