SUPPORTING INFORMATION

Halogen bonding of *N*-bromosuccinimide by grinding

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EXPERIMENTAL DETAILS

MATERIALS

The starting materials, *N*-bromosuccinimide (**nbs**) and 4,4'-bipyridine (**bpy**) were obtained from Merck, and used without further purification. Solvents were purchased from Kemika and T.T.T., Zagreb.

MECHANOCHEMICAL SYNTHESIS

Synthesis of (**nbs**)(**bpy**)

For NG experiment **nbs** (107 mg, 0.60 mmol) and **bpy** (94 mg, 0.60 mmol) were placed in a 10 mL stainless steel jar along with two stainless steel balls 7 mm in diameter. The mixture was then milled for 15 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

For LAG experiment **nbs** (107 mg, 0.60 mmol) and **bpy** (94 mg, 0.60 mmol) were placed in a 10 mL stainless steel jar along with 30 μL of acetonitrile and two stainless steel balls 7 mm in diameter. The mixture was then milled for 15 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

Synthesis of (**nbs**)$_2$(**bpy**)

For NG experiment **nbs** (139 mg, 0.78 mmol) and **bpy** (61 mg, 0.39 mmol) were placed in a 10 mL stainless steel jar along with two stainless steel balls 7 mm in diameter. The mixture was then milled for 15 minutes and 80 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

For LAG experiment **nbs** (139 mg, 0.78 mmol) and **bpy** (61 mg, 0.39 mmol) were placed in a 10 mL stainless steel jar along with 30 μL of acetonitrile and two stainless steel balls 7 mm in diameter. The mixture was then milled for 15 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

SOLUTION SYNTHESIS

Synthesis of (**nbs**)(**bpy**)

Equimolar quantities of **nbs** (60 mg, 0.34 mmol) and **bpy** (53 mg, 0.22 mmol), were dissolved in a hot acetonitrile (2.0 mL). The resulting mixture was left at room temperature. Colorless crystals appeared after one hour, and were separated from the mother liquor by filtration.

Synthesis of (**nbs**)$_2$(**bpy**)

The reactants, **nbs** (60 mg, 0.34 mmol) and **bpy** (25 mg, 0.13 mmol), were dissolved in a hot acetonitrile (3.0 mL). The resulting mixture was left at room temperature. Yellow crystals appeared after half an hour, and were separated from the mother liquor by filtration.

Preparation of single crystals

Single crystals of (**nbs**)(**bpy**) and (**nbs**)$_2$(**bpy**) suitable for X-ray diffraction were obtained by concomitant crystallization from acetone. The reactants, **nbs** (60 mg, 0.34 mmol) and **bpy** (21 mg, 0.13 mmol), were dissolved in a hot acetone (2.0 mL). The resulting solution was left at room temperature. Colorless and yellow crystals appeared after one day, and were separated from the mother liquor by filtration.

THERMAL ANALYSIS

DSC measurements were performed on a Mettler-Toledo DSC823^e module. The samples were placed in sealed aluminium pans (40 μL) with three holes made on the top cover, and heated in flowing nitrogen (150 mL min^{-1}) from 25 °C to 500 °C at a rate of 10 °C min^{-1}. The data collection and analysis was performed using the program package STAR^e Software 9.01.[1]

SINGLE-CRYSTAL X-RAY DIFFRACTION EXPERIMENTS

The crystal and molecular structures of (**nbs**)(**bpy**) and (**nbs**)$_2$(**bpy**)_were determined by single crystal X-ray diffraction. Details of data collection and crystal structure refinement are listed in Table S1. The diffraction data were collected at 293 K. Diffraction measurements were made on an Oxford Diffraction Xcalibur Kappa CCD X-ray diffractometer with graphite-monochromated MoKα (λ = 0.71073Å) radiation. The data sets were collected using the ω scan mode over the 2θ range up to 54°. Programs CrysAlis CCD and CrysAlis RED were employed for data collection, cell refinement, and data reduction.[2] The structures were solved by direct methods and refined using the SHELXS and SHELXL programs, respectively.[3] The structural refinement was performed on F^2 using all data. The hydrogen atoms not involved in hydrogen bonding were placed in calculated positions and treated as riding on their parent atoms [C–H = 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(C)] while the others were located from the electron difference map. All calculations were performed using the WINGX crystallographic suite of programs.[4] The molecular structures of compounds are presented by ORTEP-3.[5] The molecular packing projections and PXRD calculations were prepared by Mercury.[6]

POWDER X-RAY DIFFRACTION EXPERIMENTS

PXRD experiments on the samples were performed on a PHILIPS PW 1840 X-ray diffractometer with CuKα1 (1.54056 Å) radiation at 40 mA and 40 kV. The scattered intensities were measured with a scintillation counter. The angular range was from 5 to 40° (2θ) with steps of 0.02 – 0.03°, and the measuring time was 0.2 – 0.5 s per step. Data collection and analysis was performed using the program package Philips X'Pert.[7]

References

1. STARe Software V.9.01., MettlerToledo GmbH, 2006.
2. Oxford Diffraction, Oxford Diffraction Ltd., Xcalibur CCD system, CrysAlis CCD and CrysAlis RED software, Version 1.170, 2003.
3. G. M. Sheldrick, *Acta Crystallogr. Sect. C71,* **2015**, 3.
4. L. J. Farrugia, WinGX, *J. Appl. Cryst.* **1999**, 32, 837.
5. L. J. Farrugia, ORTEP-3 for Windows, *J. Appl. Cryst.* **1997**, 30, 565.
6. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. v. d. Streek and P. A. Wood, *J. Appl. Crystallogr.* **2008**, 41, 466.
7. Philips X'Pert Data Collector 1.3e, Philips Analytical B. V. Netherlands, 2001; Philips X'Pert Graphic & Identify 1.3e Philips Analytical B. V. Netherlands, 2001; Philips X'Pert Plus 1.0, Philips Analytical B. V. Netherlands, 1999.

