Supplementary Material

Template-Stereocontrolled [2+2] Photoreactions Directed by Surface Recognition on Hydrophilic Functionalized Carbon Nanomaterials. From Solution to Solid State Reactivity

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1.- Experimental section

2.- List of figures

Figure S1. (a) FT-IR spectrum of carbon spheres (CS-COOH) obtained by hydrothermal carbonization of glucose. (b) SEM images of hydrophilic carbon spheres prepared.

Figure S2. (a) Comparative FT-IR spectra of pristine carbon nanotubes. (b) and the resulting MWCNT H_2O_2 hydrothermal treatment in presence of POM :0.1g and 2 mL of H_2O_2 at 30% V/V. (b) SEM images of functionalized MWCNT-COOH.

Figure S3. Determination of surface pH (pH_{PZC}) of CS-COOH and MWCNT-COOH.

Figure S4. ¹H-NMR spectrum of products obtained from the photoreaction of *trans*-bis(2-pyridyl)ethylene (2,2'-bpe) assisted by CS-COOH in solution. [1,2,3,4-tetrakis (2-pyridyl)cyclobutane (2,2'-tpcb)]. Yield: 100% (*rctt:* 74%, *rcct:* 22% and *rtct:* 4%).

Figure S5. ¹H-NMR spectrum of products obtained from the photoreaction of *trans*-bis(2-pyridyl)ethylene (2,2'-bpe) assisted by MWCNT-COOH. [1,2,3,4-tetrakis (2-pyridyl)cyclobutane (2,2'-tpcb)]. Yield: 82% (*rctt:* 62%, *rtct:* 11% and *rcct:* 9%). Residual *trans*-1,2-(2-pyridyl)ethylene. Yield: 18%.

Figure S6. ¹H-NMR spectrum of products obtained from the photoreaction of *trans*-bis(4-pyridyl)ethylene (4,4'-bpe) assisted by CS-COOH in solution. [1,2,3,4-tetrakis (4-pyridyl)cyclobutane (4,4'-tpcb)]. Yield: 72% (*rctt:* 51%, *rcct:* 11% and *rtct:* 10%). Residual *trans*-1,2-(4-pyridyl)ethylene. Yield: 28%.

Figure S7. ¹H-NMR spectrum of products obtained from the photoreaction of trans-bis(4-pyridyl)ethylene (4,4'-bpe) assisted by MWCNT-COOH in solution. [1,2,3,4-tetrakis (4-pyridyl)cyclobutane (4,4'-tpcb)]: Yield 64% (*rctt:* 43%, *rtct:* 15% and *rcct:* 6%). Residual *trans*-1,2-(4-pyridyl)ethylene. Yield: 36%.

Figure S8. Representative ¹H-NMR spectra in CDCl₃, showing quantitative conversion of the mixture of photodimers obtained from the irradiation in solution (*rctt-*, *rcct-* and *rtct-*2,2'-tpcb isomers) (bottom) into *rtct-*isomer by heating upon hydrothermal conditions assisted either by CS-COOH or MWCNT-COOH (top). [*rtct-*1,2,3,4-tetrakis(2-pyridyl)cyclobutane (2,2'-tpcb)]: Yield 100%.

Figure S9. Representative ¹H-NMR spectra in CDCl₃, showing quantitative conversion of the mixture of photodimers obtained from the irradiation in solution (*rctt-*, *rcct-* and *rtct-*4,4'-tpcb isomers) (bottom) into *rtct-*isomer by heating upon hydrothermal conditions assisted either by CS-COOH or MWCNT-COOH (top). [*rtct-*1,2,3,4-tetrakis-(4-pyridyl)cyclobutane (4,4'-tpcb)]: Yield 100%.

Figure S10. ¹H-NMR spectrum of *rctt*-1,3-bis(carboxyl)-2,4-bis(phenyl)cyclobutane *head-to-tail* obtained from UV-irradiation of *trans*-cinammic acid assisted by CS-COOH in solution : Yield 100%.

