## The Crystal Engineering of Radiation-Sensitive Diacetylene Cocrystals and Salts

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## **Supplementary Information**



Figure S1. The experimental and calculated PXRD patterns of **1** highlighting the initial (00/) reflections. The experimental data were collected at room temperature (approx. 293 K), with the calculated data collected at 100 K.



Figure S2. A photograph of **1** before any irradiation studies. Highlighting that the surface colouration of the crystals is not representative of the bulk material (no evidence of polymerisation).



Figure S3. The experimental PXRD patterns of **1** irradiated for one hour and one day. The relative intensities are affected by differences in preferred orientation between the irradiated and non-irradiated samples.



Figure S4. CP-MAS <sup>13</sup>C NMR spectra of **1** irradiated for different durations by UV light at 254 nm.



Figure S5. The FTIR spectra of **1** irradiated for different durations by UV light at 254 nm.



Figure S6. The DSC thermogram of  $\mathbf{1}_2 \cdot \mathbf{2}$  with a peak onset endotherm at 56.9 °C.



Figure S7. The DSC thermogram of **1** with a melt onset endotherm at 62.3 °C.



Figure S8. The FTIR spectra of  $\mathbf{1}_2 \cdot \mathbf{2}$  irradiated for one hour by UV light at 365 nm.



Figure S9. The calculated and experimental PXRD pattern of  $\mathbf{1}_2 \cdot \mathbf{2}$  at different temperatures.







Figure S11. The DSC thermogram of  $\mathbf{1}_2 \cdot \mathbf{4}$  displaying a melt onset endotherm at 72.2 °C, with residual unreacted  $\mathbf{1}$  at 62.6 °C.



Figure S12. The FTIR spectra of  $1_2$ ·3 irradiated for different durations by UV light at 254 nm.



Figure S13. The FTIR spectra of  $1_2$ ·4 irradiated for different durations by UV light at 254 nm.

Cocrystal	Temp.	a / Å	b / Å	c / Å	β/°	Volume / ų
<b>1</b> <sub>2</sub> . <b>3</b>	100 K	5.4415(2)	8.9535(4)	55.673(3)	90.8823(10)	2712.1(2)
	260 K	5.4783(3)	8.9976(5)	56.951(4)	92.506(2)	2804.5(3)
	273 K	5.4761(3)	8.9950(5)	57.173(4)	92.710(2)	2813.0(5)
<b>1</b> 2· <b>4</b>	120 K	5.4494(3)	8.9235(5)	57.441(3)	92.643(2)	2790.2(3)
	260 K	5.4847(4)	8.9801(6)	58.562(4)	90.849(3)	2884.1(3)
	273 K	5.503(5)	9.023(7)	58.93(5)	90.24(3)	2927.0(7)

Table S1. The unit cell axes of  $\mathbf{1}_2 \cdot \mathbf{3}$  and  $\mathbf{1}_2 \cdot \mathbf{4}$  collected at various temperatures.



Figure S14. The calculated and experimental PXRD patterns of  $\mathbf{1}_2 \cdot \mathbf{3}$  at different temperatures.



Figure S15. The calculated and experimental PXRD patterns of  $\mathbf{1}_2 \cdot \mathbf{4}$  collected at different temperatures.



Figure S16. The FTIR spectra of  $1_2$ ·5 irradiated for different durations by UV light at 254 nm.



Figure S17. The FTIR spectra of **1**·**6** irradiated for different durations by UV light at 254 nm.



Figure S18. The FTIR spectra of  $1_2 \cdot 7$  irradiated for different durations by UV light at 254 nm.



Figure S19. The FTIR spectra of **1**·**8** irradiated for different durations by UV light at 254 nm.



Figure S20. The DSC thermogram of  $1_2 \cdot 5$  displaying a melt onset endotherm at 107.4 °C with residual unreacted 1 between 59.5-64.6 °C.



Figure S21. The DSC thermogram of 1.6 displaying a melt onset endotherm at 43.8 °C.



Figure S22. The DSC thermogram of  $1_2 \cdot 7$  displaying a melt onset endotherm at 45.8 °C.



