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A novel example of double reactivity by either photochemical [2+2] or thermal additions of an ionic organic supramolecular assembly.

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A example of double reactivity in the solid state is achieved from a single binary array directed by charge-assisted hydrogen bonds assembled via mechanochemistry: $[(HFu^{-})(Im^{+})]$ (**1**). Photochemical transformation of 1 occurs *via* a topotactic fashion with a quantitative yield then a second grinding-irradiation cycle. Recrystallisation of the photoproduct produces a novel hydrogen supramolecular isomer of [(*rctt*-H_2Cbtc^{2-})$(Im^{+})_2$] (**2**). Other example of the regioselective and quantitative preparation of *rtct*-cyclobutane isomers is isolated from the controlled isomerisation of **2** under hydrothermal conditions. Upon heating 1 produces an unexpected hydroamination product (**3**) with very nearly quantitative yield. The stereochemistry of the products **2** and **3** was confirmed by X-ray single crystal diffraction analysis.

Introduction

In recent times, diverse supramolecular strategies based on the use of H-bonding templates,[1] metal-coordination,[2] multivalent templates[3] and ionic interactions[4] have been evaluated successfully in order to control chemical reactivity of organic molecules in the solid state. In particular, the use of ionic interactions has shown to be very versatile for obtaining stereocontrolled access to single cyclobutane isomers (e.g. head-to-head or head-to-tail) either in solution or in the solid state with high yields.[4] Likewise, the self-assembly of ionic supramolecular arrays offers a convenient way to fine-tune chemical reactivity and/or to modify interesting physical properties in an interactive fashion. This possibility also allows engineering of novel ionic multicomponent assemblies based on two or more potentially reactive unsaturated molecules via directional supramolecular synthons.[5] In addition, this approach provides novel opportunities to explore unusual reactivity patterns in the solid state, depending on the resulting supramolecular organisation among the components; Cross-cycloaddition,[6] copolymerisation,[7] concomitant cycloaddition[5] and polymerisation[8] reactions into a single crystal, are potential examples of such approach.

On the other hand, mechanochemistry has received significant attention in the last years due to its attractive advantages as an alternative green approach to direct chemical reactivity.[9] Mechanically assisted transformations offer unique advantages relative to other conventional synthetic methods; Shorter reaction times, reduction of costs, energy and waste combined with high yields, in comparison with traditional synthesis in liquid-phase. It also provides the possibility of affording a greater level of complexity and sophistication in the study of solid-state transformations from sequential synthesis steps from molecular activation in order to obtain complex molecular compounds via covalent bond activation to the preparation of functional multicomponent supramolecular arrangements. Recently, such an approach has been exploited to carry-out stereocontrolled synthesis of cyclobutane derivatives from topochemical [2 + 2] cycloaddition reactions.[5, 10] Such studies have suggested potential utility in stoichiometric reactivity, supramolecular catalysis[11] and self-assembly of co-crystals. In this context, we recently reported that mechanochemical assistance via multiple grinding and irradiation steps provides an interesting green route to improvement of the yield of new and conventional cyclobutane-like stereoisomers from stoichiometric solids, allowing to overcome shortcomings imposed by the topochemical postulates in solid-state photoreactions.[12] In particular, in those photoreactions the yield of the product is seriously affected by important changes in distances and relative orientations between the pairs of photoactive species due to large molecular movements or structural rearrangements that occur during the course of the reaction. Herein, the potential