Figure S11.¹H-NMR spectrum of *rctt*-1,2-bis(carboxyl)-3,4-bis(4-chlorophenyl)cyclobutane *head-to-head* obtained from UV-irradiation of *trans*-4-chlorocinnamic acid assisted by CS-COOH in solution. Yield: 100%.

Figure S12. ¹H-NMR spectrum of *rctt*-1,2-bis(carboxyl)-3,4-bis(4-trifluoromethylphenyl)cyclobutane *head-to-head* obtained from UV-irradiation of *trans*-4-chlorocinnamic acid assisted by CS-COOH in solution. Yield 93%. Residual *trans*-4-(trifluoromethyl)-cinnamic acid: Yield 7%.

Figure S13. Comparative ¹H-NMR spectra of the photoreactivity *trans*-4-(trifluoromethyl)-cinnamic acid in solution (bottom) and the solid state reactivity under different experimental conditions (Run1: Irradiation in the solid state from mechanochemical self-assembly. Run 2: Irradiation of impregnated CS–COOH with an excess of olefin in the solid state. Run 3: Impregnation-irradiation in the solid state + two additional grinding-irradiation cycles).

Figure S14.¹H-NMR spectrum of *rctt*-1,3-bis(carboxyl)-2,4-bis(4-methylphenyl)cyclobutane head-to-tail obtained from UV-irradiation of Residual *trans*-4-methylcinnamic acid assisted by CS-COOH in solution: Yield 93%. Residual *trans*-4-methylcinnamic acid: Yield 7%.

Figure. S15. Comparative ¹H-NMR spectra of the photoreactivity of *trans*-4-methylcinnamic acid in solution (bottom) and the solid state reactivity under different experimental conditions (Run1: Irradiation in the solid state from mechanochemical self-assembly. Run 2: Irradiation of impregnated CS–COOH with an excess of olefin in the solid state. Run 3: Impregnation-irradiation in the solid state + two additional grinding-irradiation cycles).

Figure S16. ¹H-NMR spectrum of *rctt*-1,2-bis(carboxyl)-3,4-bis(4-bromophenyl)cyclobutane *head-to-head* obtained from UV-irradiation of *trans*-4-bromocinnamic acid assisted by CS-COOH in solution. Yield 85%. Residual *trans*-4-bromocinnamic acid: Yield 15%.

Figure S17. Comparative ¹H-NMR spectra of the photoreactivity of *trans*-4-bromocinnamic acid in solution (bottom) and the solid state reactivity under different experimental conditions (Run1: Irradiation in the solid state from mechanochemical self-assembly. Run 2: Irradiation of impregnated CS–COOH with an excess of olefin in the solid state. Run 3: Impregnation-irradiation in the solid state + two additional grinding-irradiation cycles).

Figure S18. ¹H-NMR spectrum of *rctt*-1,2-bis(carboxyl)-3,4-bis(4-fluorophenyl)cyclobutane *head-to-head* obtained from UV-irradiation of *trans*-4-fluorocinnamic acid assisted by CS-COOH in solution. Yield 90%. Residuals *trans*-4-fluorocinnamic acid and *cis*-4-fluorocinnamic acid: Yields 7% and 3%, respectively.

Figure S19. Comparative ¹H-NMR spectra of the photoreactivity of *trans*-4-flourocinnamic acid in solution (bottom) and the solid state reactivity under different experimental conditions (Run1: Irradiation in the solid state from mechanochemical self-assembly. Run 2: Irradiation of impregnated CS–COOH with an excess of olefin in the solid state. Run 3: Impregnation-irradiation in the solid state + two additional grinding-irradiation cycles).

Figure S20. ¹H-NMR spectrum of *rctt*-1,2-bis(carboxyl)-3,4-bis(3,4-dichlorophenyl)cyclobutane *head-to-head* obtained from UV-irradiation of *trans*-3,4-dichlorocinnamic acid assisted by CS-COOH in solution. Yield 80%. Residuals *trans*-3,4-dichlorocinnamic acid and *cis*-3,4-dichlorocinnamic acid: Yields 13% and 7% respectively.