Table S1. General and crystallographic data for (**nbs**)(**bpy**) and (**nbs**)$_2$(**bpy**).

	(**nbs**)(**bpy**)	(**nbs**)$_2$(**bpy**)
Molecular formula	$(C_4H_4BrNO_2)(C_{10}H_8N_2)$	$(C_4H_4BrNO_2)_2(C_{10}H_8N_2)$
M_r	334.18	512.17
Crystal system	monoclinic	monoclinic
Space group	$P\,2_1/c$	$P\,2_1/c$
Crystal data:		
a / Å	15.7340(6)	24.0130(10)
b / Å	7.3700(3)	4.8573(2)
c / Å	12.2070(4)	18.3684(7)
α / °	90.00	90.00
β / °	107.213(4)	110.975(4)
γ / °	90.00	90.00
V / Å^3	1352.12(9)	2000.49(14)
Z	4	4
D_{calc} / g cm^{-3}	1.642	1.701
λ(MoK_α) / Å	0.71073	0.71073
T / K	295	295
Crystal size / mm^3	0.62x0.35x0.05	0.69x0.14x0.09
μ / mm^{-1}	3.045	4.084
$F(000)$	672	1016
Refl. collected/unique	13225 / 2946	16541 / 4177
Data/restraints/parameters	181	253
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.307; −0.423	0.850; −0.344
$R[F^2>4\sigma(F^2)]$	0.0310	0.0328
$wR(F^2)$	0.0565	0.0522
Goodness-of-fit, S	0.833	0.707

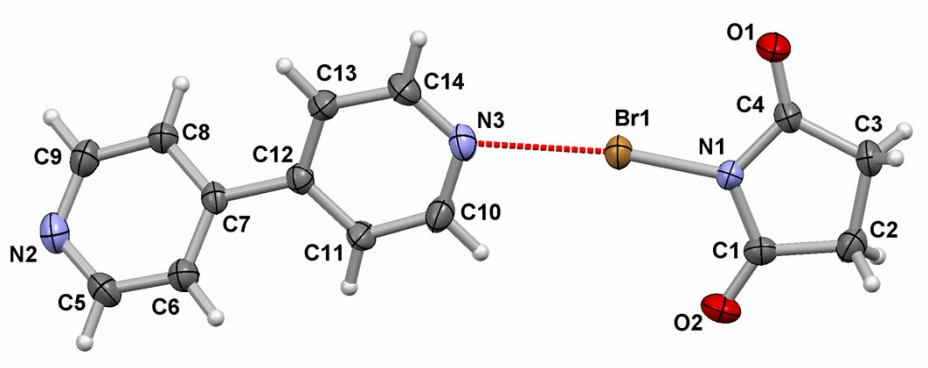

Figure S1. Molecular structures of (**nbs**)(**bpy**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40 % probability level and H atoms are shown as small spheres of arbitrary radius.

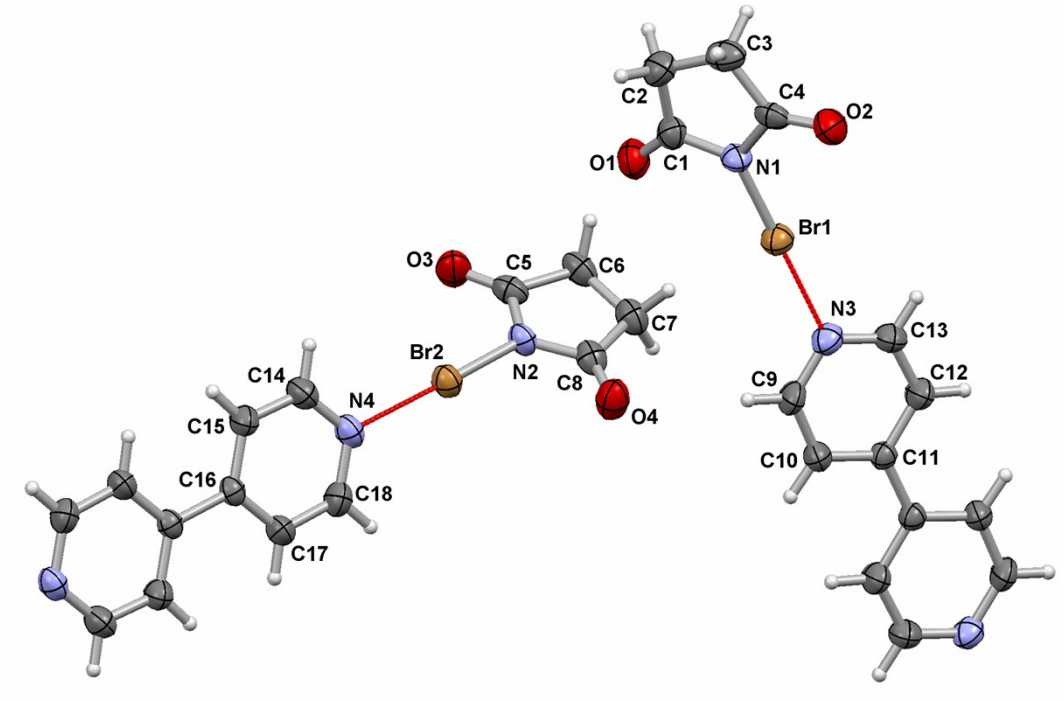

Figure S2. Molecular structures of (**nbs**)$_2$(**bpy**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40 % probability level and H atoms are shown as small spheres of arbitrary radius.