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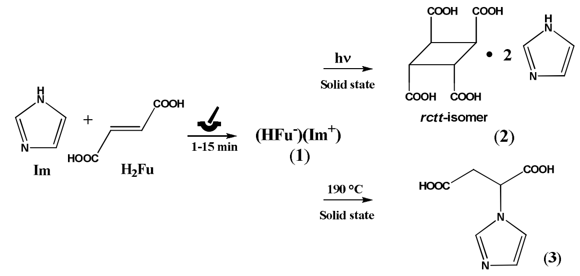
Electronic Supplementary Information (ESI) available: [Experimental details. FT-IR, PXRD and ^{1}H-NMR spectra]. See DOI: 10.1039/x0xx00000x of this approach is shown with the self-assembly of a binary ionic organic phase via mechanochemistry: [(HFu$^-$)(Im$^+$)] (HFu$^-$: Hydrogen fumarate and Im$^+$: Imidazolium), and its re-investigation in the solid state,[13] which provides an unprecedented example that exhibits the formation of two different addition products in the solid state with high yields, depending on whether **1** irradiated or heated (scheme 1). The UV-irradiation leads to the photodimer from fumaric acid with ca. 92% yield. Such yield is improved until near quantitative yield after a second grinding-irradiation cycle. The resulting photoproduct is crystalline, which suggests that such transformation occurs in a topotactic fashion. Recrystallisation of the photoproduct in methanol produces a novel hydrogen supramolecular isomer [(*rctt*-H_2Cbtc^{2-})(Im$^+$)$_2$]: *rctt*-1,2,3,4-Cyclobutanetetracarboxylic acid (**H_4Cbtc**). Upon heating **1** can also undergo an unexpected hydroamination addition reaction in the solid state, leading to (*R*,*S*)-2-(1H-Imidazol-1-yl)succinic acid, with very nearly quantitative yield.



Scheme 1. Schematic preparation of **1** via mechanochemistry and formation of **2** and **3** in the solid state.

Results and discussion

Compound 1 can be obtained as a single crystalline phase by solvent-free mechanical grinding of fumaric acid (H_2Fu) and imidazole (Im) compounds at least for 1 min. (Scheme 1) The resulting phase was characterised by XRD, FT-IR and TGA/DSC. The PXRD pattern of the crystalline solid is consistent with the simulated powder pattern from single crystal data (Fig.1) previously reported by Ito and co-workers.[13] The FT-IR spectrum reveals the presence either of the adsorption bands associated to the carboxylic group or the bands characteristics of the formation of a carboxylate, confirming the proton transfer between the components.

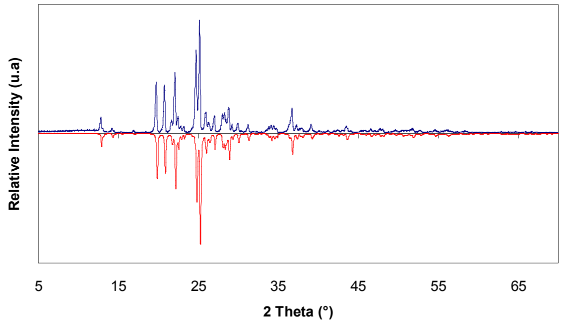


Fig. 1 Powder XRD patterns from ground mixture of H_2Fu + Im for 5 min (blue) and simulated from single crystal structure of [(HFu$^-$)(Im$^+$)] (**1**) (red).

In order to show the origin of the photoreactivity of **1** a brief description of this compound is given. The crystal structure consists of 1D supramolecular chains built-up from self-assembly of hydrogen fumarate anions via O–H···O$^-$ charge-assisted hydrogen bond between carboxylic and carboxylate groups along the *a*-axis (Fig 3). These chains are stacked in a parallel fashion templated by imidazolium cations trough N$^+$–H···O and C–H···O hydrogen bonding interactions. This organisation shows short contacts between the double bonds with distances of 3.76 Å (centroid-to-centroid).[12]

The reactivity was monitored and verified by FT-IR and PXRD at different UV irradiation time periods at 254 nm (See Fig. S1). The FT-IR of **1**-irradiated displays the shift of C=O absorption from 1700 to 1740 cm^{-1} and the disappearance of the bands associated to C=C bonds of the fumaric acid at 1635 cm^{-1} (Fig. S1b). The yield of the reaction was estimated from ^{1}H-NMR integration, which is consistent with the result reported by Ito and co-workers[13] (ca 90% yield). The yield of the photoreaction was improved very close to the quantitative conversion applying a second grinding cycle to compound **1**-irradiated for 10 min and after irradiated at 254 nm during 24 h again (Fig. S2). The monitoring of the photoreaction by PXRD revealed significant structural changes, observing the concomitant appearance of an unidentified phase together with progressive disappearance of **1**, after 18 hours only **2** persists (Fig S3). This result reveals the formation of a crystalline product, which suggests that such transformation occurred in a topotactic fashion within the microcrystals obtained from the mechanochemical self-assembly of **1**. On the other hand, the comparison of the PXRD pattern of the resulting photoproduct with simulated powder pattern from the crystal structure of a supramolecular assembly previously reported by MacDonald,[14] obtained by direct co-crystallisation of imidazole and *rctt*-1,2,3,4-Cyclobutanetetracarboxylic acid (H_4Cbtc) from a 2:1 molar ratio in methanol (**2a**), reveals a surprisingly similarity between the patterns.

