Towards an environmentally-friendly laboratory: dimensionality and reactivity in the mechanosynthesis of metal-organic compounds

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Supplementary Material

Experimental

Mechanosynthesis

All materials were purchased from Sigma-Aldrich Chemical Co. and were used without further purification. Mechanochemical reactions were performed by using 200 mg of the mixture of solid reactants. For LAG experiments additional 50 μL of ethanol or nitromethane were added. The reaction mixture was placed in a 10 mL stainless steel jar and ground either using a pair of 7 mm diameter stainless steel balls (standard conditions, each ball weighing 1.4 g) or using a single 12 mm diameter stainless steel ball (harsh conditions, ball weighing 4.0 g). The mixture was then ground for 5-30 min in a Retsch MM200 grinder mill operating at 30 Hz. The temperature of the grinding jar during grinding was monitored via thermocouples embedded in the walls of the jar.

Powder X-ray diffraction

PXRD data was collected on a laboratory Philips X'Pert Pro diffractometer, equipped with an X'celerator RTMS detector, using Ni-filtered CuKα radiation, using a flat plate configuration. Data were typically collected in the 2θ range 5-40^{o} or 5-20^{o}. Data stuitable for structure solution and refinement were collected in the angular range 4-60^{o} over a period of 8 hours.

FTIR reflectance spectroscopy

Reflectance FTIR spectra of all samples were recorded on a ThermoNicolet NEXUS spectrometer equipped with the Golden Gate ATR accessory, in the range 4000-600 cm^{-1}.

Solid-state NMR

Experiments were performed on a Bruker Avance 400 spectrometer operating at 100.7 MHz (^{13}C), 40.5 MHz (^{15}N) and 88.7 MHz (Cd-113) using a Bruker 4 mm double-resonance probe under magic angle spinning at 12.5 kHz (for ^{113}Cd) and 6 MHz (^{15}N). ^{13}C spectra were referenced externally to solid glycine (methylene signal at 43.1 ppm relative to TMS at 0 ppm), ^{15}N experiments were referenced externally to ^{15}N-enriched solid glycine (signal at 10 ppm relative to ammonium ion at 0 ppm) and ^{113}Cd was referenced to 0.1 M aqueous cadmium perchlorate at 0 ppm. Spectra were acquired with ramped cross polarization (2.5 ms) from protons (400.0 MHz) and TPPM15 broad band decoupling.

