

Fig.S3 IR spectra of **1** (a), desolventized sample **1'** (b), and irradiated sample **1-i** (c).

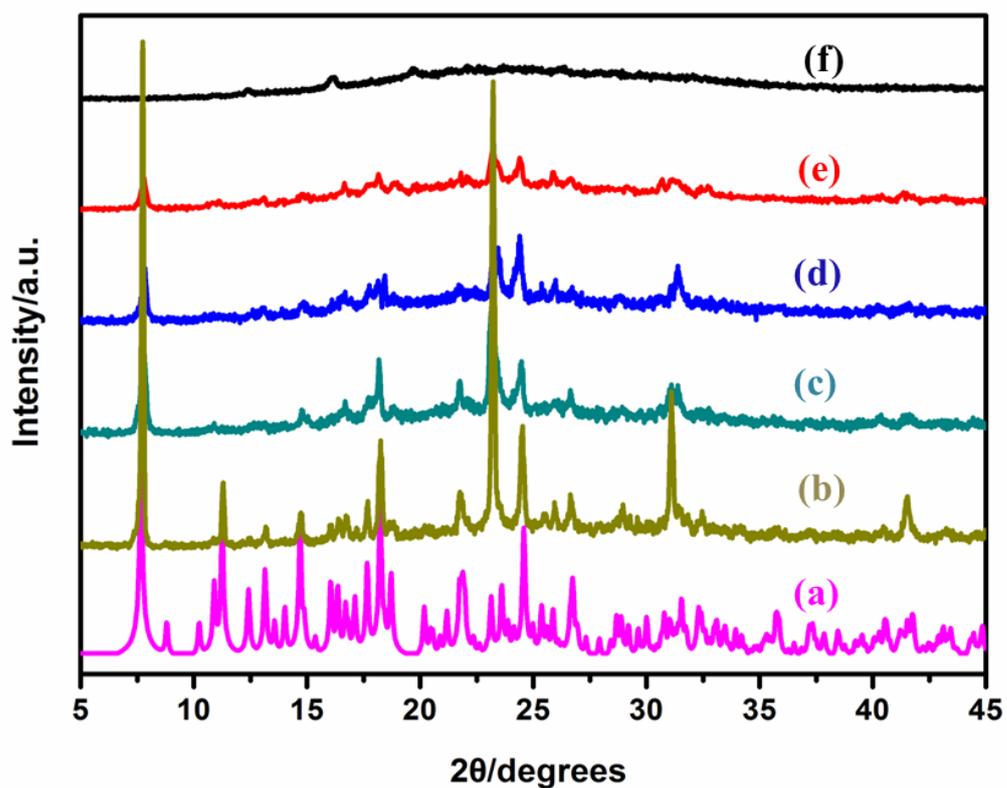


Fig.S4 PXRD patterns of simulated **1** (a), as-synthesized **1** (b), **1** exposed to UV light for 2 h (c), **1** exposed to UV light for 4 h (d), **1** exposed to UV light for 6 h (e), **1** is exposed to UV light for 38 h (f).