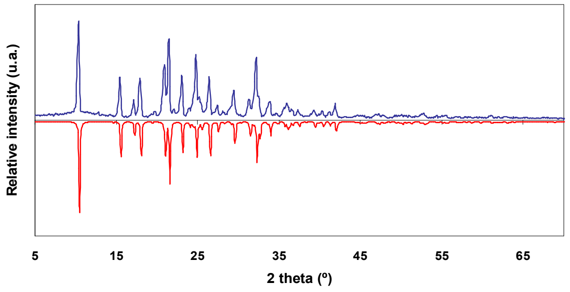


Fig. 2. Powder XRD patterns from UV-irradiated mixture of H_2Fu + Im for 18h (blue) and simulated from single crystal structure reported by MacDonald during the co-crystallisation of Im and *rctt*-1,2,3,4- (H_4CBTC) from a 2:1 molar ratio in methanol (red).

These observations, prompted us to evaluate the possibility of monitoring the reaction to assess if it were a single crystal-to-single crystal manner. However, different attempts with single crystals irradiated with UV light revealed evident changes in shape and colour. During exposure with UV light, the crystals showed a gradual formation of anisotropic internal fractures and the crystals became opaque, such changes are commonly associated to the release of accumulated strain in the crystals. This macroscopic feature suggests that photoreaction does not proceed completely via single crystal-to-single crystal process. Nevertheless, it is possible that such transformation only occurs in an efficient way in smaller crystals. Similar results have been reported by MacGillivray and co-workers in nanocrystalline co-crystals of 2(resorcinol)·2(4,4´-bpe) formed via sonocrystallization[15] [Where: 4,4´-bpe = *trans*-1,2-bis(4-pyridyl)ethylene].

In order to understand such structural similitude between both arrays obtained in different ways either from solid-state reactivity or by direct co-crystallisation of both components in solution and to find a plausible explanation for such an observation, a further analysis of the structure of **1** was done.

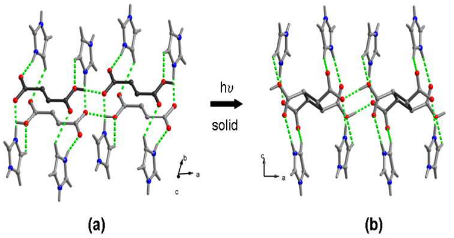


Fig. 3. Comparative similitude view between array of **1** before the UV irradiation (a) and the structure reported by MacDonal (b). Schematic evolution of photocycloaddition reaction from **1** to **2a.**

Supported by the close geometric features found in both structures, it is possible to expect that such [2+2] photocycloaddition could occur via topotactic transformation with a minimum of molecular motion in the structure of **1** (Fig. 3(a)). This rearrangement of the components either of the photoproduct or imidazolium cations permits to achieve a geometrical orientation very close to the molecules found in the structure of **2a** (Fig 3(b)).