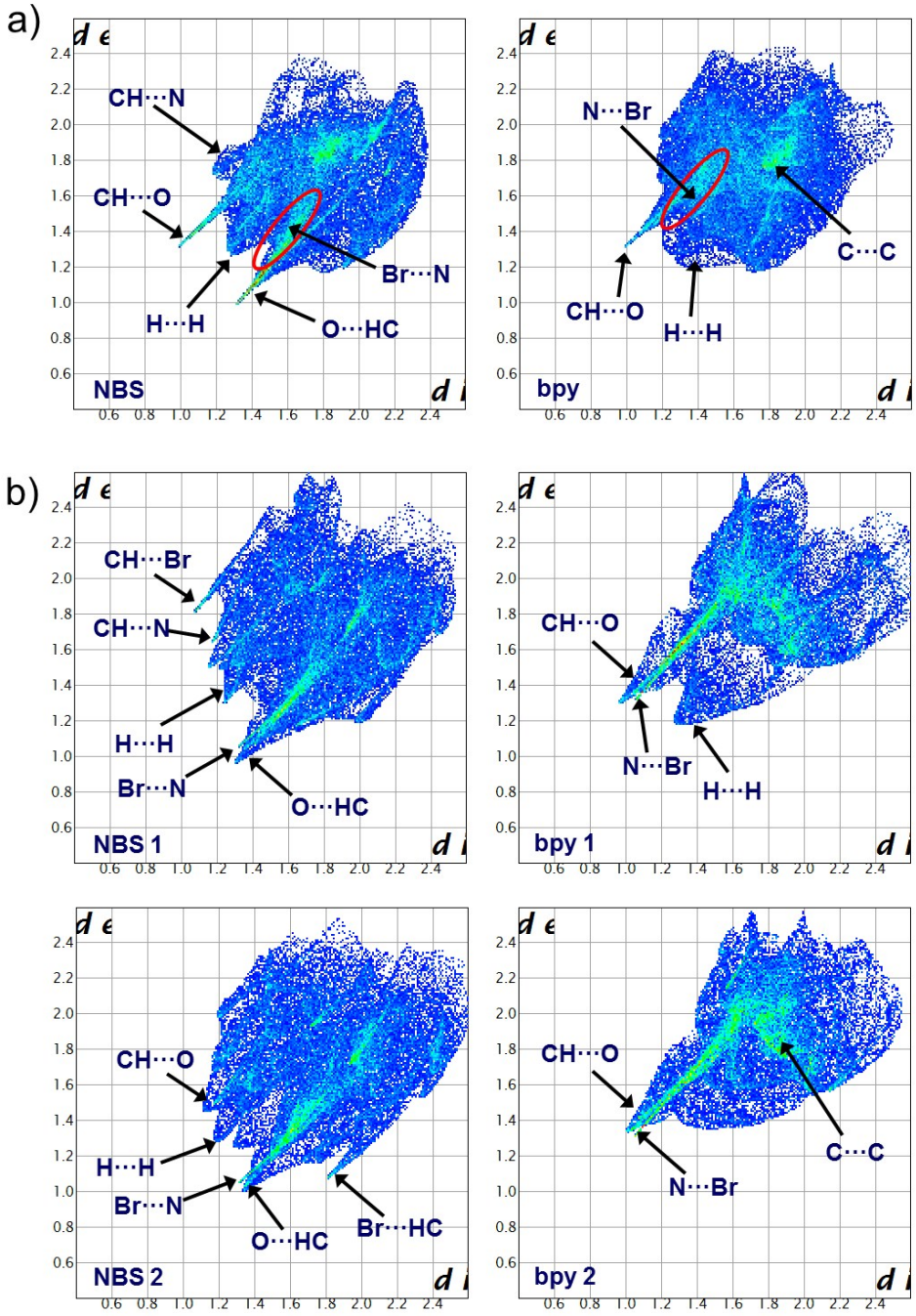

Figure S3. Two-dimensional fingerprint plot derived from the Hirshfeld surface of the **nbs** and **bpy** molecule of: a) (**nbs**)(**bpy**) and b) (**nbs**)$_2$(**bpy**).