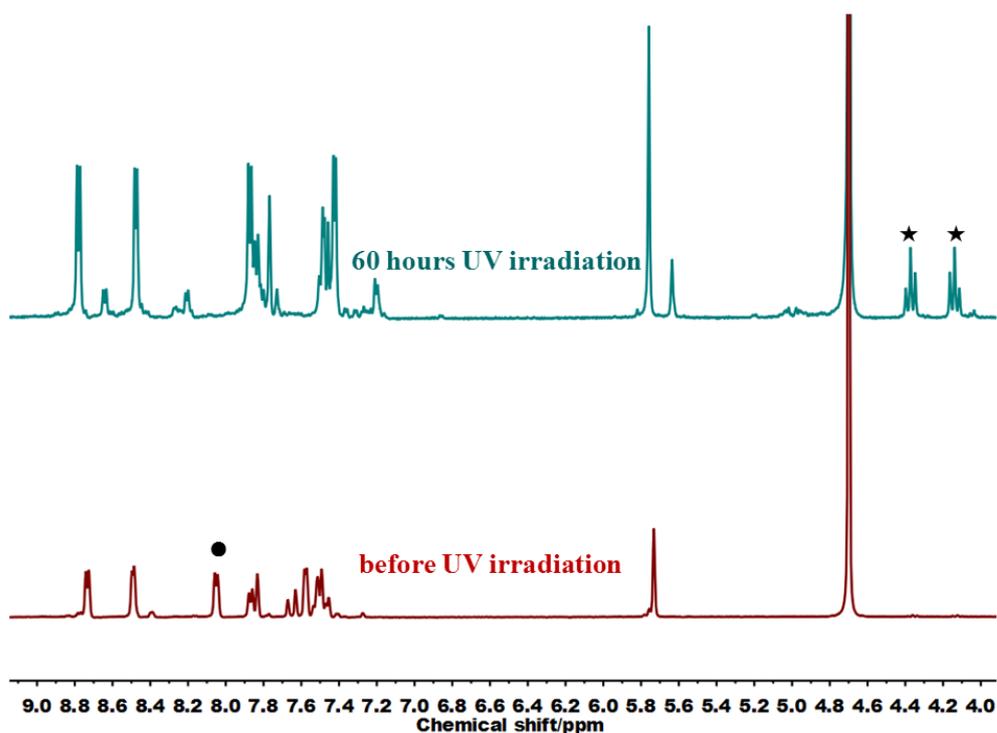


Fig.S5 ^1H NMR spectra of *m*-BCbpe in D_2O before and after 365 nm UV irradiation for 60 hours. The vinyl and cyclobutane protons are represented by (●) and (★), respectively. It shows that almost complete conversion has taken place.

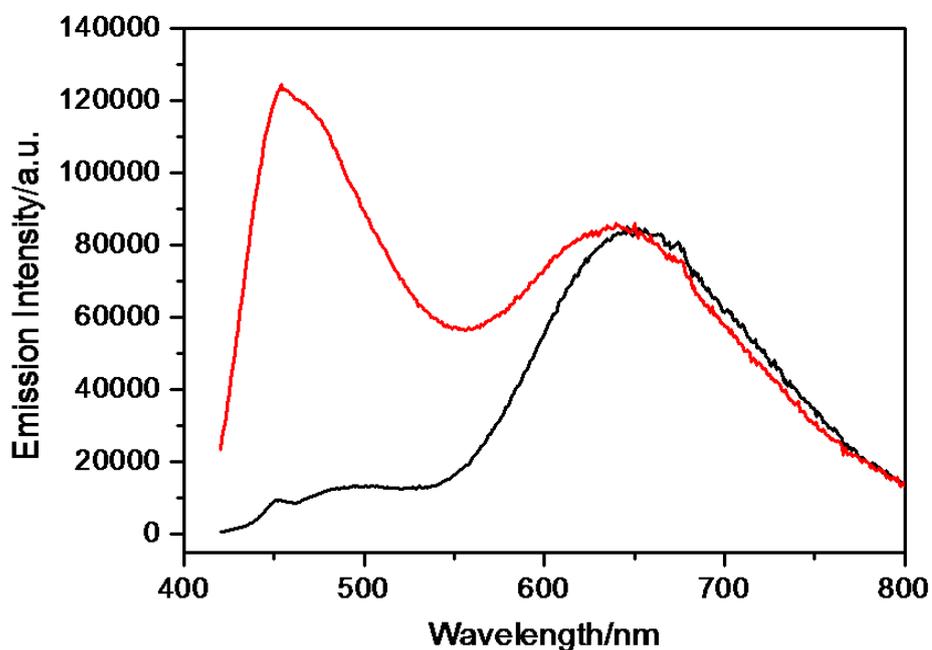


Fig.S6 Emission profiles of *m*-BCbpe (black line) and its photodimer product obtained through exposing the sample to 365 nm UV light for 60 hours (red line) in H_2O ($\lambda_{\text{ex}} = 390 \text{ nm}$).

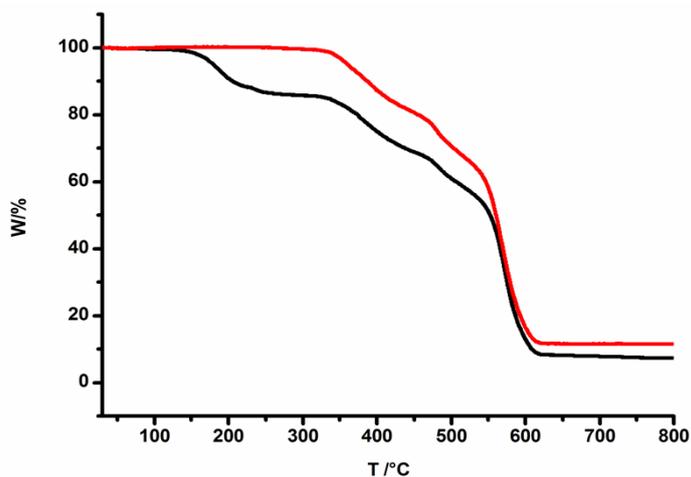


Fig.S7 The TG Plots of compound **1** (black) and desolventized sample **1'** (red).