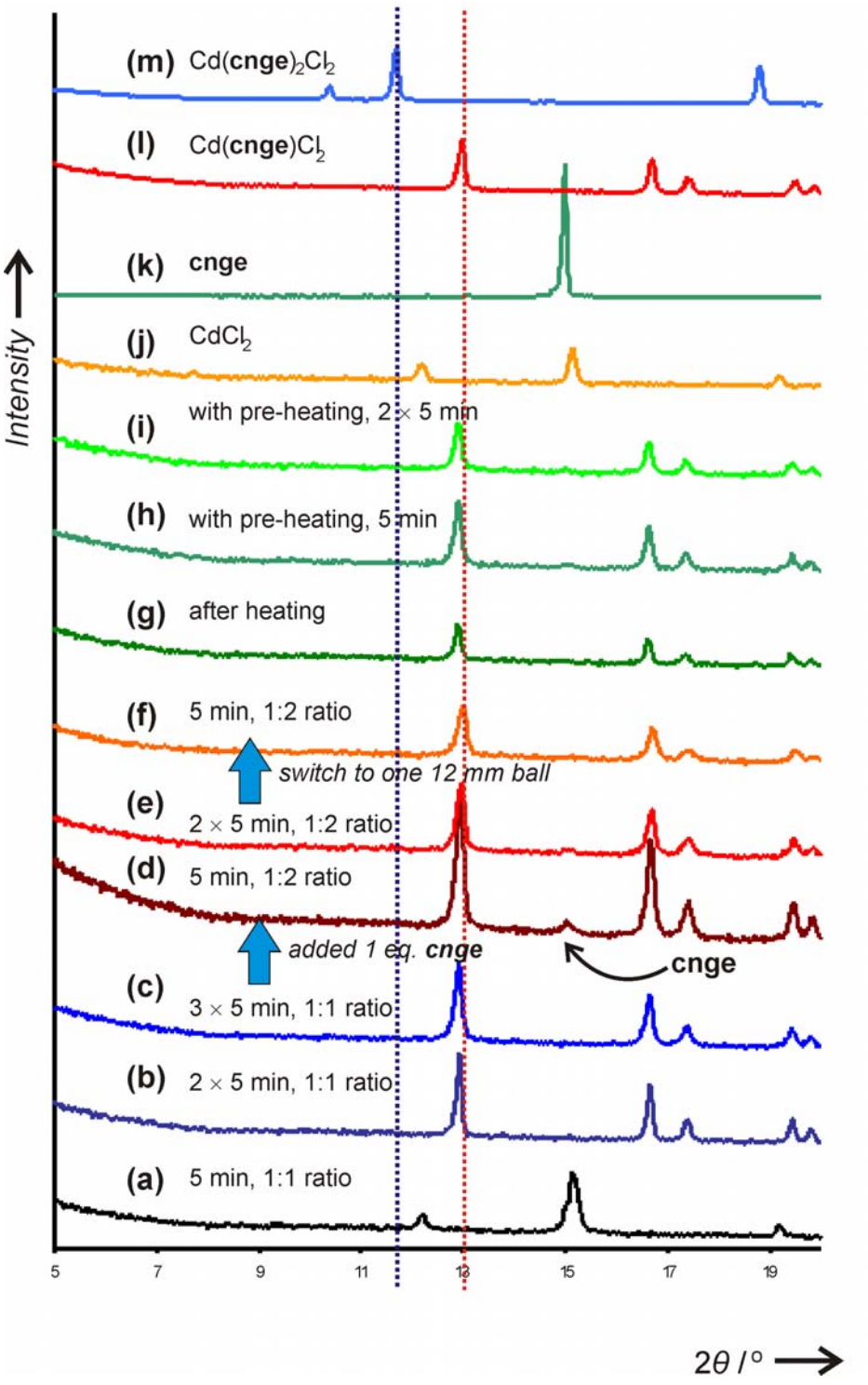

Figure S1. PXRD patterns for neat grinding reactions of $CdCl_2$ and **cnge** involving (unless otherwise stated) a pair of 7 mm grinding balls (bottom to top): (**a**) after 5 min grinding with a $CdCl_2$:**cnge** ratio 1:1; (**b**) after 2×5 min grinding with a $CdCl_2$:**cnge** ratio 1:1; (**c**) after 3×5 min grinding with a $CdCl_2$:**cnge** ratio 1:1; (**d**) sample under (**c**) after the addition of 1 equivalent of **cnge** and 5 min grinding; (**e**) after 2×5 min grinding with a $CdCl_2$:**cnge** ratio 1:2; (**f**) same as under (**e**), but after switching to a 12 mm grinding ball and 5 min grinding; (**g**) sample under (**f**) after ageing for 3 hours at 85°C; (**h**) after one cycle of pre-heating to 85 °C and grinding for 5 min, $CdCl_2$:**cnge** ratio 1:2; (**i**) after two cycles of pre-heating to 85 °C and grinding for 5 min, $CdCl_2$:**cnge** ratio 1:2; (**j**) $CdCl_2$ starting material; (**k**) **cnge** starting material; (**l**) pure Cd(**cnge**)Cl_2 and (**m**) pure Cd(**cnge**)$_2Cl_2$. The vertical lines indicate the approximate positions of the characteristic PXRD reflections for Cd(**cnge**)Cl_2 (red) and Cd(**cnge**)$_2Cl_2$ (blue)

