Electronic Supplementary Material (ESI) for CrystEngComm

Supplementary Material

Switching between halogen- and hydrogen-bonding in stoichiometric modifications of a cocrystal of a phosphine oxide

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Experimental details

Mechanochemical LAG screening Mechanochemical experiments were conducted in a Retsch MM400 mixer mill. For each experiment, the mixture of reactants in an appropriate stoichiometric ratio (200 mg total weight) was placed in a 10 mL stainless steel grinding jar along with two stainless steel balls of 7 mm diameter. The reaction mixture was then milled for 30 minutes at a frequency of 30 Hz. The samples were then analysed using powder X-ray diffraction, FTIR-ATR as well as DSC.

Powder X-ray diffraction (PXRD) Room temperature PXRD patterns were collected either on a Bruker D8 Discovery X-ray diffractometer using a Cu-K_α (λ=1.54 Å) source, equipped with a Vantech area detector and a nickel filter (McGill University) or on a Philips X'Pert Pro diffractometer, equipped with an X'celerator RTMS detector, using Ni-filtered CuKα radiation, using a flat plate configuration (University of Cambridge). In all cases the X-ray tube was operated at 40 kV and 40 mA and data analysis was carried out using the Panalytical X'pert Highscore Plus program

Single crystal diffraction Single crystal diffraction data were collected on a Nonius Kappa CCD diffractometer equipped with a graphite monochromator and an Oxford cryostream, using Mo*K*α radiation. Structure solution and refinement was perfromed using SHELX available with the WinGX package of crystallographic tools, running on a Pentium-based PC under MS Windows XP.

Infrared Spectroscopy Fourier transform infrared spectra were collected using a Perkin Elmer Fourier Transform-Infrared Attenuated Total Reflection spectrometer in the range 400 cm^{-1} to 4000 cm^{-1}.

Differential Scanning Calorimetry (DSC) DSC measurements were conducted either on a TA Instruments Q1000 Differential Scanning Calorimeter with a standard aluminum pan of 40 μL volume and nitrogen flow rate set at 50 ml/min (McGill University) or on a Mettler DSC30 instrument (University of Cambridge) in aluminum pans of 40 μL volume.

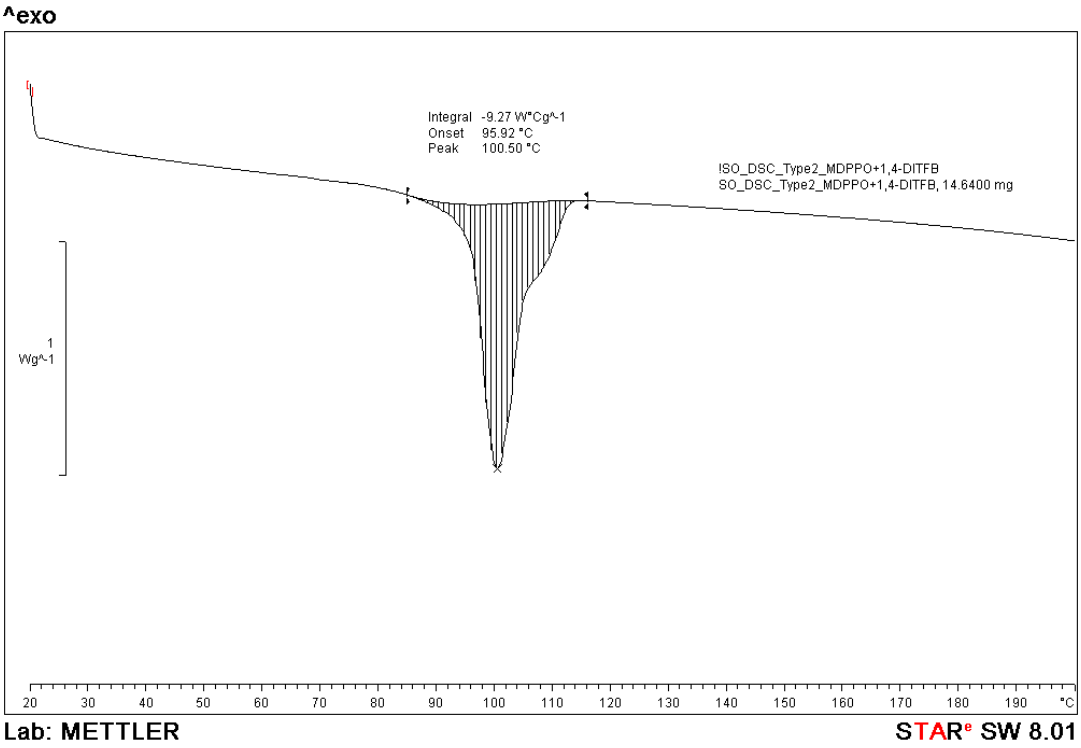

Figure S1. DSC thermogram of (**mdppo**)·(**tfib**) collected on 14.6 mg of sample in a dynamic flow of nitrogen, heating rate 10 K min^{-1}