The stereochemistry of the photoproduct was confirmed by X-ray single crystal diffraction analysis. Crystals of **2b** were obtained by recrystallisation from a hot methanol solution at RT. The structure of **2b** consists of a new supramolecular isomer of the assembly reported by MacDonald and co-workers.[14] The unit asymmetric of **2b** contains one imidazolium cation and a half of the $(H_2Cbtc)^{2-}$ dianion located on a special position (Fig. 4). The crystal structure consists of the self assembly of cations and anions via N^+–H···O and O–H···O^- charge-assisted hydrogen bonding interactions [N2–H2N2···O1: 2.695(2), N1–H1N1···O3: 2.894(2) and O4–H4OH···O1: 2.512(2) Å]. These interactions lead to the formation of a 2D H-bonded network formed by 1D zigzag supramolecular ribbons formed by centrosymmetric pairs of $(H_2Cbtc)^{2-}$ anions linked by O–H···O^- charge-assisted hydrogen bonds between carboxylic and carboxylate groups along the *a*-axis. These ribbons are stacked in a parallel fashion through imidazolium cations via N^+–H···O and C–H···O hydrogen bonding interactions (Fig.5). The cyclobutane ring is perfectly planar the carboxylate (C5–C4–O2–O1) and carboxylic groups (C7–C6–O3–O4) are twisted 56.48(13)º and 83.56(12)º, with respect to the mean plane of the cyclobutane ring.

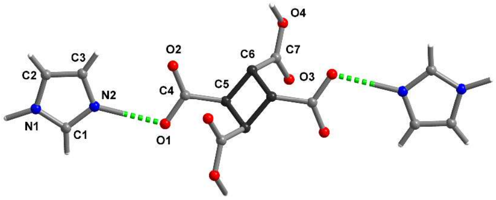


Fig. 4. Molecular structure of compound **2b**

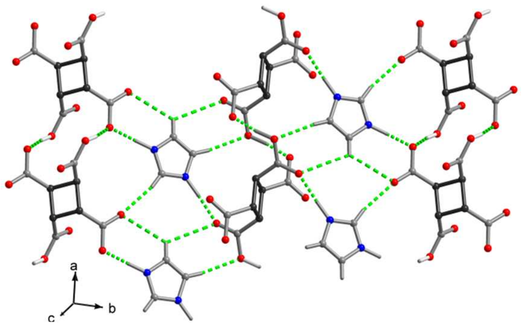


Fig. 5. View of the 2D H-bonded network in the structure of **2**.

A comparative analysis with the isomer **2a** reveals remarkable structural differences. For example: a) the connectivity between the dianions is different in both cases; in the structure **2a**, these 1D ribbons are formed also through of the same kind of complementary O–H···O^- charge-assisted hydrogen bonds between pairs of carboxylate and carboxylic groups , however the relative orientation of the proton acidic in the structure of **2a** is planar in contrast to that antiplanar orientation found in the structure of the isomer **2b** (Figs. 6 (a) and (b)). Likewise, the relative orientation of the imidazolium cations regarding to the supramolecular ribbons in the structure of **2a** is near parallel, unlike to that perpendicular orientation observed for **2b**.

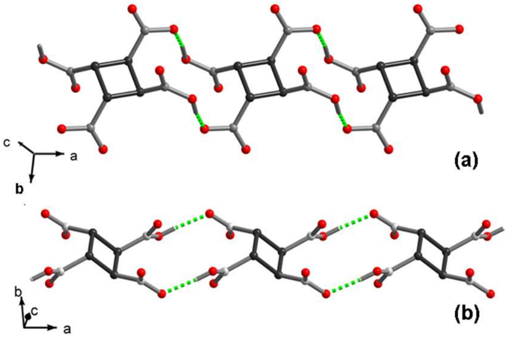


Fig. 6. Comparative hydrogen bond interactions between ribbons found for the supramolecular isomers **2a** (a) and **2b** (b).

Another interesting behaviour of this assembly was investigated. Ito and co-workers reported the following observations “crystals showed a complex melting behaviour, starting to melt above 192

°C, then resolidified around 210 °C, and finally decomposed at 278–281 °C."[13] Based on these antecedents, we carried-out a TGA/DSC analysis in order to evaluate such changes (Fig. 7). The TG curve shows that solid **1** is stable until 180 °C a small weight loss up to ca 250 °C then an abrupt weight loss is observed up to 290 °C. The DSC curve reveals the presence of some thermal transitions related to these events, an endothermic transition at 172 °C and exotherms at ca 178 °C and finally a second endothermic transition related to decomposition of the solid at 250 °C. The first endothermic process is attributed to a possible chemical change whereas the second exothermic process is associated to the possible crystallisation of a metastable intermediary. In order to gain insight about the first exothermic process a fresh sample was heated at 190 °C and kept at this temperature during short time periods (10-30 min). This sample was cooled down to 100 °C temperature and heated again until 600 °C. The thermal analysis showed a thermal behaviour totally different with respect to the original sample. These results revealed that such changes undergo for 1 until 190 °C are irreversible (Fig. S4).