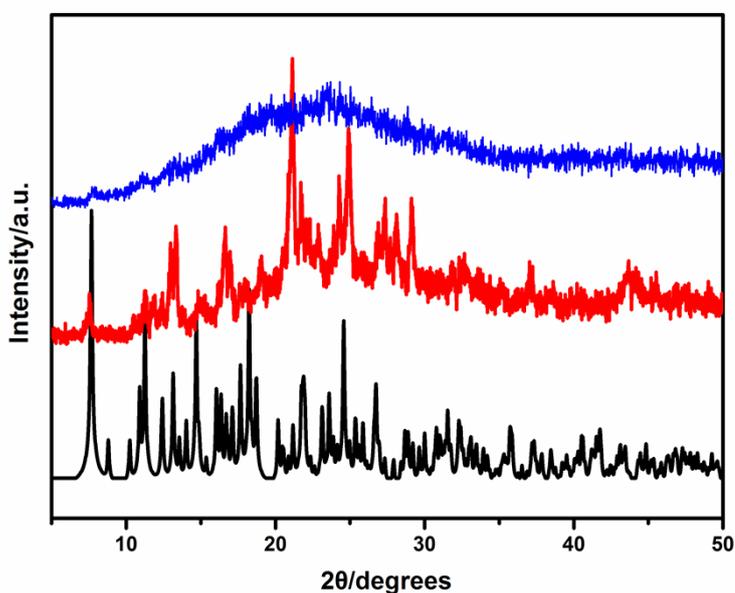


Fig.S8 PXRD patterns of simulated **1** (black), desolventized sample **1'** (red) and irradiated sample **1'-i** after activation (blue).

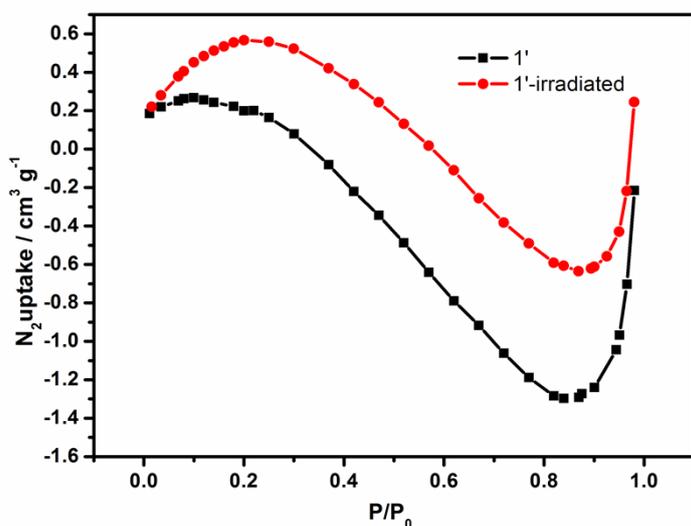


Fig.S9 N₂ sorption isotherms for desolventized sample **1'** (black) and irradiated sample **1'-i** (red).

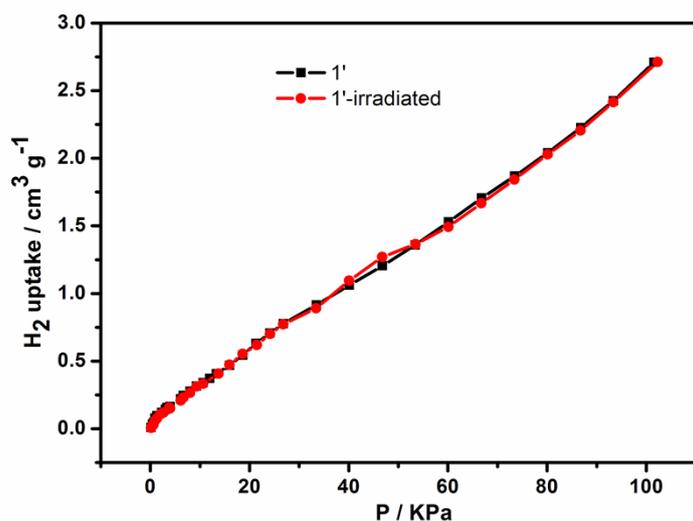


Fig.S10 H₂ sorption isotherms for desolventized sample **1'** (black) and irradiated sample **1'-i** (red).