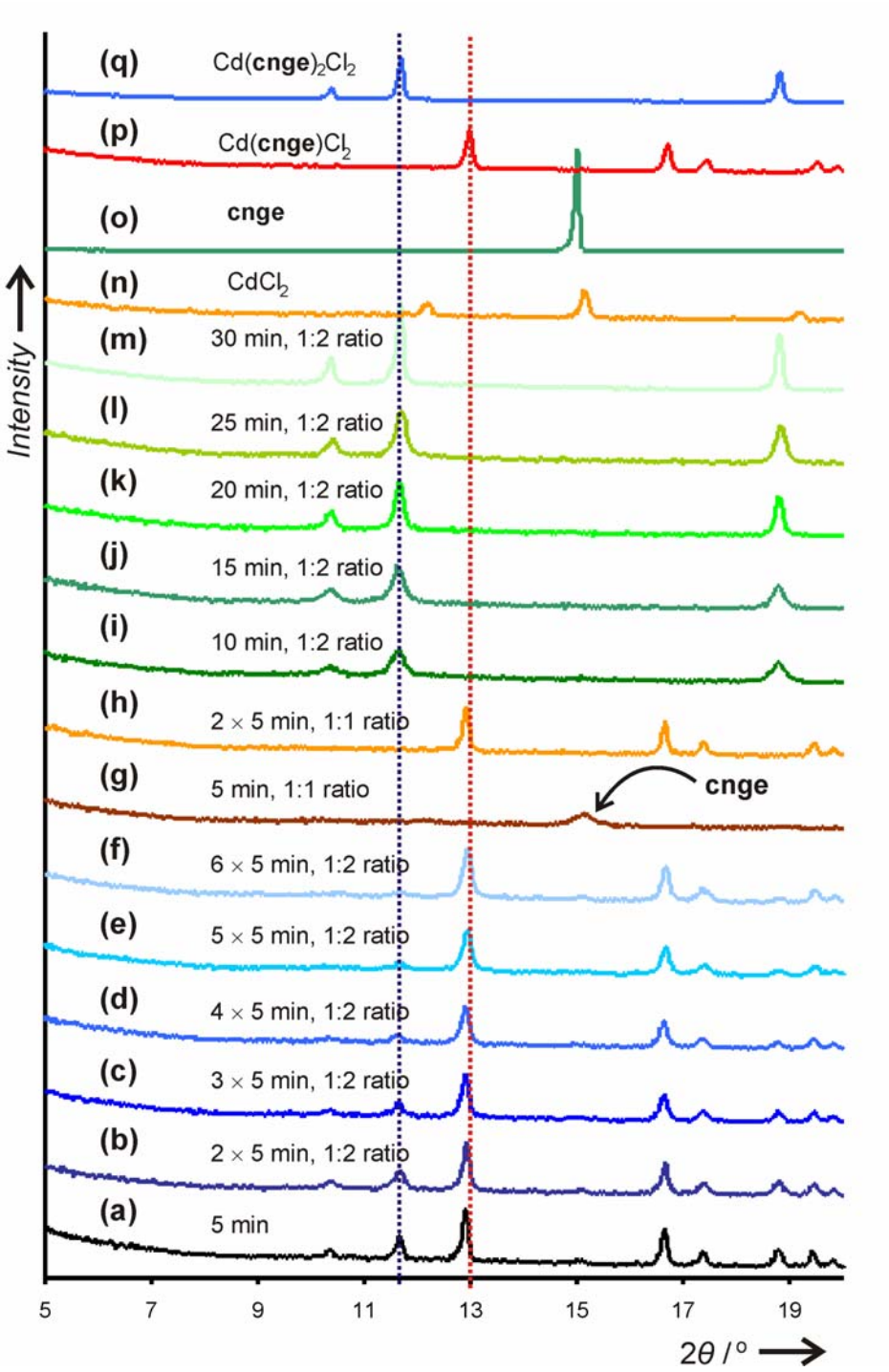

Figure S2. PXRD patterns for neat grinding reactions of $CdCl_2$ and **cnge** involving (unless otherwise stated) a single 12 mm grinding ball (bottom to top): (**a**) after 5 min grinding with a $CdCl_2$:**cnge** ratio 1:2; (**b**) after 2×5 min grinding with a $CdCl_2$:**cnge** ratio 1:2; (**c**) after 3×5 min grinding with a $CdCl_2$:**cnge** ratio 1:2; (**d**) after 4×5 min grinding with a $CdCl_2$:**cnge** ratio 1:2; (**e**) after 5×5 min grinding with a $CdCl_2$:**cnge** ratio 1:2; (**f**) after 6×5 min grinding with a $CdCl_2$:**cnge** ratio 1:2; (**g**) after 5 min grinding with a $CdCl_2$:**cnge** ratio 1:1; (**h**) after 2×5 min grinding with a $CdCl_2$:**cnge** ratio 1:1; (**i**) after 10 min grinding with a $CdCl_2$:**cnge** ratio 1:2; (**j**) after 15 min grinding with a $CdCl_2$:**cnge** ratio 1:2; (**k**) after 20 min grinding with a $CdCl_2$:**cnge** ratio 1:2; (**l**) after 25 min grinding with a $CdCl_2$:**cnge** ratio 1:2; (**m**) after 30 min grinding with a $CdCl_2$:**cnge** ratio 1:2; (**n**) $CdCl_2$ starting material; (**o**) **cnge** starting material; (**p**) pure Cd(**cnge**)Cl_2 and (**q**) pure Cd(**cnge**)$_2Cl_2$. The vertical lines indicate the approximate positions of the characteristic PXRD reflections for Cd(**cnge**)Cl_2 (red) and Cd(**cnge**)$_2Cl_2$ (blue)