Figure S21. Comparative ¹H-NMR spectra of the photoreactivity of *trans*-3,4-dichlorocinnamic acid in solution (bottom) and the solid state reactivity under different experimental conditions (Run1: Irradiation in the solid state from mechanochemical self-assembly. Run 2: Irradiation of impregnated CS–COOH with an excess of olefin in the solid state. Run 3: Impregnation-irradiation in the solid state + two additional grinding-irradiation cycles).

Figure S22. Comparative ¹H-NMR spectra of the photoreactivity of *trans*-cinnamic acid in solution: (a) ¹H-NMR spectrum obtained from UV-irradiation of *trans*-cinnamic acid assisted by MWCNT-blank in solution. Photoproducts: *trans*-cinnamic acid and *cis*-cinnamic acid: Yields 33% and 67%, respectively. (b) ¹H-NMR spectrum obtained from UV-irradiation of *trans*-cinnamic acid assisted by functionalized MWCNT-COOH in solution. Photoproducts: *rctt*-1,3-bis(carboxyl)-2,4-bis(phenyl) cyclobutane *head-to-tail*: Yield 28%. Residual *trans*-cinnamic acid: Yield 72%

Figure S23. Comparative FT-IR spectra of fresh CS-COOH, cinnamic acid free and impregnated Cinnamic acid/ CS-COOH.

Figure S24. (a) Comparative UV-visible spectra of ethanol dispersion of CS-COOH (2 mg/mL), (b) Impregnated cinnamic acid/CS-COOH in ethanol (mass ratio of 3:1).

1.- Experimental section

Preparation and characterization of carbon spheres and functionalization of MWCNT

All reagents were of analytical grade and used without further purification. The preparation of CS-COOH were obtained using the method previously reported in a previous study.²⁰ Anhydrous α -D-glucose, phosphotungstinic acid [H₃PW₁₂O₄₀] (PTA) and hydrogen peroxide (H₂O₂) were obtained from Aldrich Co. The reaction was carried out in a 23 mL capacity Teflon-lined stainless steel autoclave, which was introduced into a programmable oven. In a typical experiment, 1 g of glucose was dissolved in 10 mL of distilled water together with 150 mg of PTA and 2 mL of H₂O₂ at 30% V/V were added to the glucose solution. The autoclave was sealed and heated at 180 °C for 12-24 h and then allowed to cool to room temperature. The solid products were filtered off, washed several times with distilled water, and finally dried in a vacuum oven at 60 °C overnight. Similar experimental condition were used for the functionalization of MWCNT.

FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm⁻¹ on a Thermo-Scientific Nicolet spectrometer. The point of zero charge (pHpzc) of CS-COOH and MWCNT-COOH was measured by using the pH drift method. The surface morphology was performed on a FEI Inspect F50 scanning electron microscopy, operating at 20-30 KeV. ¹H-NMR spectra were recorder on a Bruker 300 and 500 MHz spectrometers from solution in CDCl₃ or d_6 -DMSO.

Photochemical reactivity studies

For the photolysis in aqueos solution, the MWCNT-COOH or CS-COOH were water dispersed in 10 mL of H_2O under ultrasonication during 10-15 min and then mixed with a solution of stilbene or cinnamic derivatives previously dissolved in 10 mL of Ethanol in a mass ratio of 1:3, respectively. The mixture were kept under magnetic stirring overnight to assure the interaction substrate/surface. Photoirradiation was carried-out in a sealed glass vial with a 8 Watt mercury lamp at 302 nm for 48 h. Prior to irradiation, the samples were desgassed with N_2 gas for 15-20 min. The samples were kept under magnetic stirring during the irradiation process. For the photolysis in the solid state, either the impregnated spheres or self-assembled via mechanochemistry were crushed and spread between two pyrex plates. These plates were flipped back at regular intervals of time to assure the uniform exposure of UV irradiation. Effect of irradiation times on the photoreaction was not optimized due to the low power of the lamp used. However, the yield of some tested reactions do not show significant differences when irradiated for 24 or 48 h.