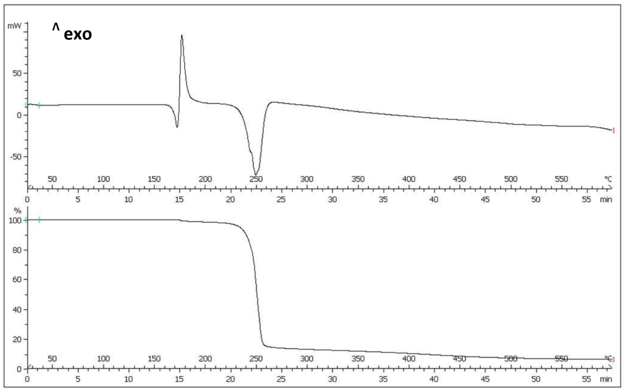


Fig. 7. Thermal analyses TGA/DSC of **1** fresh prepared via mecanochemistry.

A preliminary study by FT-IR of a sample of 1 heated at 190 °C for 30 min revealed significant changes on initial absorption bands of **1**. In particular, a shift of absorption band from 1700 to 1713 cm^{-1} related to carbonyl group is observed. This value is different to that observed for **1**-irradiated (Fig. S5). This change together with the disappearance of the band associated to C=C bonds supported a possible chemical transformation on the double bond of hydrogen fumate anion. Nevertheless, such changes are not associated to [2+2] photocycloaddition reaction found for **1** when the solid is exposed to UV irradiation. This one is not allowed thermally, due to orbital symmetry elements do not match between the HOMO and LUMO of double bonds for cycloaddition to occur in a concerted suprafacial-suprafacial mode.[16] This presumption and chemical change were confirmed from a solution ^{1}H –NMR spectrum of the resulting solid (Fig. 8). This spectrum revealed the almost complete disappearance of the bands of the starting components and the appearance of six new bands at 7.93, 7.29, 7.0, 5.27, 3.16, 2.93 ppm, respectively. This NMR pattern is consistent with the formation of an unexpected hydroamination product[17] with a yield of ca 98% (Scheme 1).

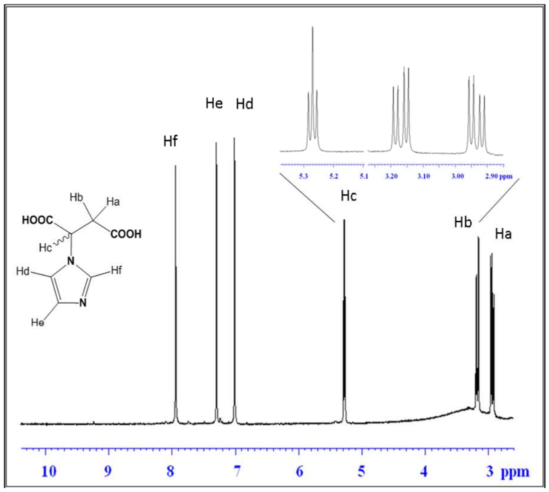


Fig.8. ^{1}H NMR spectrum of **1** fresh in DMSO-D$_6$ heated in the solid state upon nitrogen atmosphere at 190 °C for 30 min

Although it is not clear that this reaction is directed via topochemical control, a naked eye monitoring of such reaction did not reveal an apparent complete fusion of the sample. However it is possible that such reaction occurred via a possible eutectic phase. This mechanism has been observed in similar addition reactions induced in the solid state under mechanochemical activation[18]or in other thermal transformations observed by us in the isomerisation of itaconate to citraconate anion in the solid state.[19]