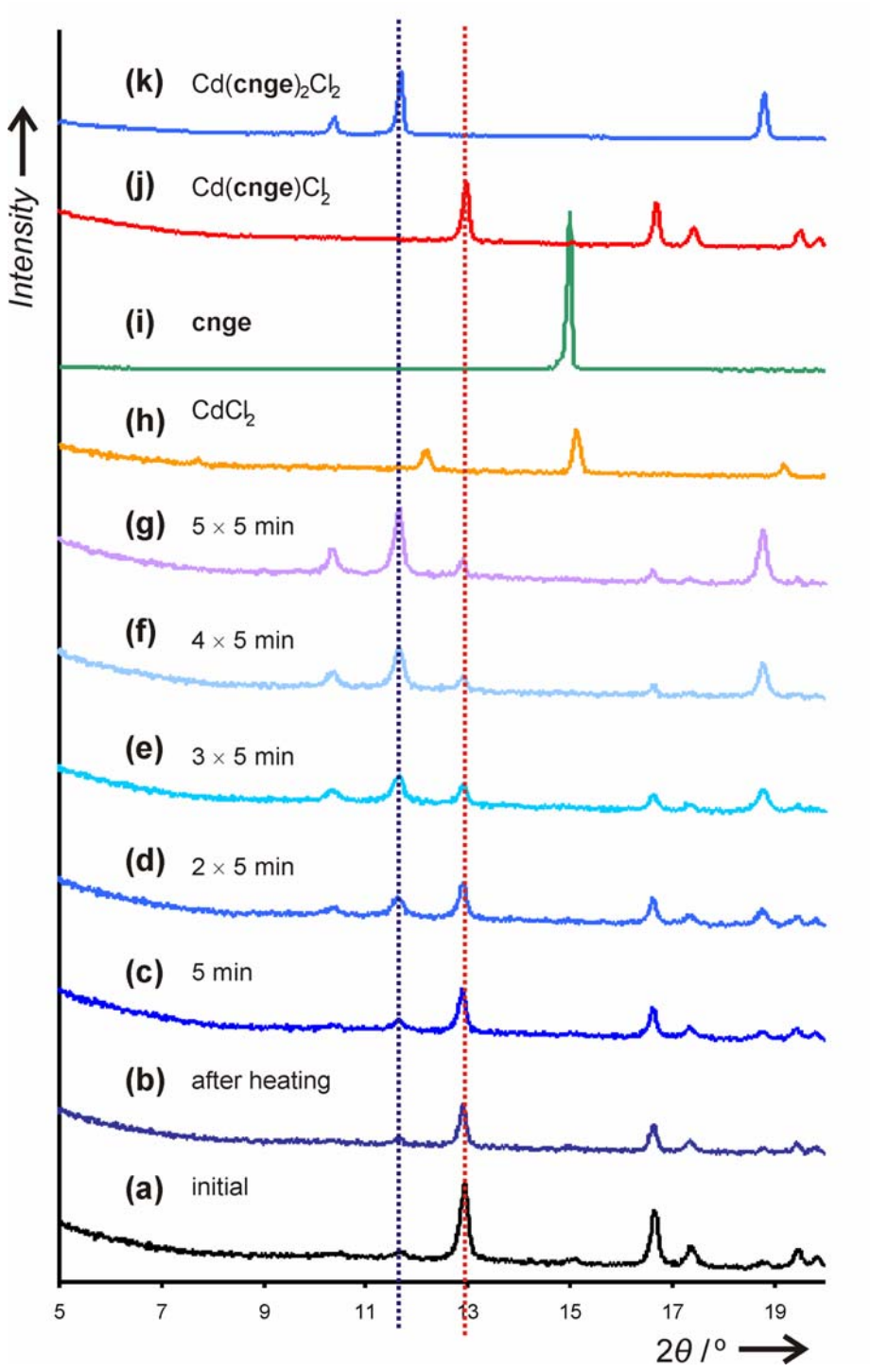

Figure S3. PXRD patterns for neat grinding reactions of $CdCl_2$ and **cnge** involving (unless otherwise stated) a single 12 mm grinding ball. Each sample was heated for 1h at 85°C immediately before grinding (bottom to top): (**a**) initial sample, obtained by exposing the 1:2 mixture of $CdCl_2$ and cnge to **six** 5 min grinding periods at room temperature; (**b**) the initial sample after ageing overnight at 85°C; (**c**) after one cycle of heating to 85°C and grinding for 5 min; (**d**) after two cycles of heating to 85°C and grinding for 5 min; (**e**) after three cycles of heating to 85°C and grinding for 5 min; (**f**) after four cycles of heating to 85°C and grinding for 5 min; (**g**) after five cycles of heating to 85°C and grinding for 5 min; (**h**) $CdCl_2$ starting material; (**i**) **cnge** starting material; (**j**) pure Cd(**cnge**)Cl_2 and (**k**) pure Cd(**cnge**)$_2Cl_2$. The vertical lines indicate the approximate positions of the characteristic PXRD reflections for Cd(**cnge**)Cl_2 (red) and Cd(**cnge**)$_2Cl_2$ (blue)

