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A rock tumbler for mechanochemistry: generation of a photoactive cocrystal and a metal–organic framework

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A rock tumbler used in the field of geology is developed as an apparatus for mechanochemistry performed in the chemistry laboratory. The apparatus supports the formation of a photoactive organic cocrystal and a metal–organic framework, as well as photochemical reactions to be performed within the confines of the assembly.

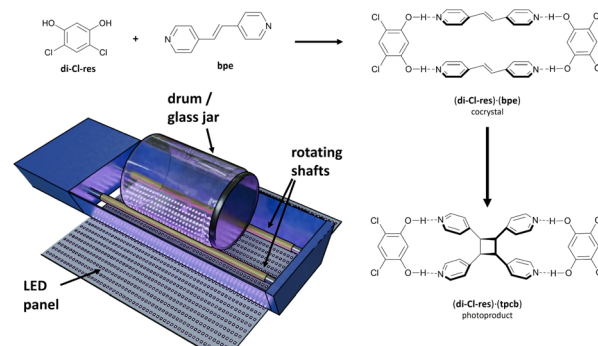
Mechanochemistry is developing as an increasingly mainstream approach to perform organic synthesis, offering benefits of green organic synthesis and the preparation of novel materials.^{1–4} In addition to facilitating reactions in ways akin to the liquid phase, the method allows for the manipulation of molecular crystalline phases to form covalent bonds⁵ and facilitate cocrystal exchange reactions.^{6,7} While reactions performed mechanochemically are, arguably, often associated as being conducted on small scales (*e.g.*, <0.5 g), mechanochemical processes performed on increasingly large scales (*e.g.*, >1 g) are becoming more commonplace.^{8–10} The field can also be expected to benefit from high throughput methods and combinatorial syntheses, wherein there are developing needs to introduce new approaches to grinding.

Herein, we report the development and application of a rock tumbler to perform mechanochemical syntheses (Scheme 1). Specifically, we demonstrate how a rock tumbler outfitted with commercial glass jars can generate supramolecular materials in the form of: (i) a photoactive organic cocrystal and (ii) a metal–organic framework (MOF). Both targeted materials form in high yields, in reasonable time periods, and in gram scale amounts. The apparatus is also demonstrated to allow for application of UV-radiation to materials, specifically to perform an intermolecular [2 + 2] photodimerization in the solid state. Given the relative ease of accessibility of the rock tumbler apparatus, we expect the use of the tumbler to become a feasible method to

perform mechanochemical reactions, particularly at increasingly large scales.

A rock tumbler is a common milling apparatus used and applied in the field of geology. The tumbler is used for polishing mineral samples prepared for observation, characterization, and general scientific inquiry.¹¹ Given our efforts to develop multicomponent solids in the form of cocrystals to direct [2 + 2] photodimerizations in the solid state, we were motivated to develop an apparatus that would allow for facile scale-up of solid-state reactions and, ultimately, make available the cyclobutane (CB) photoproducts in up to gram scale amounts.

We hypothesized that the action of a rock tumbler when used in combination with large sample vials could be utilized as a ball mill in the chemistry laboratory (Fig. 1). A commercially available jar would serve as the sample vial and house steel ball bearings to facilitate grinding. The interior of the jar coupled with the rotating motion of the drum of the tumbler shafts would allow for the ball bearings to impact upon a solid chemical sample with the assistance of gravity. An ordinary straight-sided glass jar would be employed as it would be expected to fit along the shafts affixed to the surface of the drum assembly. The radial motion of the tumbler could then be



Scheme 1 UV-equipped rock tumbler for mechanochemistry (bottom left). Schematic representation of the cocrystal formation and the photochemical reaction.

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Fig. 1 Photo of scalable mechanochemical synthesis featuring a high-capacity milling chamber with a glass jar affixed to a rock tumbler and incorporated LED lights (365 nm).

converted to mechanochemical force and effectively drive the crystallization. The scale of the reaction would be largely determined by the size of the drum and glass, which can be easily modified and scaled to at least gram quantities. When modified to be equipped with an LED panel, the tumbler could also be utilized for photochemical reactions mediated by mechanochemistry.

To test our hypothesis, we first turned to determine if the cocrystal **(di-Cl-res)·(bpe)** can be generated in the rock tumbler (Scheme 1) (*i.e.*, in the absence of light). The diol **di-Cl-res** (4,6-dichlorobenzene-1,3-diol) and bipyridine **bpe** (*trans*-1,2-di(pyridin-4-yl)ethene) assemble in the solid state to form the binary cocrystal **(di-Cl-res)·(bpe)**, wherein the components are sustained by discrete hydrogen-bonded macrocycles. In the experiment, **di-Cl-res** (982 mg, 5.49 mmol) and **bpe** (1.0 g, 5.49 mmol) were placed in a straight-sided glass jar (capacity: 266 mL) along with 20 stainless steel ball bearings (diameter: 13 mm).¹² The tumbler was then allowed to rotate (single setting rotation: 15 rpm) for a period of up to 24 hours. When the rotating motion was stopped, a resulting white-to-light yellow solid was observed to adhere along the inner surface of the jar. The solid was then removed using a spatula and transferred to a scintillation vial (15 mL).