After the irradiation the products were extracted with CHCl₃ and characterized by ¹H-NMR spectroscopy without further chemical purification. The products could be almost quantitatively extracted from the surface, and the mass balance was generally near 95-100% in the majority of the cases.

Figure S1. (a) FT-IR spectrum of Carbon spheres (CS-COOH) obtained by hydrothermal carbonization of glucose. (b) SEM images of hydrophilic carbon spheres prepared.



FT-IR [KBr, cm⁻¹] A (3418, vO-H), B (2952, vC-H), C (1702, vC=O), D (1625, C=C), E (1384, δCH₃), F (1293, vC-O), G (1024, 800, γC-H y O-H).



Figure S2. (a) Comparative FT-IR spectra of pristine carbon nanotubes. (b) and the resulting MWCNT H_2O_2 hydrothermal treatment in presence of POM :0.1 and 2 mL of H_2O_2 at 30% V/V. (b) SEM images of functionalized MWCNT-COOH.



FT-IR [KBr, cm⁻¹] A (3444, vO-H), B (1632, vC=O), C (1400, C–O–H), D (1075, vC-O).







[2+2] photocycloaddition of trans-bis(2-pyridyl)ethylene (2,2'-bpe) direct by CS-COOH and MWCNT-COOH in solution.

Figure S4. ¹H-NMR spectrum of products obtained from the photoreaction of *trans*-bis(2-pyridyl)ethylene (2,2'-bpe) assisted by CS-COOH in solution. [1,2,3,4-tetrakis (2-pyridyl)cyclobutane (2,2'-tpcb)]. Yield: 100% (*rctt:* 74%, *rcct:* 22% and *rtct:* 4%).



300 MHz / CDCl₃

Figure S5. ¹H-NMR spectrum of products obtained from the photoreaction of *trans*-bis(2-pyridyl)ethylene (2,2'-bpe) assisted by MWCNT-COOH. [1,2,3,4-tetrakis (2-pyridyl)cyclobutane (2,2'-tpcb)]. Yield: 82% (*rctt:* 62%, *rtct:* 11% and *rcct:* 9%). Residual *trans*-1,2-(2-pyridyl)ethylene. Yield: 18%.



300 MHz / CDCl₃

• Spectroscopic data

rctt-2,2'-tpcb: ¹H-NMR [CDCl₃-*d*, 300 MHz, *J* (Hz)] δ 8.38 (dd, *J*a₁b₁ = 4.9, *J*a₁c₁ = 1.7, Ha₁), 7.34 (ddd, *J*c₁b₁ = *J*c₁d₁ = 7.9, Hc₁), 7.06 (d, Hd₁), 6.89 (ddd, *J*b₁d₁ = 1.0, Hb₁), 5.05 (s, He₁) ppm.

rcct-2,2'-tpcb: ¹H-NMR [CDCl₃-*d*₁ 300 MHz, *J* (Hz)] δ 8.29 (d, *J*a₂b₂ = 4.6, Ha₂), 7.34 (solp, *J*c₂a₂ = 1.8, *J*c₂b₂ = *J*c₂d₂ = 7.8, Hc₂), 7.06 (solp, Hd₂), 6.89 (solp, *J*b₂d₂ = 1.1, Hb₂), 5.56 (t, *J*g₂e₂ = *J*g₂f₂ = 10.1, Hg₂), 4.84 (m, Hf₂), 4.70 (m, *J*e₂f₂ = 9.4, He₂), 8.00 (d, *J*a₃b₃ = 4.0, Ha₃), 7.14 (solp, Hc₃), 7.00 (d, *J*d₃c₃ = 7.9, Hd₃), 6.66 (ddd, *J*b₃d₃ = 1.8, Hb₃), 8.61 (d, *J*a₄b₄ = 4.6, *J*a₄c₄ = 1.6, Ha₄), 7.63 (solp, Hc₄), 7.12 (solp, Hd₄), 7.10 (solp, Hb₄) ppm.