Figure S23. The DSC thermogram of **1**·**8** displaying a melt onset endotherm at 57.3 °C.



Figure S24. The FTIR spectra of  $\mathbf{1}_2 \cdot \mathbf{2}$  irradiated for one hour by UV light at 254 nm.



Figure S25. The experimental PXRD patterns of  $\mathbf{1}_2 \cdot \mathbf{2}$  irradiated for one hour by UV light at 254 nm.



Figure S26. The experimental PXRD patterns of  $\mathbf{1}_2 \cdot \mathbf{2}$  irradiated for different durations by UV light at 365 nm. Additional peak at 23.0 2 $\vartheta$  in the one hour and one day patterns correlate to  $\mathbf{1}$ .



Figure S27. The experimental PXRD patterns of  $\mathbf{1}_2 \cdot \mathbf{3}$  irradiated for different durations by UV light at 254 nm.



Figure S28. The experimental PXRD patterns of  $\mathbf{1}_2 \cdot \mathbf{4}$  irradiated for different durations by UV light at 254 nm. The peaks emerging in the one-day irradiated patterns at 5.7, 17.5, and 23.0  $2\vartheta$ , correlate to peaks of  $\mathbf{1}$ .



Figure S29. CP-MAS <sup>13</sup>C NMR spectra of  $1_2 \cdot 2$  irradiated for different durations by UV light at 254 nm.



Figure S30. CP-MAS <sup>13</sup>C NMR spectra of  $1_2 \cdot 2$  irradiated for one hour by UV light at 365 nm. The additional peak at 182.5 ppm which correlates to the carboxylate peak of **1**.



Figure S31. CP-MAS <sup>13</sup>C NMR spectra of  $1_2$ ·**3** irradiated for different durations by UV light at 254 nm.



Figure S32. CP-MAS <sup>13</sup>C NMR spectra of  $1_2 \cdot 4$  irradiated for different durations by UV light at 254 nm. The additional peak at 180.3 ppm in the one-day irradiated spectra corresponds to the carboxylate peak of **1**.



Figure S33. The experimental PXRD patterns of  $1_2 \cdot 5$  irradiated for different durations by UV light at 254 nm.



Figure S34. CP-MAS <sup>13</sup>C NMR spectra of  $1_2$ ·5 irradiated for different durations by UV light at 254 nm.



Figure S35. CP-MAS <sup>13</sup>C NMR spectra of **1**·**6** irradiated for different durations by UV light at 254 nm.



Figure S36. CP-MAS <sup>13</sup>C NMR spectra of  $1_2$ ·7 irradiated for different durations by UV light at 254 nm.



Figure S37. CP-MAS <sup>13</sup>C NMR spectra of  $1\cdot 8$  irradiated for different durations by UV light at 254 nm.



Figure S38. The experimental PXRD patterns of 1.6 irradiated for different durations by UV light at 254 nm.



Figure S39. The experimental PXRD patterns of  $\mathbf{1}_2 \cdot \mathbf{7}$  irradiated for different durations by UV light at 254 nm.



Figure S40. The experimental PXRD patterns of **1**·**8** irradiated for different durations by UV light at 254 nm.



Figure S41. The Raman spectra of **1** before and after 100 Gy of X-ray radiation.



Figure S42. The Raman spectra of  $\mathbf{1}_2 \cdot \mathbf{2}$  before and after 10 Gy of X-ray radiation.



Figure S43. The Raman spectra of  $1_2 \cdot 3$  before and after 10 Gy of X-ray radiation.



Figure S44. The Raman spectra of  $\mathbf{1}_2 \cdot \mathbf{4}$  before and after 10 Gy of X-ray radiation.



Figure S45. The Raman spectra of  $1_2 \cdot 5$  before and after 100 Gy of X-ray radiation.



Figure S46. The Raman spectra of **1**·**6** before and after 100 Gy of X-ray radiation.



Figure S47. The Raman spectra of  $1_2 \cdot 7$  before and after 100 Gy of X-ray radiation, highlighting the pre-resonance Raman effect by the differences in relative intensities of bands.



Figure S48. The Raman spectra of **1**·**8** before and after 100 Gy of X-ray radiation.