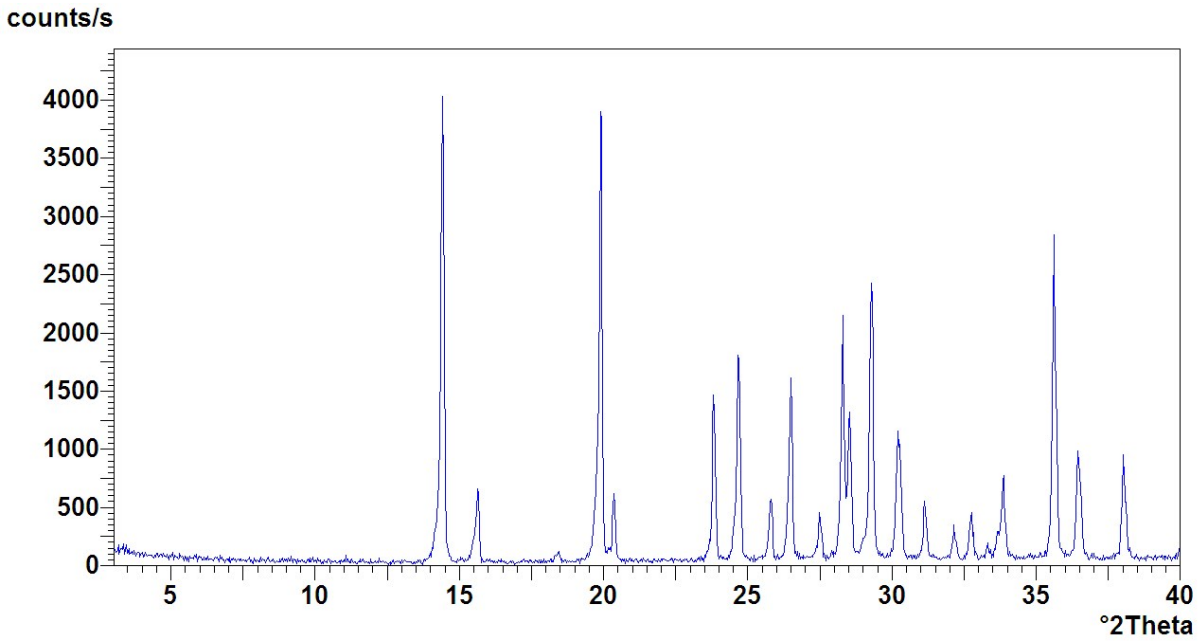

Figure S4. PXRD pattern of pure **nbs** reactant.

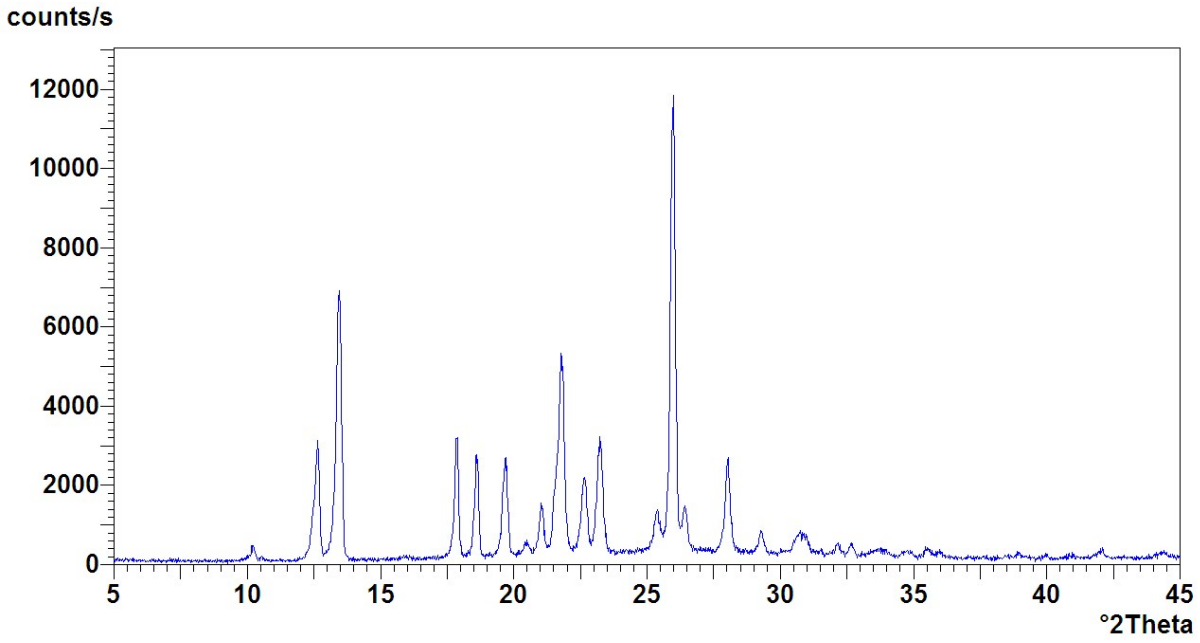

Figure S5. PXRD pattern of pure **bpy** reactant.

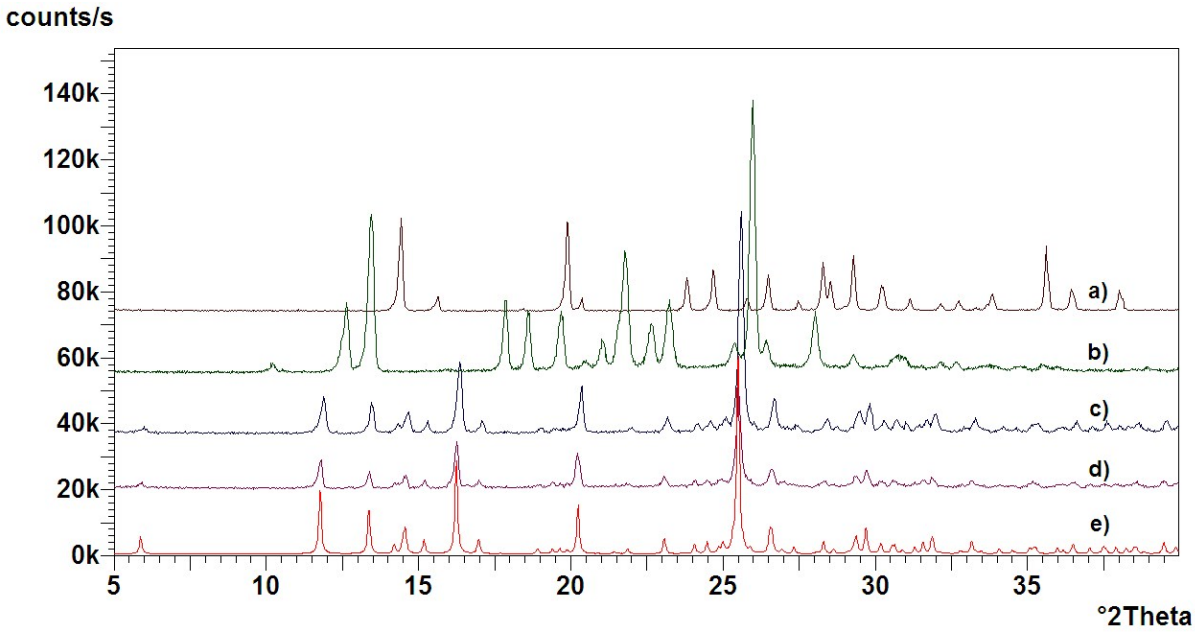

Figure S6. PXRD patterns for mechanochemical experiment involving **nbs** and **bpy**: a) **nbs**, b) **bpy**, c) product obtained by neat grinding an equimolar amount of **nbs** and **bpy** in a ball mill for 15 min d) product obtained by neat grinding an equimolar amount of **nbs** and **bpy** in a ball mill for 80 min, e) calculated pattern for compound (**nbs**)(**bpy**).