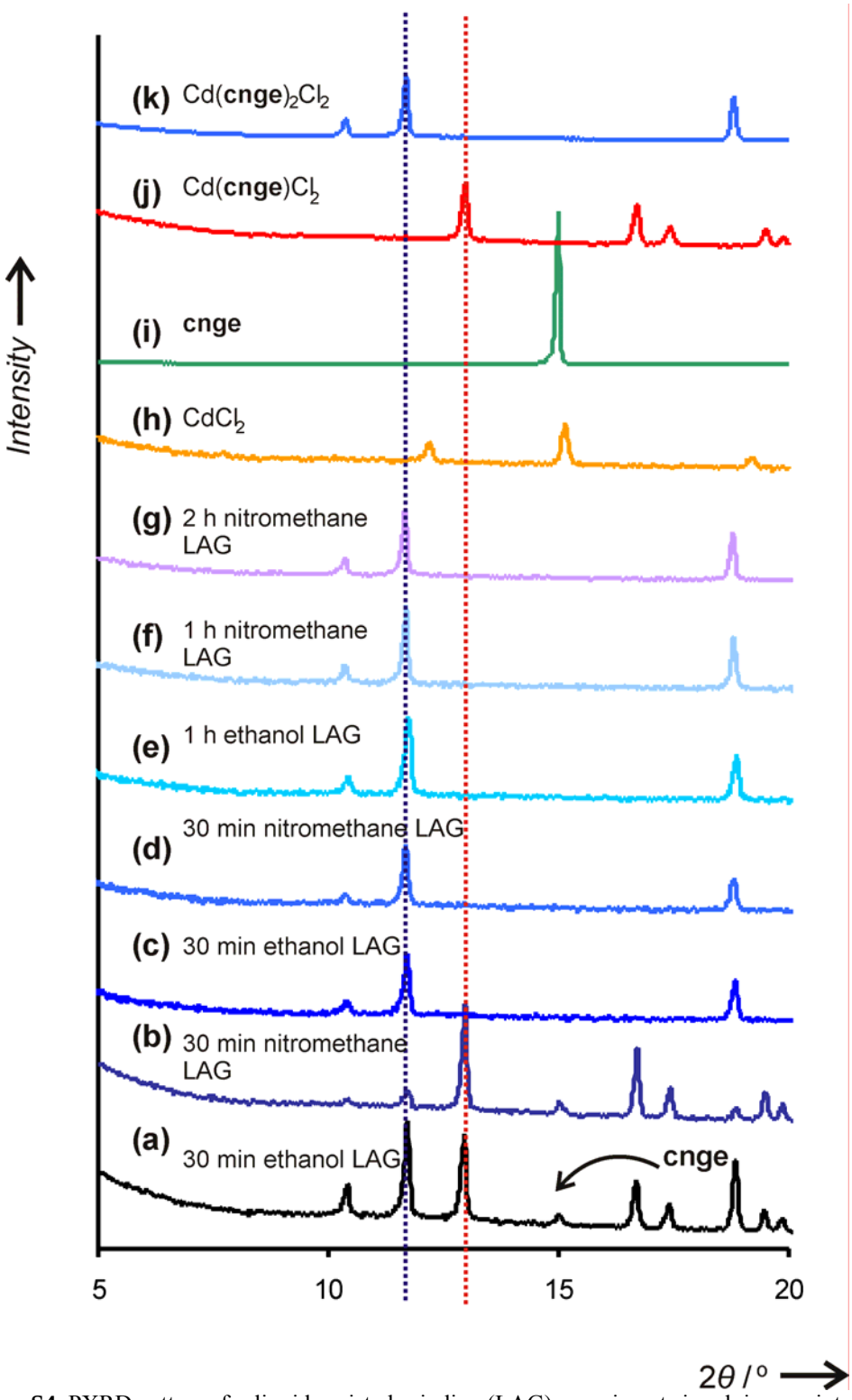

Figure S4. PXRD patterns for liquid-assisted grinding (LAG) experiments involving a mixture of $CdCl_2$ and **cnge** in a 1:2 stoichiometric ratio: (**a**) 30 min LAG using 50 µL ethanol and two 7 mm diameter balls; (**b**) 30 min LAG using 50 µL nitromethane and two 7 mm diameter balls; (**c**) 30 min LAG using 50 µL ethanol and a single 12 mm diameter ball; (**d**) 30 min LAG using 50 µL nitromethane and a single 12 mm diameter ball; (**e**) sample (**c**) after addtional 30 min LAG using 50 µL EtOH and a pair of 7 mm dimater balls; (**f**) sample (**d**) after addtional 30 min LAG using 50 µL nitromethane and a pair of 7 mm dimater balls; (**g**) sample (**d**) after addtional 90 min LAG using 50 µL nitromethane and a pair of 7 mm dimater balls; (**h**) $CdCl_2$ starting material; (**i**) **cnge** starting material; (**j**) pure Cd(**cnge**)Cl_2 and (**k**) pure Cd(**cnge**)$_2Cl_2$. The vertical lines indicate the approximate positions of the characteristic PXRD reflections for Cd(**cnge**)Cl_2 (red) and Cd(**cnge**)$_2Cl_2$ (blue).