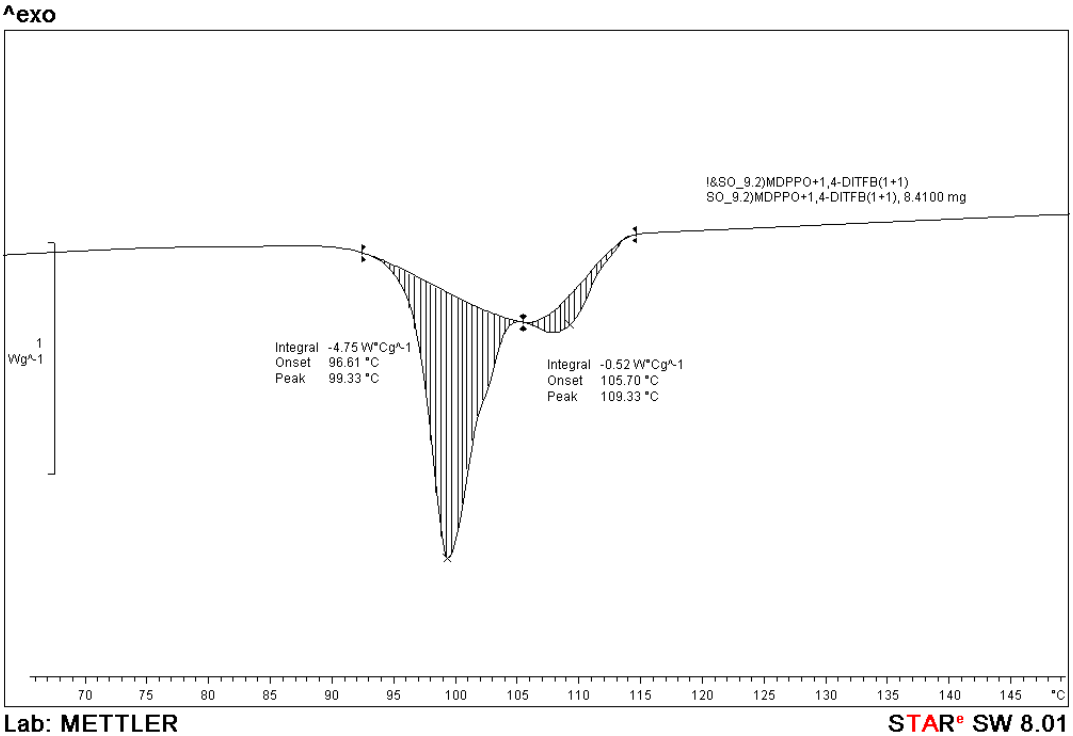

Figure S2. DSC thermogram of (**mdppo**)·(**tfib**) collected on 8.4 mg of sample in a dynamic flow of nitrogen, heating rate 10 K min^{-1}.