rtct-2,2'-tpcb: ¹H-NMR [CDCl₃-*d*₃ 300 MHz, *J* (Hz)] δ 8.65 (solp, *J*a₅b₅ = 4.6, Ha₅), 7.52 (ddd, *J*a₅c₅ = 1.9, *J*c₅b₅ = *J*c₅d₅ = 7.6, Hc₅), 7.15 (solp, Hd₅), 7.06 (solp, Hb₅), 4.36 (s, He₅) ppm.

2,2'-bpe: ¹H-NMR [CDCl₃- d_{1} 300 MHz, J (Hz)] δ 8.94 (dd, $Ja_{6}b_{6} = 4.4$, $Ja_{6}c_{6} = 1.4$, Ha₆), 8.84 (dd, $Jc_{6}b_{6} = Jc_{6}d_{6} = 7.8$, Hc₆), 8.44 (m, Hb₆, Hd₆), 8.18 (s, He₆) ppm.

[2+2] photocycloaddition of trans-bis(4-pyridyl)ethylene (4,4'-bpe) direct by carbon CS-COOH and MWCNT-COOH.

Figure S6. ¹H-NMR spectrum of products obtained from the photoreaction of *trans*-bis(4-pyridyl)ethylene (4,4'-bpe) assisted by CS-COOH in solution. [1,2,3,4-tetrakis (4-pyridyl)cyclobutane (4,4'-tpcb)]. Yield: 72% (*rctt:* 51%, *rcct:* 11% and *rtct:* 10%). Residual *trans*-1,2-(4-pyridyl)ethylene. Yield: 28%.



500 MHz / CDCl₃

Figure S7. ¹H-NMR spectrum of products obtained from the photoreaction of trans-bis(4-pyridyl)ethylene (4,4'-bpe) assisted by MWCNT-COOH in solution. [1,2,3,4-tetrakis (4-pyridyl)cyclobutane (4,4'-tpcb)]: Yield 64% (*rctt:* 43%, *rtct:* 15% and *rcct:* 6%). Residual *trans*-1,2-(4-pyridyl)ethylene. Yield: 36%.



500 MHz / CDCl₃

• Spectroscopic data

rctt-4,4'-tpcb: ¹H-NMR [CDCl₃- d_{1} 500 MHz, J (Hz)] δ 8.41 (d, $Ja_{1}b_{1} = 5.9$, Ha₁), 6.99 (d, Hb₁), 5.05 (s, Hc₁) ppm.

rcct-4,4'-tpcb: ¹H-NMR [CDCl₃-*d*₁ 500 MHz, *J* (Hz)] δ 8.60 (solp, Ha₂), 7.32 (d, *J*b₂a₂ = 5.9, Hb₂), 4.62 (t, *J*c₂c₂ = 10.4, *J*c₂d₂ = 9.3, He₂), 4.55 (t, *J*d₂c₂ = 10.4, Hd₂), 4.36 (t, Hc₂), 8.17 (d, *J*a₃b₃ = 6.0, Ha₃), 6.69 (m, Hb₃), 8.38 (d, *J*a₄b₄ = 5.8, Ha₄), 6.93 (d, Hb₄) ppm.

rtct-4,4'-tpcb: ¹H-NMR [CDCl₃- d_{2} 500 MHz, J (Hz)] δ 8.57 (d, $Ja_{5}b_{5} = 6.0$, Ha₅), 7.17 (d, Hb₅), 3.71 (s, Hc₅) ppm.

4,4'-bpe: ¹H-NMR [CDCl₃-*d*₃ 500 MHz, *J* (Hz)] δ 8.77 (d, *J*a₆b₆ = 5.3, Ha₆), 7.90 (s, Hc₆), 7.76 (d, Hb₆) ppm.