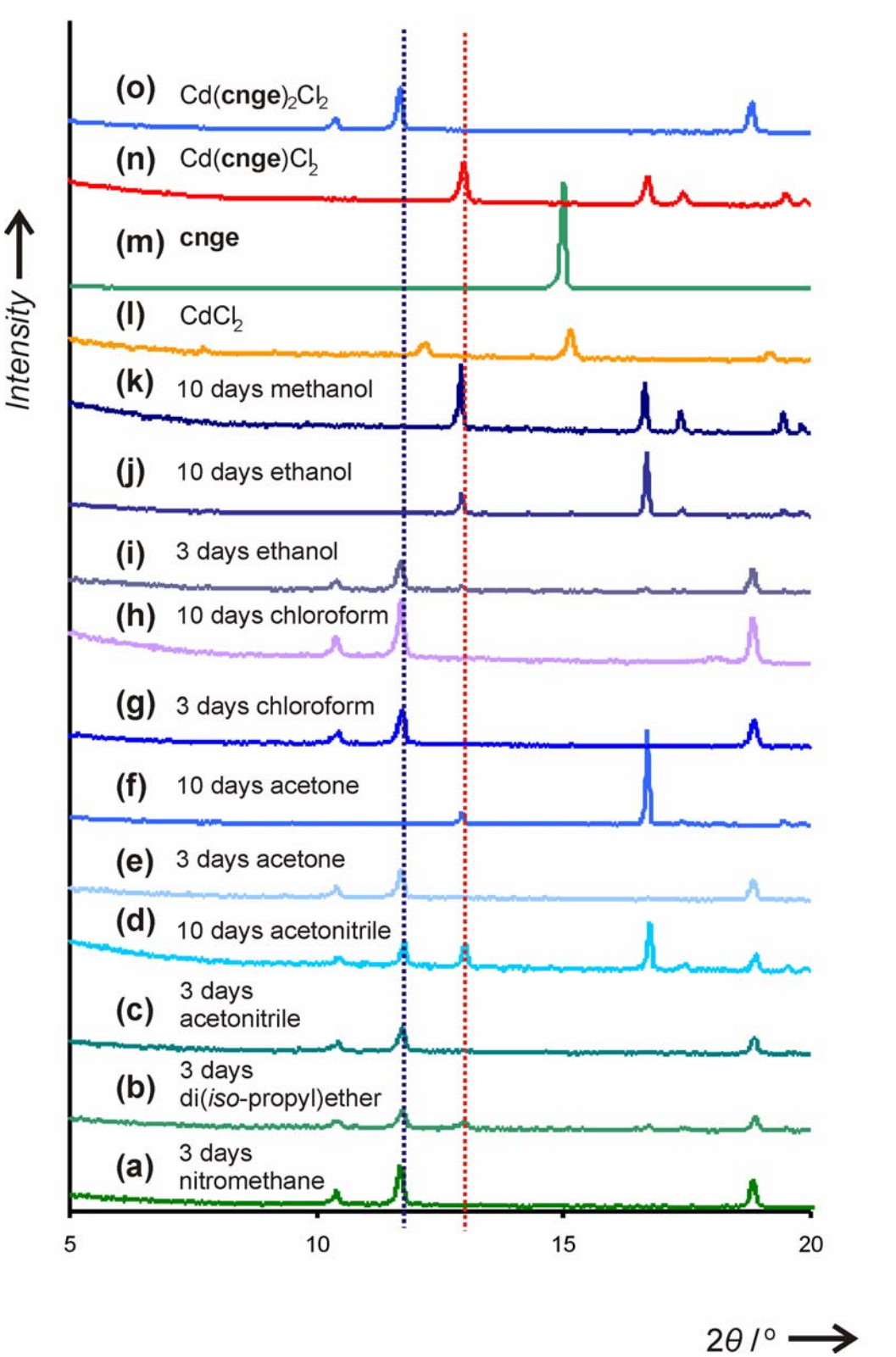

Figure S5. PXRD patterns for slurrying samples of pure Cd(**cnge**)$_2$Cl$_2$ (50 mg) in different solvents (2 mL) (bottom to top): (**a**) nitromethane for 3 days; (**b**) di(*iso*propyl)ether for 3 days; (**c**) acetonitrile for 3 days; (**d**) acetonitrile for 10 days; (**e**) acetone for 3 days; (**f**) acetone for 10 days; (**g**) chloroform for 3 days; (**h**) chloroform for 10 days; (**i**) ethanol for 3 days; (**j**) ethanol for 10 days; (**k**) ethanol for 10 days; (**l**) $CdCl_2$ starting material; (**m**) **cnge** starting material; (**n**) pure Cd(**cnge**)Cl_2 and (**o**) pure Cd(**cnge**)$_2Cl_2$. The vertical lines indicate the approximate positions of the characteristic PXRD reflections for Cd(**cnge**)Cl_2 (red) and Cd(**cnge**)$_2Cl_2$ (blue).