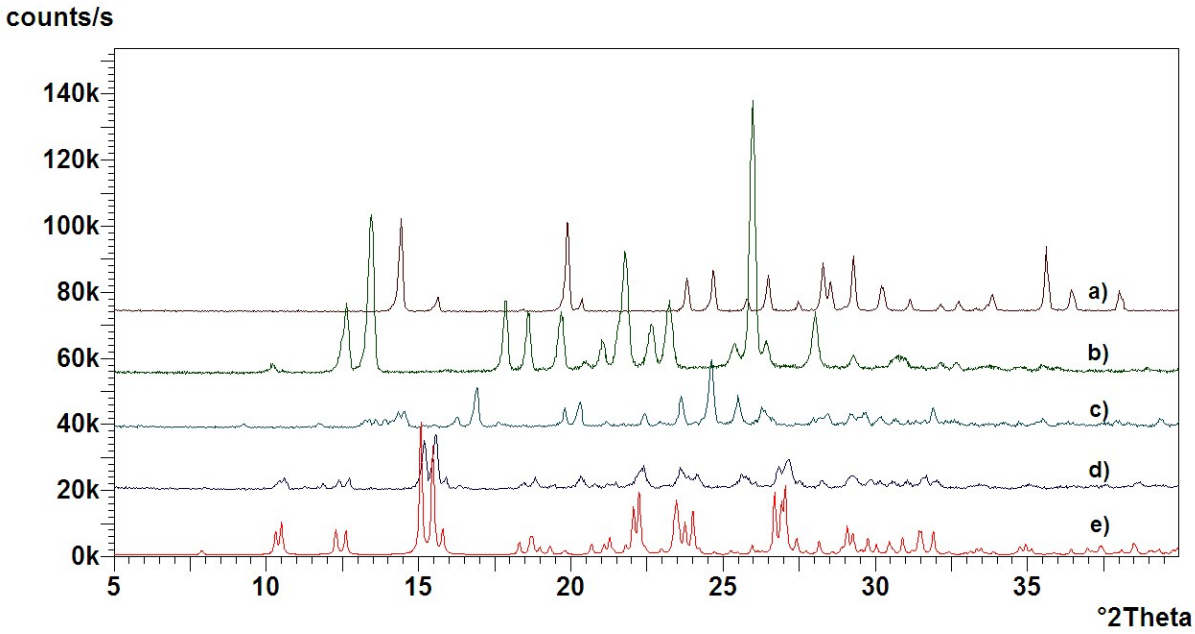

Figure S7. PXRD patterns for mechanochemical experiment involving **nbs** and **bpy**: a) **nbs**, b) **bpy**, c) product obtained by neat grinding a mixture with a 2:1 molar ratio of **nbs** and **bpy** in a ball mill for 15 min, d) product obtained by neat grinding a mixture with a 2:1 molar ratio of **nbs** and **bpy** in a ball mill for 80 min, e) calculated pattern for compound (**nbs**)$_2$(**bpy**).

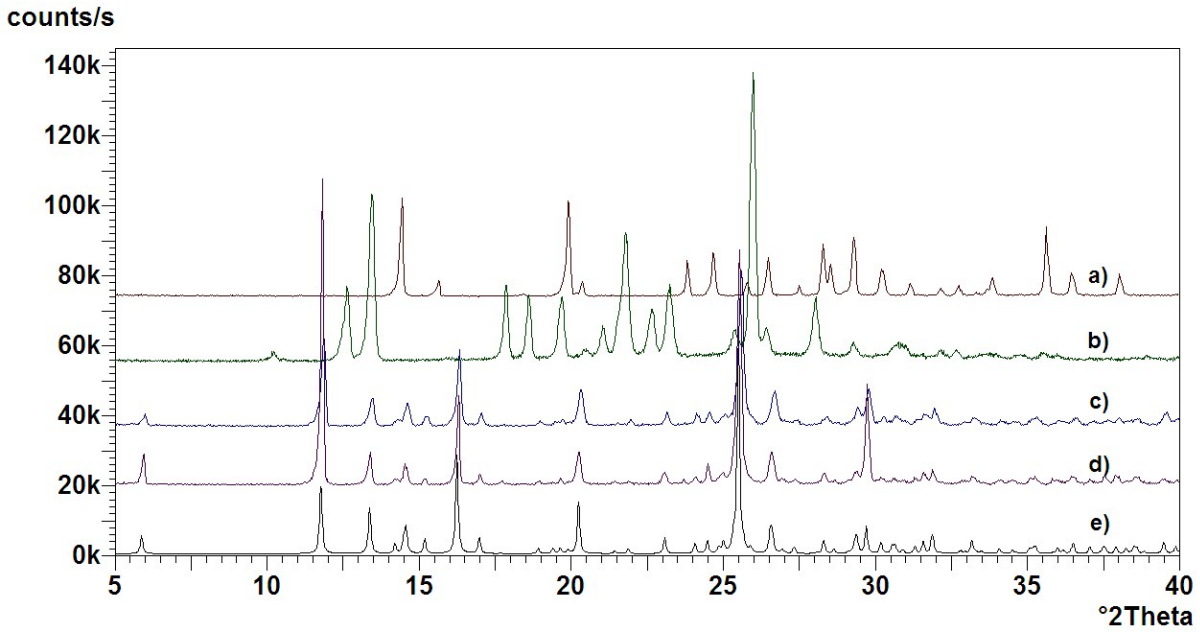

Figure S8. PXRD patterns for mechanochemical experiment involving **nbs** and **bpy**: a) **nbs**, b) **bpy**, c) product obtained by grinding an equimolar amount of **nbs** and **bpy** in a ball mill for 15 min in the presence a small quantity of acetonitrile, d) (**nbs**)(**bpy**) obtained by solution synthesis from acetonitrile, e) calculated pattern for compound (**nbs**)(**bpy**).