Cyclobutane isomerisation upon hydrothermal conditions

Figure S8. Representative ¹H-NMR spectra in CDCl₃, showing quantitative conversion of the mixture of photodimers obtained from the irradiation in solution (*rctt-*, *rcct-* and *rtct-*2,2'-tpcb isomers) (bottom) into *rtct-*isomer by heating upon hydrothermal conditions assisted either by CS-COOH or MWCNT-COOH (top). [*rtct-*1,2,3,4-tetrakis(2-pyridyl)cyclobutane (2,2'-tpcb)]: Yield 100%.



Figure S9. Representative ¹H-NMR spectra in CDCl₃, showing quantitative conversion of the mixture of photodimers obtained from the irradiation in solution (*rctt-*, *rcct-* and *rtct-*4,4'-tpcb isomers) (bottom) into *rtct-*isomer by heating upon hydrothermal conditions assisted either by CS-COOH or MWCNT-COOH (top). [*rtct-*1,2,3,4-tetrakis-(4-pyridyl)cyclobutane (4,4'-tpcb)]: Yield 100%.



500 MHz / CDCl₃

[2+2] photocycloaddition of cinnamic acid derivatives direct by CS-COOH in solution.

Figure S10. ¹H-NMR spectrum of *rctt*-1,3-bis(carboxyl)-2,4-bis(phenyl)cyclobutane *head-to-tail* obtained from UV-irradiation of *trans*-cinammic acid assisted by CS-COOH in solution : Yield 100%.



500 MHz / DMSO

¹H-NMR [DMSO- d_6 , 500 MHz, J (Hz)] δ 12.10 (s, Hf), 7.33 (m, Jab = Jbc = 7.2, Jca = 3.5, Hb, Hc), 7.22 (t, Ha), 4.27 (dd, Jed = 7.4, Jdd' = Jee' = 10.2, He), 3.81 (dd, Hd) ppm.

Figure S11.¹H-NMR spectrum of *rctt*-1,2-bis(carboxyl)-3,4-bis(4-chlorophenyl)cyclobutane *head-to-head* obtained from UV-irradiation of *trans*-4-chlorocinnamic acid assisted by CS-COOH in solution.Yield: 100%.



500 MHz / DMSO

¹H-NMR [DMSO- d_{6} , 500 MHz, J (Hz)] δ 12.50 (s, He), 7.17 (d, Jab = 8.5, Ha), 7.08 (d, Hb), 4.22 (d, Jcd = 6.1, Hc), 3.81 (d, Hd) ppm.

Figure S12. ¹H-NMR spectrum of *rctt*-1,2-bis(carboxyl)-3,4-bis(4-trifluoromethylphenyl)cyclobutane *head-to-head* obtained from UV-irradiation of *trans*-4-trifluoromethylcinnamic acid assisted by CS-COOH in solution. Yield 93%. Residual *trans*-4-(trifluoromethyl)-cinnamic acid: Yield 7%.



300 MHz / DMSO

¹H-NMR [DMSO- d_{6} 300 MHz, J (Hz)] δ 12.58 (s, He), 7.42 (d, Jab = 8.2, Ha), 7.28 (d, Hb), 4.38 (d, Jcd = 6.2, Hc), 3.91 (d, Hd) ppm.

Figure S13. Comparative ¹H-NMR spectra of the photoreactivity *trans*-4-(trifluoromethyl)-cinnamic acid in solution (bottom) and the solid state reactivity under different experimental conditions (Run1: Irradiation in the solid state from mechanochemical self-assembly. Run 2: Irradiation of impregnated CS–COOH with an excess of olefin in the solid state. Run 3: Impregnation-irradiation in the solid state + two additional grinding-irradiation cycles).



Figure S14.¹H-NMR spectrum of *rctt*-1,3-bis(carboxyl)-2,4-bis(4-methylphenyl)cyclobutane *head-to-tail* obtained from UV-irradiation of Residual *trans*-4-methylcinnamic acid assisted by CS-COOH in solution: Yield 93%. Residual *trans*-4-methylcinnamic acid: Yield 7%.