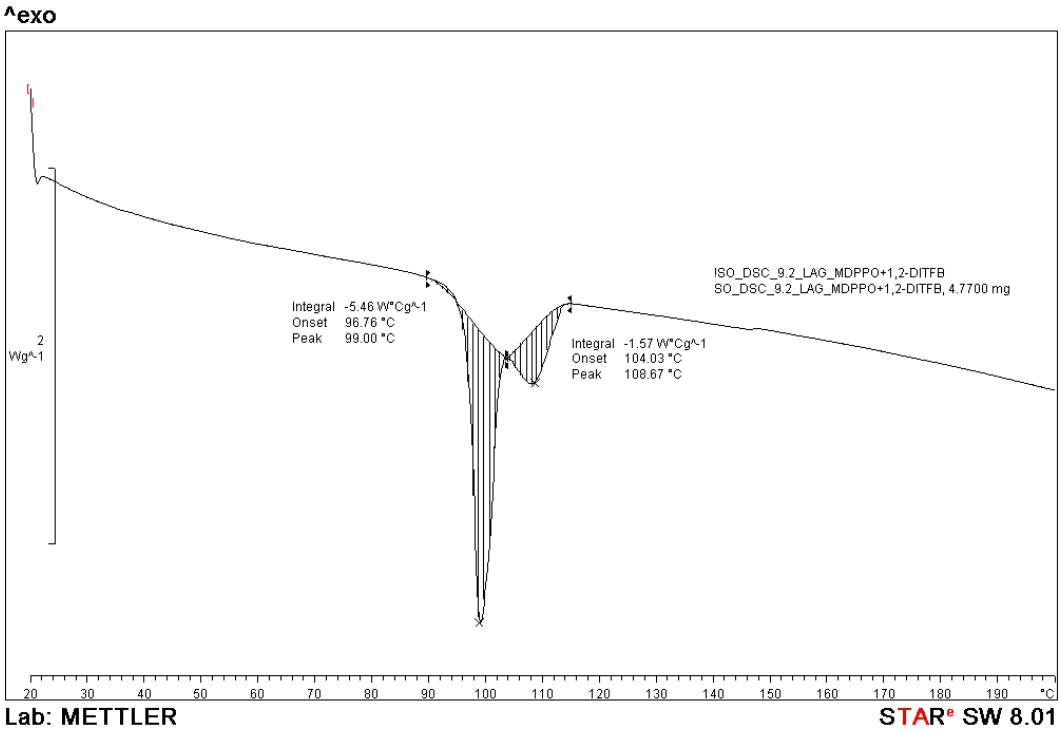

Figure S3. DSC thermogram of (**mdppo**)·(**tfib**) collected on 4.8 mg of sample in a dynamic flow of nitrogen, heating rate 10 K min^{-1}.

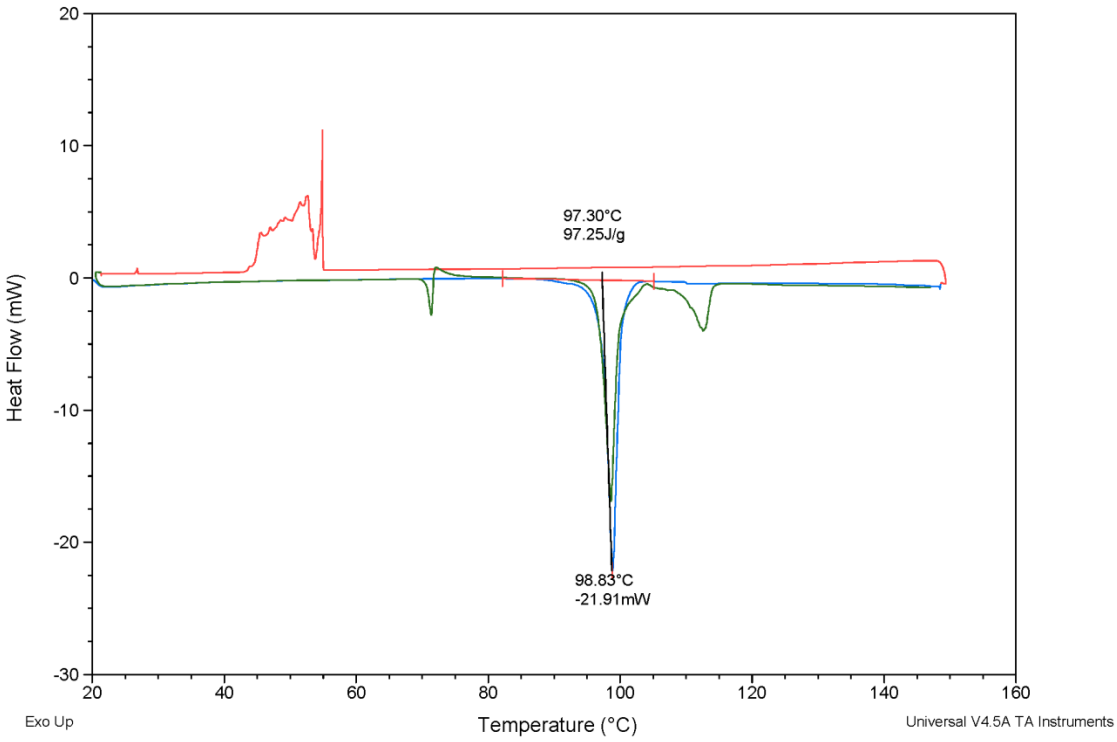

Figure S4. DSC thermogram of (**mdppo**)$_2$·(**tfbb**) collected on 3.6 mg of sample in a dynamic flow of nitrogen. The sample was heated (blue line), cooled (red line) and then heated again (green line) at a rate 10 K min^{-1}.