The stereochemistry of the thermal product was confirmed by single crystal X-ray diffraction analysis. Crystals of **3** were obtained by recrystallisation from a methanol-water solution at RT. Compound **3** crystallised as a zwitterion, which is observed the formation of the carboxylate group with distances C–O similar [C4–O1: 1.241(4) and C4–O2: 1.251(4) Å] in contrast with asymmetric C–O distances found in the other oxygenated group [(C7–O3: 1.310(4) and C7–O4: 1.200(4) Å]. Besides the protonation of N2 atom on imidazolyl ring was depicted from localization of H atom from Fourier map (Fig. 9(a)). The proton transfer is also confirmed by FT-IR spectrum. The crystal structure consists of the self assembly of the racemate via N^+–H···O and O–H···O^- charge-assisted hydrogen bonding interactions [N2–H2···O1: 2.729(4) and O3–H3OH···O2: 2.547(4) Å]. These interactions lead to the formation of a 2D H-bonded network formed by 1D supramolecular chains formed by pairs of zwitterions linked by O–H···O^- hydrogen bonds between carboxylic and carboxylate groups along the *a*-axis. These chains are stacked in a parallel fashion in the *ab*-plane through imidazolium cations via N^+–H···O hydrogen bonding interactions (Fig. 9(b)). Similar H-bonded organisation is found in the crystal structure of pure enantiomeric compound (S)-2-(1H-Imidazol-1-yl)succinic acid previously reported[20] (**3b**). The fundamental difference between both structures displays in the stacking organisation of the H-bonded layer in our structure the layers are related between them by inversion centres, whereas in the structure of **3b** the stacking is oriented by a screw axis.

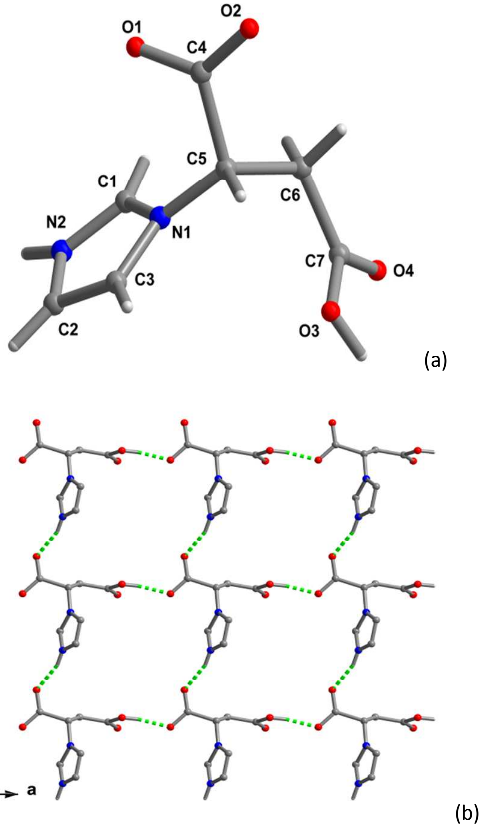
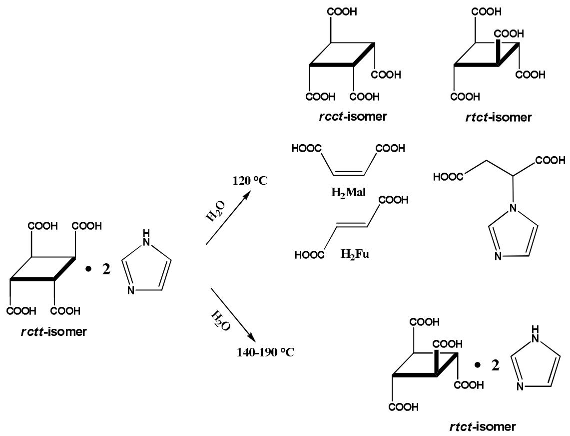


Fig.9. (a) Molecular structure of the hydroamination product (**3**). (b) View of the 2D H-bonded network found in the structure of **3**.