¹H-NMR [DMSO- d_6 , 300 MHz, J (Hz)] δ 12.02 (s, Hf), 7.22 (d, Jcb = 8.0, Hc), 7.11 (d, Hb), 4.21 (dd, Jde = 7.3, Jdd = Jee = 10.3, Hd), 3.73 (dd, He), 2.27 (s, Ha) ppm.

Figure. S15. Comparative ¹H-NMR spectra of the photoreactivity of *trans*-4-methylcinnamic acid in solution (bottom) and the solid state reactivity under different experimental conditions (Run1: Irradiation in the solid state from mechanochemical self-assembly. Run 2: Irradiation of impregnated CS–COOH with an excess of olefin in the solid state. Run 3: Impregnation-irradiation in the solid state + two additional grinding-irradiation cycles).



Figure S16. ¹H-NMR spectrum of *rctt*-1,2-bis(carboxyl)-3,4-bis(4-bromophenyl)cyclobutane *head-to-head* obtained from UV-irradiation of *trans*-4-bromocinnamic acid assisted by CS-COOH in solution. Yield 85%. Residual *trans*-4-bromocinnamic acid: Yield 15%.



¹H-NMR [DMSO- d_{6} 300 MHz, J (Hz)] δ 12.49 (s, He₁, He₂), 7.65 (m, Ha₂, Hb₂, Hc₂), 7.29 (d, $Ja_1b_1 = 8.5$, Ha₁), 7.01 (d, Hb₁), 6.55 (d, $Jd_2c_2 = 16.1$, Hd₂), 4.18 (d, $Jc_1d_1 = 7.0$, Hc₁), 3.78 (d, Hd₁) ppm.

Figure S17. Comparative ¹H-NMR spectra of the photoreactivity of *trans*-4-bromocinnamic acid in solution (bottom) and the solid state reactivity under different experimental conditions (Run1: Irradiation in the solid state from mechanochemical self-assembly. Run 2: Irradiation of impregnated CS–COOH with an excess of olefin in the solid state. Run 3: Impregnation-irradiation in the solid state + two additional grinding-irradiation cycles).



Figure S18. ¹H-NMR spectrum of *rctt*-1,2-bis(carboxyl)-3,4-bis(4-fluorophenyl)cyclobutane *head-to-head* obtained from UV-irradiation of *trans*-4-fluorocinnamic acid assisted by CS-COOH in solution. Yield 90%. Residuals *trans*-4-fluorocinnamic acid and *cis*-4-fluorocinnamic acid: Yields 7% and 3%, respectively.



¹H-NMR [DMSO- d_6 , 300 MHz, J (Hz)] δ 7.74 (m, Hc₂, Hc₃), 7.58 (d, $Jd_2e_2 = 16.0$, Hd₂), 7.20 (m, Hb₂, Hb₃, Hd₃), 7.05 (dd, $Jc_1b_1 = 8.7$, $Jc_1a_1 = 6.1$, Hc₁), 6.88 (t, $Jb_1a_1 = 8.8$, Hb₁), 6.49 (d, He₂), 5.93 (d, $Je_3d_3 = 12.8$, He₃), 4.21 (d, $Jd_1e_1 = 6.1$, Hd₁), 3.79 (d, He₁) ppm.

Figure S19. Comparative ¹H-NMR spectra of the photoreactivity of *trans*-4-flourocinnamic acid in solution (bottom) and the solid state reactivity under different experimental conditions (Run1: Irradiation in the solid state from mechanochemical self-assembly. Run 2: Irradiation of impregnated CS–COOH with an excess of olefin in the solid state. Run 3: Impregnation-irradiation in the solid state + two additional grinding-irradiation cycles).