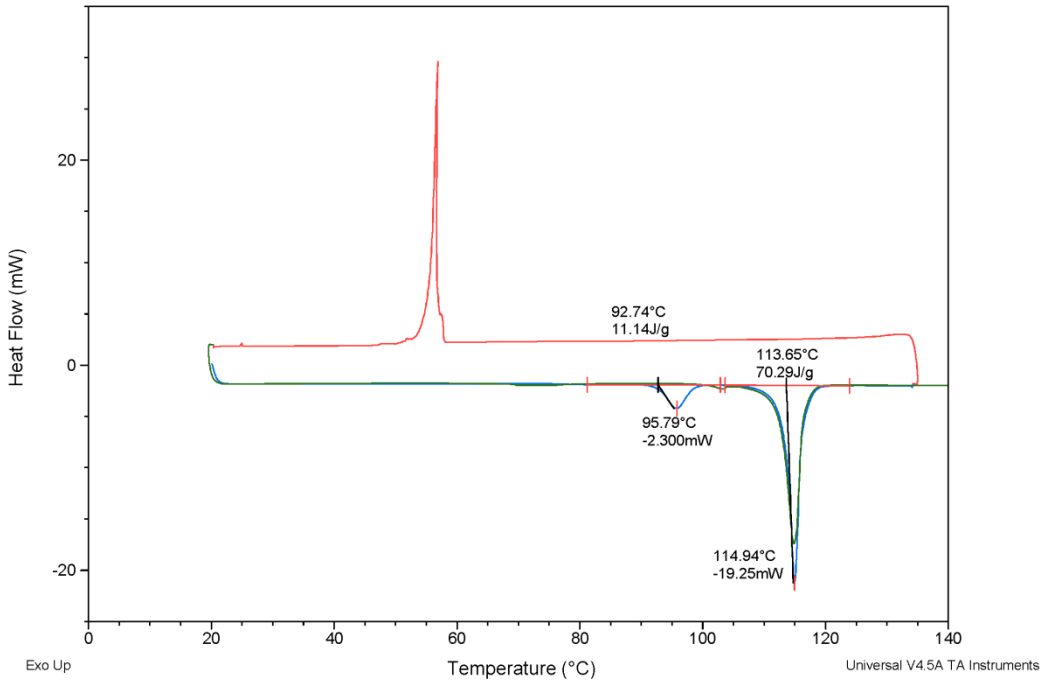

Figure S5. DSC thermogram of (**mdppo**)$_2$·(**tfib**) collected on 4.6 mg of sample in a dynamic flow of nitrogen. The sample was heated (blue line), cooled (red line) and then heated again (green line) at a rate 10 K min^{-1}.

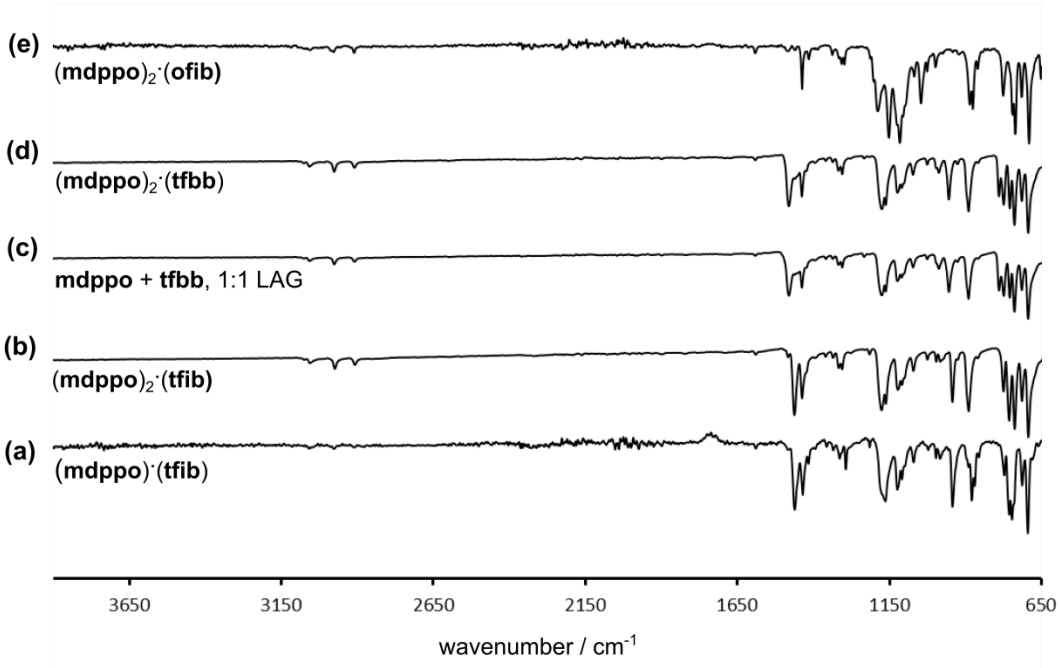

Figure S6. FTIR-ATR spectra of: (a) (**mddpo**)·(**tfib**) cocrystal prepared by LAG; (b) (**mddpo**)$_2$·(**tfib**) cocrystal prepared by LAG; (c) 1:1 mixture of **mdppo** and **tfbb** after LAG with acetonitrile; (d) (**mddpo**)$_2$·(**tfbb**) cocrystal prepared by LAG and (e) (**mddpo**)$_2$·(**ofib**) cocrystal prepared by grinding.