Taking advantage of our ongoing studies about the non-photochemical route to prepare quantitatively and regio- and stereoselectively *rtct*-cyclobutanes compounds via hydrothermal-assisted isomerisation.[21] According to our results the presence of ionisable groups on cyclobutane ring favour the isomerisation process together with previous works reported in the literature, prompted us to evaluate the isomerisation of this tetrameric acid. Thus, the isomerisation of **2b** was studied under hydrothermal conditions at 120, 140 and 190 °C for 2 days. The ^{1}H-NMR characterisation of the product obtained either at 140 °C or 190 °C from controlled evaporation of the solvent after heated at RT revealed the selective and quantitative isomerisation of the *rctt*-into *rtct*-isomer (**2c**), observing a shift of the singlet corresponding to methine proton absorption from 3.45 to 3.02 ppm (Fig. S6). The chemical shift is consistent with the reported ^{1}H NMR pattern for such an isomer.[22]

To our surprise, when **2b** is heated at 120 °C led to complex mixture of products where were identified the stereoisomers: *rctt* (3.42 ppm, 17%) and the products of its isomerisation to *rcct* with characteristic three novel signals at 3.25, 3.35 and 3.64 ppm (26%) and *rtct*-isomer (3.05 ppm, 21%) together with the presence of traces of fumaric acid (H_2Fu) and maleic acid (H_2Mal) as products of the thermal cycloreversion (sheme 2). The presence of such acids suggests ring-cleavage of H_4Cbtc molecule in two ways to drive the formation of *cis–trans*-isomers (Fig S7). Similar examples have been reported recently by Vittal and co-workers in the solid state upon heating.[23] In addition, the formation of the hydroamination product (HYAP) of fumaric acid above described was also identified, as consequence of the reaction between fumaric acid free and imidazole generated *in situ* in solution with ca 31% (scheme 2).



Scheme 2. Product formation under hydrothermal treatment depending on temperature.

Conclusions

In summary a novel example of a binary organic assembly that exhibits different addition reactions in the solid state was characterized, such examples are rare in the literature.[24] The dimerisation of hydrogen fumarate anion occurs via a topotactic process, in which the yield of the photoreaction was improved in the solid state until quantitative yield, applying a second grinding-irradiation cycle. In addition, a novel genuine supramolecular isomer of [(*rctt*-H_2Cbtc^{2-})(Im^+)$_2$] (**2**) was isolated from the recrystallisation of the photoproduct obtained. Likewise, the quantitative and regioselective isomerisation of the *rctt*-cyclobutane derivative to *rtct*-isomer was observed upon hydrothermal conditions in the range of temperature 140-190 °C. On the other hand, the product obtained under heating, to the best of our knowledge represents the first example of hydroamination addition via a solvent- and catalyst-free process.[25] Further works on the self-assembly of multi-component supramolecular arrays capable of showing different reactivity when irradiated or heated in the solid state are in progress, as well as the possibility to access novel hydroamination products from co-crystals or ionic organic assemblies.

Experimental section

General considerations

All reagents were obtained from commercial sources and used without further purification. The FT-IR spectra were recorded from KBr discs, using a Nicolet Magna-IR 560 spectrophotometer. PXRD patterns were recorded on a Siemens 5005 Diffractometer with Cu(Kα) (1.5418 Å) radiation, with a scan speed of 2 deg/min. The ^{1}H

NMR spectra were recorded on a Bruker AVANCE-300 Spectrometer in DMSO-D_6. Simultaneous Thermogravimetric analyses TGA/DCS were carried-out on a Mettler Toledo thermal analyzer (heating rate of 10 °C min^{-1} and under N_2 Atmosphere).

Preparation of [(HFu⁻)(Im⁺)] (1). Compound **1** was prepared according to previously published procedure[13] and can also be obtained as a highly pure single-phase by direct solvent-free co-grinding of the starting compounds for a period of 1-15 min (See Fig 1b). IR (cm^{-1}): ν(N-H): 3425, ν(COOH): 3150-2000, ν(C=O): 1692, $\nu(C=C)_{acid}$: 1635, $\nu(COO^{-}_{asym})$: 1587, $\nu(COO^{-}_{sym})$: 1400, ν(=C–H): 985.