Figure S20. ¹H-NMR spectrum of *rctt*-1,2-bis(carboxyl)-3,4-bis(3,4-dichlorophenyl)cyclobutane *head-to-head* obtained from UV-irradiation of *trans*-3,4-dichlorocinnamic acid assisted by CS-COOH in solution. Yield 80%. Residuals *trans*-3,4-dichlorocinnamic acid and *cis*-3,4-dichlorocinnamic acid: Yields 13% and 7% respectively.



¹H-NMR [DMSO- d_{6} 300 MHz, J (Hz)] δ 8.03 (d, $Ja_2b_2 = 1.9$, Ha₂), 7.88 (dd, $Jb_2c_2 = 8.4$, Hb₂), 7.85 (d, Hc₂), 7.75 (d, $Jd_2e_2 = 16.0$, Hd₂), 7.65 (m, Ha₃, Hb₃, Hc₃, Hd₃), 7.37 (m, $Jb_1c_1 = 8.8$, $Jb_1a_1 = 2.0$, Ha₁, Hc₁), 7.06 (dd, Hb₁), 6.63 (d, He₂), 6.05 (d, $Je_3d_3 = 12.7$, He₃), 4.23 (d, $Jd_1e_1 = 6.2$, Hd₁), 3.85 (d, He₁) ppm.

Figure S21. Comparative ¹H-NMR spectra of the photoreactivity of *trans*-3,4-dichlorocinnamic acid in solution (bottom) and the solid state reactivity under different experimental conditions (Run1: Irradiation in the solid state from mechanochemical self-assembly. Run 2: Irradiation of impregnated CS–COOH with an excess of olefin in the solid state. Run 3: Impregnation-irradiation in the solid state + two additional grinding-irradiation cycles).



Figure S22. Comparative ¹H-NMR spectra of the photoreactivity of *trans*-cinnamic acid in solution: (a) ¹H-NMR spectrum obtained from UV-irradiation of *trans*-cinammic acid assisted by MWCNT-blank in solution. Photoproducts: *trans*-cinnamic acid and *cis*-cinnamic acid: Yields 33% and 67%, respectively. (b) ¹H-NMR spectrum obtained from UV-irradiation of *trans*-cinammic acid assisted by functionalized MWCNT-COOH in solution. Photoproducts: *rctt*-1,3-bis(carboxyl)-2,4-bis(phenyl) cyclobutane *head-to-tail*: Yield 28%. Residual *trans*-cinnamic acid: Yield 72%.



300 MHz/DMSO

¹H NMR [DMSO-*d*6, 300 MHz, *J* (Hz)] δ 12.46 (s, Hf₁, Hf₂), 7.63 (m, *J*a₁b₁ = *J*a₂b₂ = 7.9, *J*a₁c₁ = *J*a₂c₂ = 3.6, *J*d₁e₁ = 16.0, Ha₁, Ha₂, Hd₁), 7.35 (m, Hb₁, Hb₂, Hc₁, Hc₂), 6.89 (d, *J*d₂e₂ = 12.1, Hd₂), 6.53 (d, *J*e₁d₁ = 16.0, He₁), 5.96 (d, He₂) ppm.



300 MHz/DMSO

¹H NMR [DMSO-*d*6, 300 MHz, *J* (Hz)] δ 12.31 (s, Hf₁, Hf₂), 7.67 (m, *J*a₁b₁ = 7.8, *J*a₁c₁ = 3.4, Ha₁), 7.58 (d, *J*d₁e₁ = 16.0, Hd₁), 7.41 (m, Hb₁, Hc₁), 7.33 (m, *J*b₂a₂ = 7.5, *J*c₂a₂ = 3.5, Hb₂, Hc₂), 7.22 (m, Ha₂), 6.52 (d, He₁), 4.27 (dd, *J*d₂e₂ = 7.4, *J*d₁d₁' = *J*e₁e₁' = 10.2, Hd₂), 3.80 (dd, He₂) ppm.

Figure S23. Comparative FT-IR spectra of fresh CS-COOH, cinnamic acid free and impregnated Cinnamic acid/CS-COOH.







(b)