A powder X-ray diffraction (PXRD) pattern of the solid removed from the glass jar showed the appearance of prominent peaks ($2\theta = 15.6, 20.5, 25.8$) to indicate the complete formation of **(di-Cl-res)·(bpe)** following the 24 hour time period (Fig. 2, green).¹³ When PXRD data were collected in a shorter two hour time period (blue), the cocrystal was present along with crystalline **bpe**. A pattern comparable to the diffractogram at 2 hours was also obtained in as little as 30 minutes (red).

The cocrystal **(di-Cl-res)·(bpe)** when generated in the rock tumbler was photoactive as reported. Specifically, when the tumbler containing a mixture of **di-Cl-res** (0.982 mg) and **bpe** (1.0 g) was rotated and continuously exposed to UV-radiation for

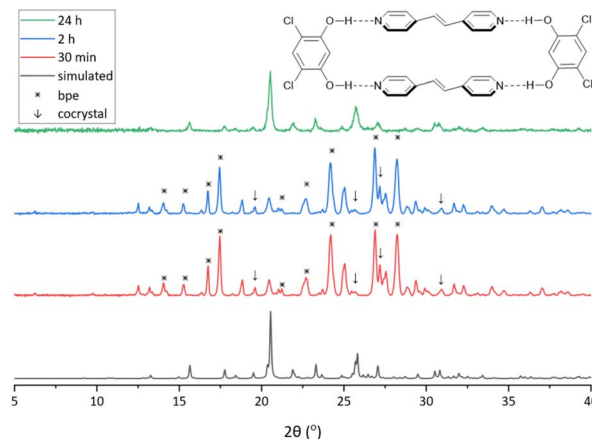


Fig. 2 Stacked PXRD patterns showing the formation of **(di-Cl-res)·(bpe)** in a rock tumbler at 30 min (red), 2 h (blue), and 24 h (green).¹³

a period of 60 hours, **tpcb** formed stereospecifically and in up to 88.5% yield (LED panel with 365 nm lights). The generation of the photoproduct was evidenced by a decrease in the intensity of the olefinic peak at 7.37 ppm and emergence of a peak for **tpcb** at 4.67 ppm in the ¹H NMR spectrum (Fig. S1). We note that when the cocrystal **(di-Cl-res)·(bpe)** was formed manually by mortar-and-pestle grinding and then subjected to UV-radiation, **tpcb** formed in quantitative yield in 80 hours as reported (Hg medium-pressure lamp).¹³ An increase in the formation of **tpcb** to 96.6% yield from 88.5% yield was realized using up to 45 ball bearings in the tumbler (Fig. S1–S3). We also note that when the presynthesized cocrystal **(di-Cl-res)·(bpe)** generated using a ball mill was subjected to UV-radiation in the tumbler, **tpcb** formed in 90.9% yield in a comparable 72 hours (Fig. S5 and 6).

The photoproduct **tpcb** can also be generated catalytically using the rock tumbler. Specifically, when 50% **di-Cl-res** (269 mg) was employed as a catalyst (relative to 1 : 1 stoichiometry), **bpe**

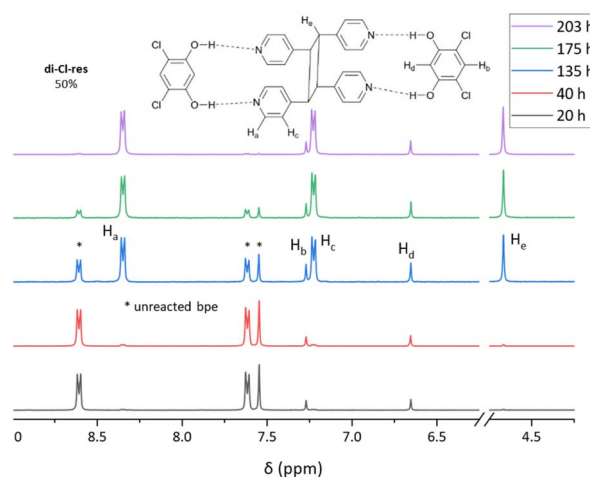


Fig. 3 Stacked ¹H NMR spectra showing the generation of **tpcb** using a catalytic amount of **di-Cl-res** (50%).



(547 mg) reacted to generate **tpcb** in up to 97% yield in a period of approximately 8 days (Fig. 3 and Table S1). When conducted using **bpe** (72.9 mg) on a smaller scale, **tpcb** formed in up to 73.4% yield in a comparable period (Fig. S4 and Table S2).