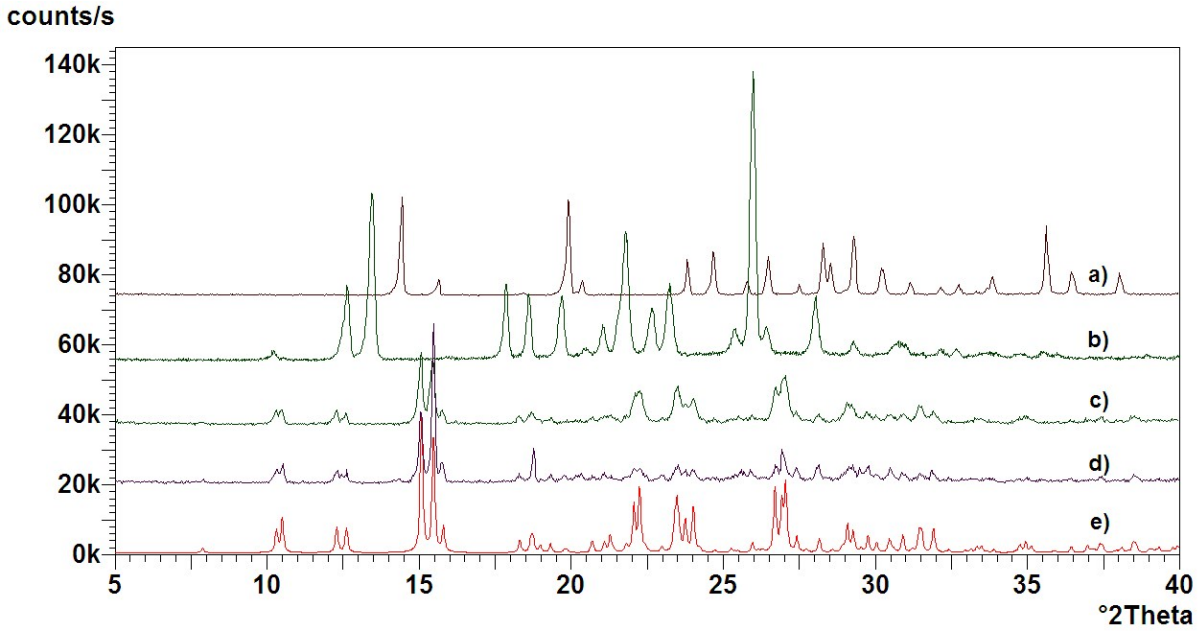

Figure S9. PXRD patterns for mechanochemical experiment involving **nbs** and **bpy**: a) **nbs**, b) **bpy**, c) product obtained by grinding a mixture with a 2:1 molar ratio of **nbs** and **bpy** in a ball mill for 15 min in the presence a small quantity of acetonitrile, d) $(\mathbf{nbs})_2(\mathbf{bpy})$ obtained by solution synthesis from acetonitrile, e) calculated pattern for compound $(\mathbf{nbs})_2(\mathbf{bpy})$.