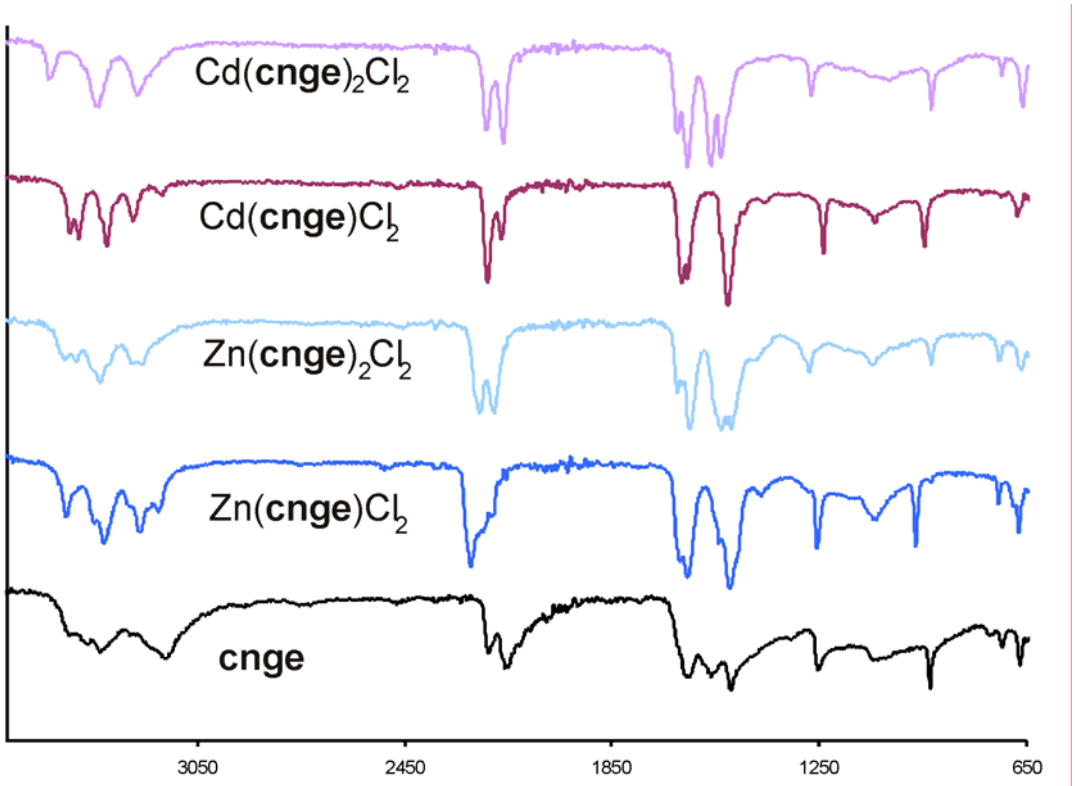

Figure S6. FTIR-ATR spectra of solid samples (top to bottom): (**a**) **cnge** reactant; (**b**) Zn(**cnge**)Cl_2; (**c**) Zn(**cnge**)$_2Cl_2$; (**d**) Cd(**cnge**)Cl_2; (**e**) Cd(**cnge**)$_2Cl_2$.

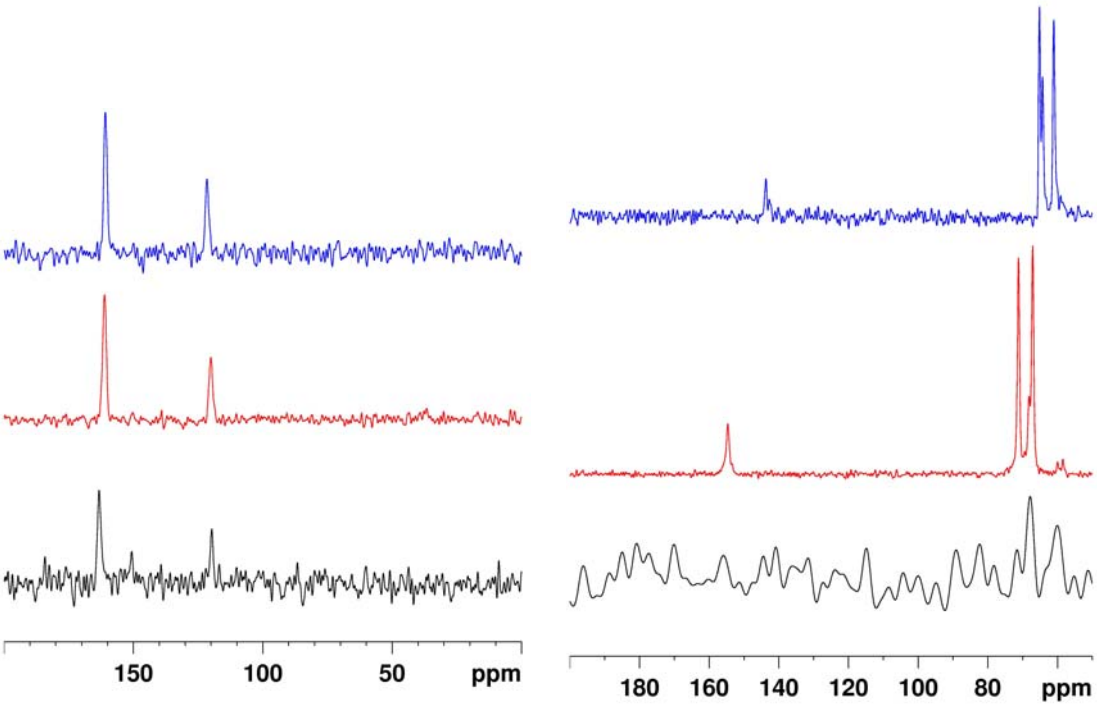

Figure S7. (Left) Solid-state natural abundance ^{13}C CP-MAS NMR spectra of **cnge** (bottom), Cd(**cnge**)Cl_2 (middle) and Cd(**cnge**)$_2Cl_2$ (top). (Right) Solid-state natural abundance ^{15}N CP-MAS NMR spectra of **cnge** (bottom), Cd(**cnge**)Cl_2 (middle) and Cd(**cnge**)$_2Cl_2$ (top).