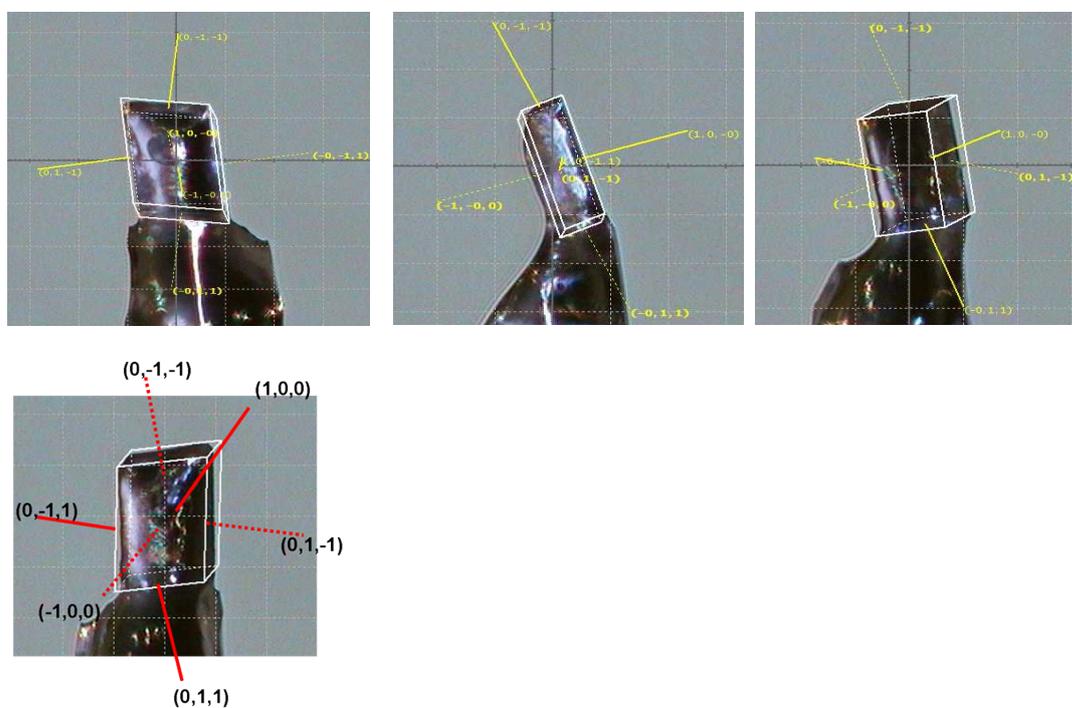


Fig.S11 Face indexing images of the crystal **1**.

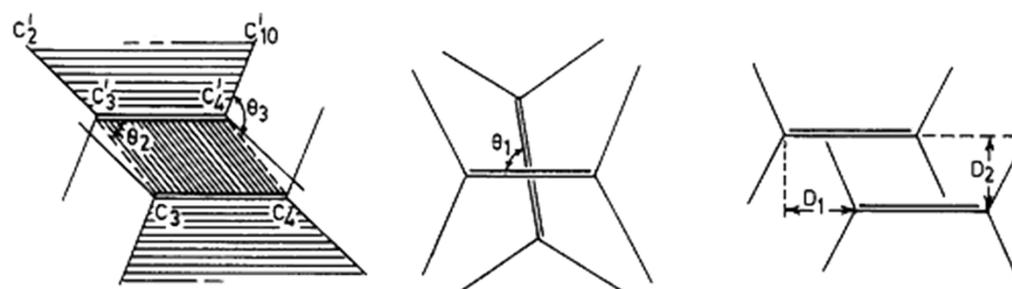


Chart S1. Definitions of the Parameters Usually Considered To Be Geometric Criteria for [2+2] Photodimerization of Double Bonds (According to Ref: V.Ramamurthy, K.Venkatesan, *Chem. Rev.* **1987**, 87, 433–481; θ_3 is the Angle between the $>C=C<$ and $C=C-C=C$ Planes).