From eqn (1) and (2), we determined¹⁴ that the action of the rock tumbler in providing mechanical energy was on the order of four orders of magnitude less than a conventional ball mill (Table S3). Specifically, we calculated 0.0055 kJ, as total mechanical energy, to be provided by the 20 ball bearings when confined within the jar, as facilitated by the rotary motion of the drum. A significant percentage (up to 80%) of energy offered to a reaction mixture in a shaker or planetary mill was considered to be mostly dissipated as heat.¹⁵ Owing to the relatively low rotation speed and milder grinding conditions of the rock tumbler, a majority of the energy can be expected to be directed to the reaction. Using an infrared thermometer, we measured the temperature in the glass jar of the tumbler to generally not exceed 40 °C. With heat loss being minimized, product formation using the tumbler for mechanochemistry can, thus, be considered cost efficient and sustainable.

$$E_{\text{impact}} = \frac{1}{2} m_b v_{\text{eff}}^2 \quad (1)$$

$$E_{\text{total}} = \phi E_{\text{impact}} N_b f_b t \quad (2)$$

The morphology of the cocrystals formed in the rock was studied by scanning electron microscopy (SEM). The solid was determined to be composed of nanosized particles with rounded edges and approximate prism-like morphologies (Fig. 4) with an average base size of 140 ± 40 nm (analysis was based on ~50 crystals). The sizes were found to be larger compared to a case using a vortex mixer,¹² which may be attributed to milder forces inside the tumbler.

The rock tumbler was also used to generate the metal-organic framework (MOF) ZIF-67. When $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (82 mg, 0.282 mmol), 2-methyl-imidazole (1.0 g, 12.18 mmol), and KOH (150 mg, 2.67 mmol)¹⁶ were subjected to tumbling with 25 stainless steel ball bearings (diameter: 13 mm) and in a smaller jar (capacity: 140 mL) for a period of 3 hours, an optical inspection revealed the combined solids to undergo a rapid colour change to purple upon mixing. The resulting solid was then washed with methanol (3×10 mL) and dried in an oven (80 °C) to remove excess ligand and water molecules for BET analysis.¹⁶ The PXRD pattern of the solid was consistent

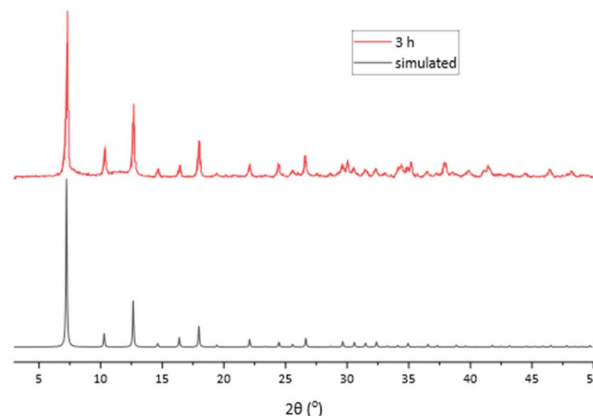


Fig. 5 Stacked PXRD patterns of as-synthesised ZIF-67 following wash (red) and the simulated from the crystal structure (black).²⁰

with the formation of ZIF-67 (Fig. 5). The weaker peaks observed at higher angles (35.4°, 38.5°, and 39.8°) can be attributed to unreacted traces of ligand (Fig. S7 and S8).¹⁷ The porosity of the solid was also confirmed by Brunauer–Emmett–Teller (BET) surface area measurements using N_2 gas (Fig. S9), with the determined surface area ($945 \text{ m}^2 \text{ g}^{-1}$) comparing favourably to similarly produced ZIF-67 (ref. 18) (Table S4). With the surface area being affected by synthetic procedures and/or morphologies of products,¹⁹ our results are consistent with ZIF-67 generated in the tumbler being a fine crystalline powder.

Conclusions

We have reported an approach to perform mechanochemical syntheses using a rock tumbler. The method allows for generation of organic cocrystals and MOFs, with the solids being formed in gram-scale amounts. An *in situ* [2 + 2] photodimerization was also performed using the tumbler. With attempts to scale-up synthesis using mechanochemistry confronting challenges such as heat management, equipment limitations, process control and cost efficiency,^{21–26} the approach reported here in addition to scale-up offers an element for visual monitoring. We have an ongoing goal to apply the method to generate additional multi-component materials.

Author contributions

CH: investigation, methodology, writing – original draft; KAP: investigation, methodology, writing – original draft; AKP: data curation, investigation, methodology, validation, visualization, writing – original draft, writing – review & editing; ABE: data curation, investigation, visualization; CK: investigation; MAS: investigation; AVT: resources, supervision, validation, writing – review & editing; LRM: conceptualization, funding acquisition, investigation, methodology, project administration, resources, supervision, validation, writing – original draft, writing – review & editing.

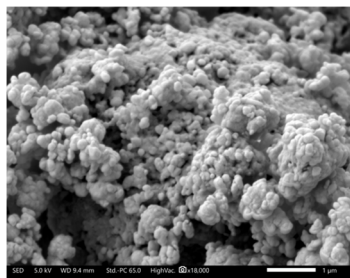


Fig. 4 SEM image of the solid cocrystal (di-Cl-res)·(bpe) showing nanosized particles formed in the tumbler.



Conflicts of interest

The authors declare no conflicts of interest.

Data availability

All experimental and characterization data and detailed experimental procedures are available in the published article and supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5mr00108k>.

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