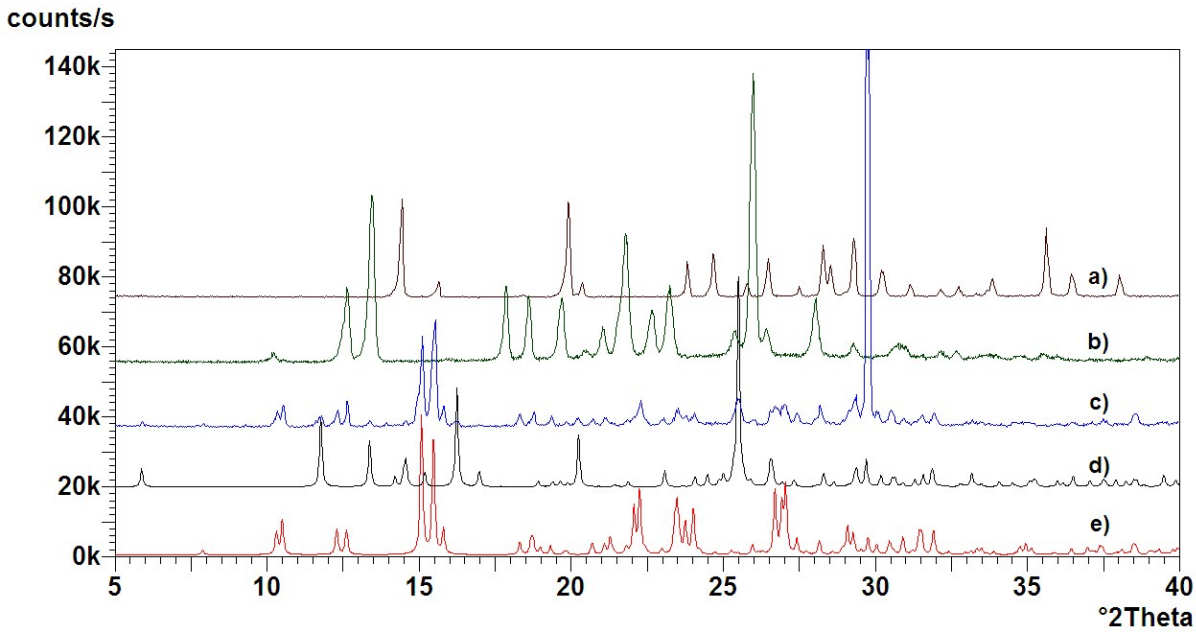

Figure S10. PXRD patterns for mechanochemical experiment involving **nbs** and **bpy**: a) **nbs**, b) **bpy**, c) crystal product obtained by solution synthesis from acetone, d) calculated pattern for compound (**nbs**)(**bpy**), e) calculated pattern for compound (**nbs**)$_2$(**bpy**).

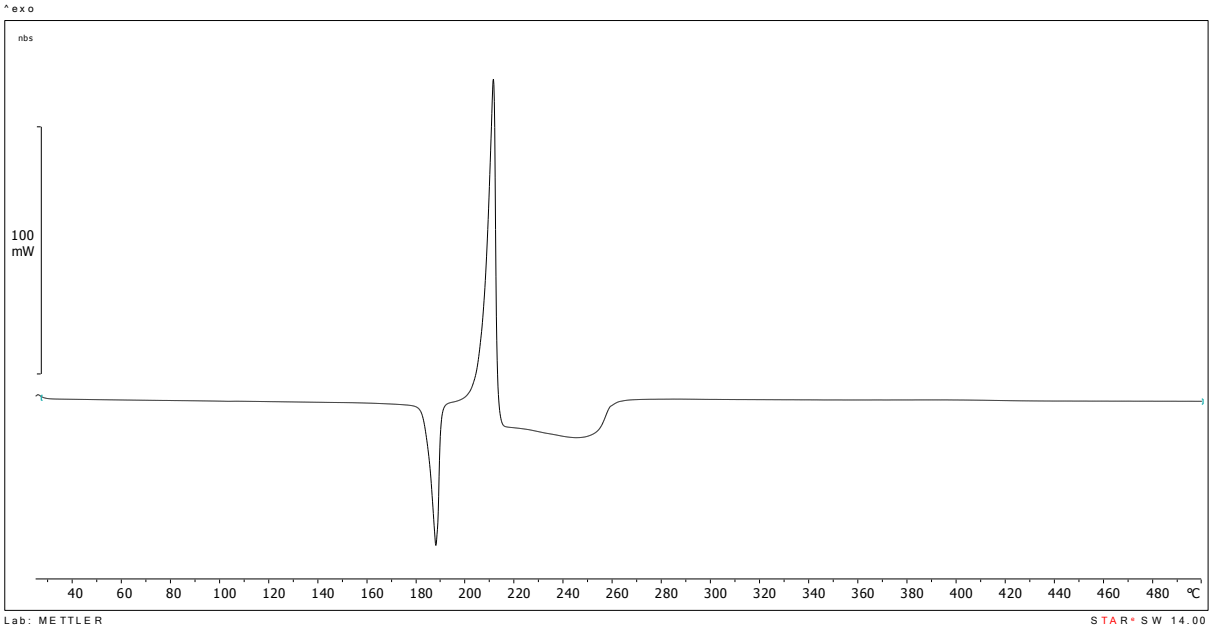

Figure S11. DSC curve for pure **nbs** reactant.

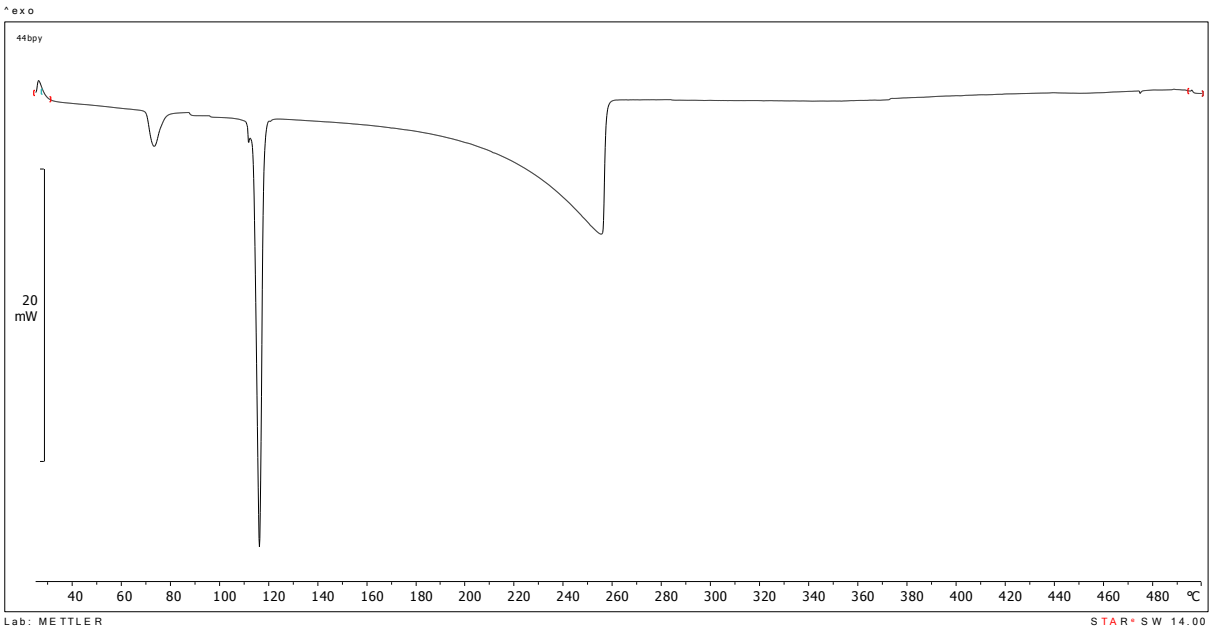

Figure S12. DSC curve for pure **bpy** reactant.