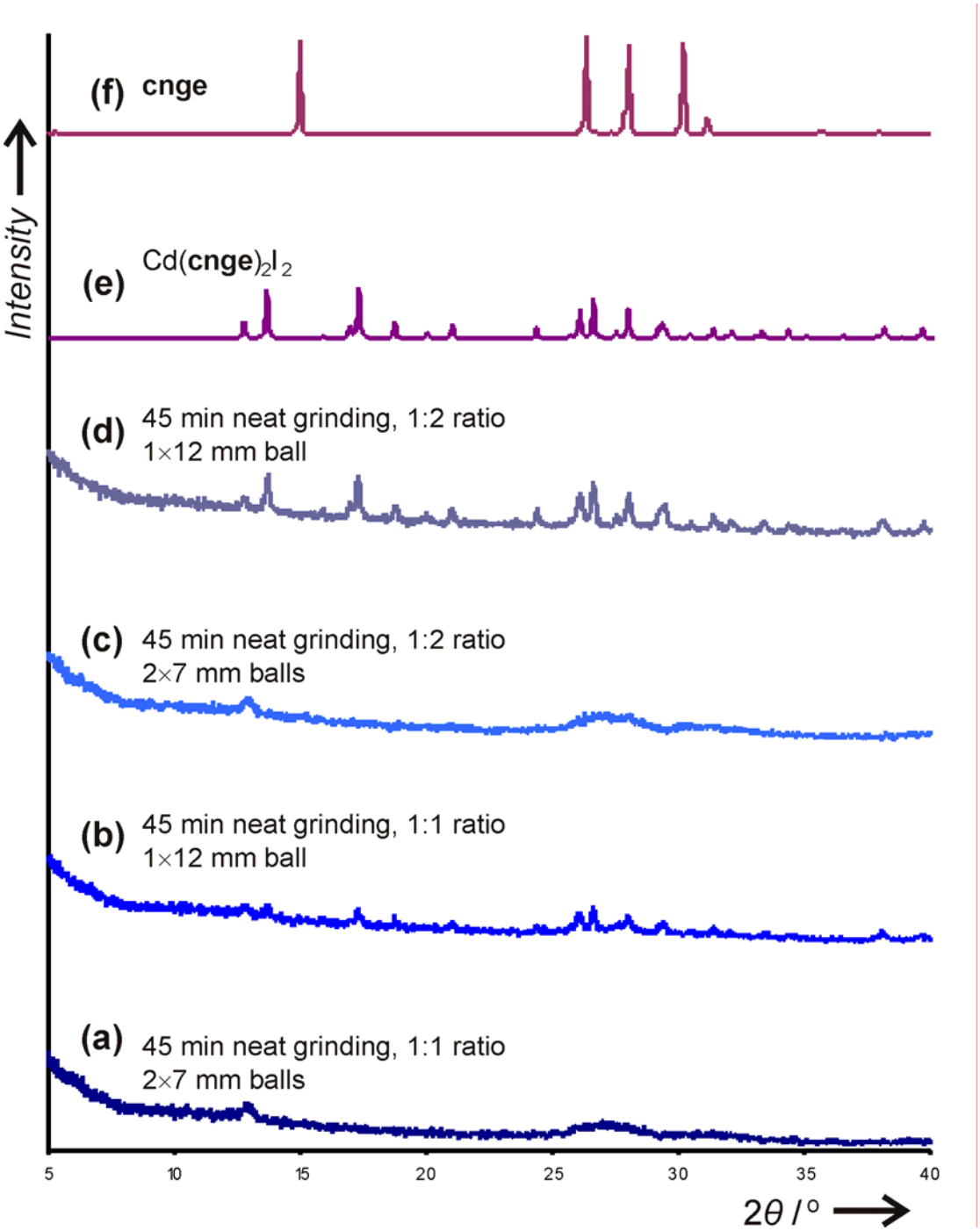

Figure S8. PXRD patterns for neat grinding reactions of CdI_2 and **cnge** (bottom to top): (**a**) CdI_2:**cnge** ratio 1:1, using two grinding balls of 7 mm diameter; (**b**) CdI_2:**cnge** ratio 1:1, using a single grinding ball of 12 mm diameter; (**c**) CdI_2:**cnge** ratio 1:2, using two grinding balls of 7 mm diameter; (**d**) CdI_2:**cnge** ratio 1:2, using a single grinding ball of 12 mm diameter; (e) simulated pattern for Cd(**cnge**)$_2I_2$ (CCDC code ICYDAC); (**g**) **cnge** starting material.