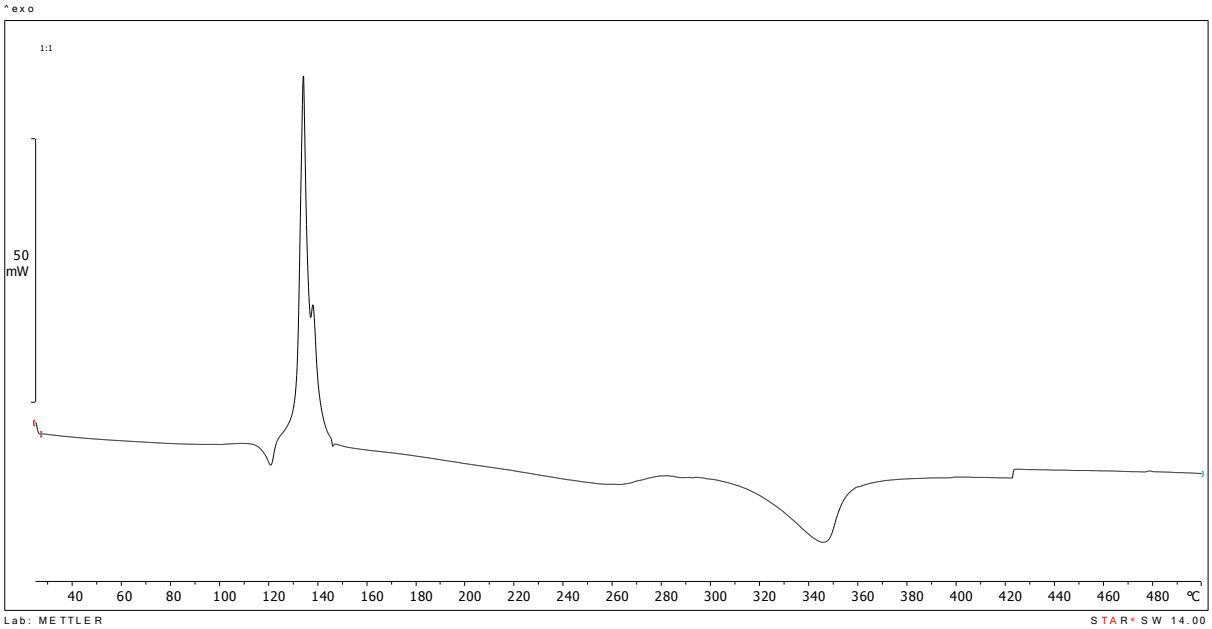

Figure S13. DSC curve for (**nbs**)(**bpy**) synthesised by LAG.

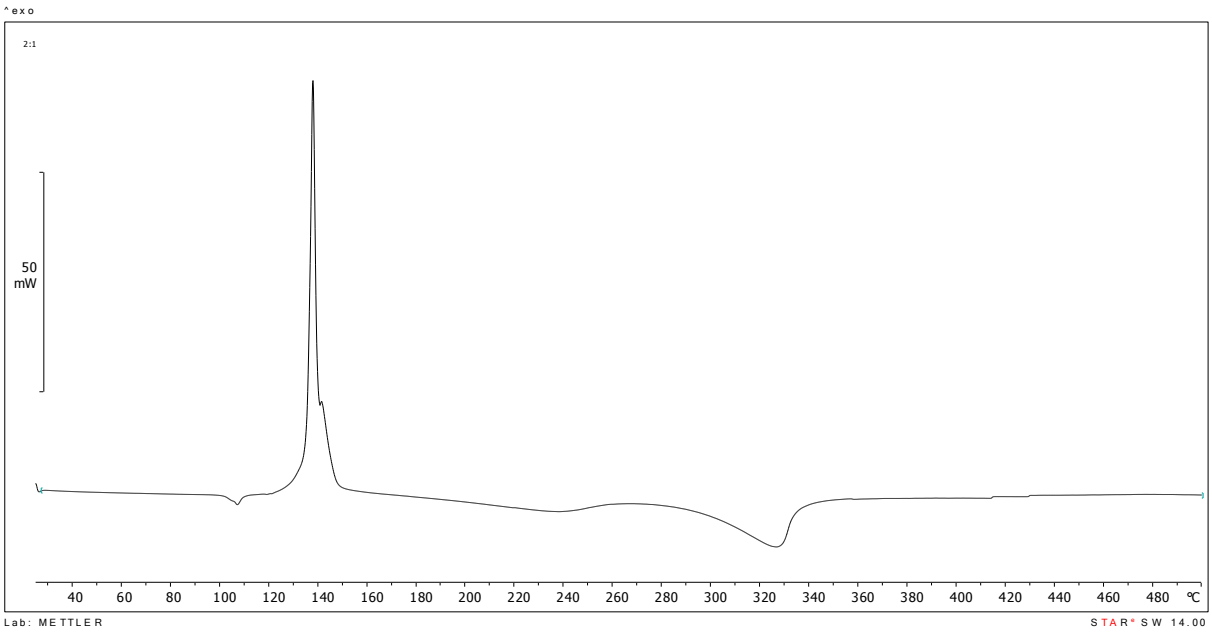

Figure S14. DSC curve for (**nbs**)$_2$(**bpy**) synthesised by LAG.