Solid state reactivity. The reactivity of compounds **1** was studied upon irradiation with UV light. A powdered crystalline sample (100 mg) was irradiated at 254 nm during 2h - 2 days. The irradiated samples were characterised by FT-IR and ^1H NMR spectroscopy. X-ray powder diffraction was also used for monitoring the respective topochemical transformation of **1**.

Compound [(*rctt*-H_2Cbtc^{2-}) $(Im^+)_2$] (2): ^1H NMR (300 MHz, DMSO-D_6), δ_H(ppm): 7.84(H_{Im}, s), 7.10(H_{Im}, s) and 3.42 (H_{dimer}, s). IR (cm^{-1}): ν(N-H): 3425, ν(COOH): 3150-2000, ν(C=O): 1692, $\nu(C=C)_{acid}$: 1635, $\nu(COO^{-}_{asym})$: 1587, $\nu(COO^{-}_{sym})$: 1400, ν(=C–H): 985.

Preparation of compound [(*rtct*-H_2Cbtc^{2-})$(Im^+)_2$] (2c): A powdered crystalline sample of **2** (50 mg) was heated under hydrothermal conditions at 140 and 190 °C for 2 days. Slow evaporation of the resulting solutions at room temperature gave a white solid bearing the *rtct*-isomer with a quantitative conversion. ^1H NMR (300 MHz, DMSO-D_6), δ_H(ppm): 7.89(H_{Im}, s), 7.12(H_{Im}, s) and 3.04 (H_{dimer}, s)

Preparation of (*R*,*S*)-2-(1H-Imidazol-1-yl)succinic acid (3): A fresh sample of **1** heated at 190 °C and kept at this temperature during short time periods (10-30 min) under N_2 atmosphere. ^1H NMR (300 MHz, DMSO-D_6), δ_H(ppm): , *J* (Hz): 7.93(H_f, s), 7.29(H_e, s), 7.00(H_d, s), 5.27(H_c, t, J_{bc}= 7.05, J_{ac} = 7.01), 3.16(H_b, dd, J_{ab} = 16.70, J_{ed} = 7.0) and 2.93(H_a, dd). ν(N-H): 3425, ν(COOH): 3190-2000, $\nu(C=O)_{acid}$: 1713, $\nu(COO^{-}_{asym})$: 1583, $\nu(COO^{-}_{sym})$: 1388.

Crystal structure determination. Intensity data were recorded at room temperature on a Rigaku AFC-7S diffractometer equipped with a CCD bidimensional detector using monochromated Mo(Kα) radiation (λ = 0.71073 Å). An empirical absorption correction (multi-scan) was applied using the package CrystalClear.[26] The structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL-PLUS package.[27] Hydrogen atoms on the carbon atoms were placed at fixed positions using the HFIX instruction. H-atoms on carboxylic groups were found from the Difference Fourier map. They were refined with isotropic displacement parameters set to 1.2 × *U*eq of the attached atom.

Table 1. Crystal, Intensity collection and refinement data

	2	**3**
Crystal data		
Chemical formula	$C_{14}H_{16}N_4O_8$	$C_7H_8N_2O_4$
Formula weight	368.31	184.15
Crystal system, Space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	295(2)	295(2)
***a*/Å**	6.4203(11)	7.646 (5),
***b*/Å**	18.901 (3)	7.480 (5),
***c* /Å**	6.5776 (11)	13.756 (10)
***β* (°)**	104.022 (4)	96.52 (2)
***V* (Å³)**	774.4 (2)	781.6 (9)
Z	2	4
***μ* (Mo Kα, mm⁻¹)**	0.13	0.13
Crystal size (mm)	0.40 × 0.20 × 0.15	0.48 × 0.33 × 0.25
ρ_{calc} (mg.m⁻³)	1.580	1.565
Data collection		
No. of measured, independent and observed [*I* > 2σ(*I*)] reflections	8297, 1504, 1280	9613, 1650, 1137
R_{int}	0.037	0.075
Refinement		
$R1[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.046, 0.12, 1.07	0.079, 0.22, 1.16
No. of reflections	1504	160
No. of parameters	118	118
No. of restraints	0	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (*e*Å⁻³)	0.17, −0.28	0.27, −0.33
CCDC code	1048351	1048352

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Notes and references

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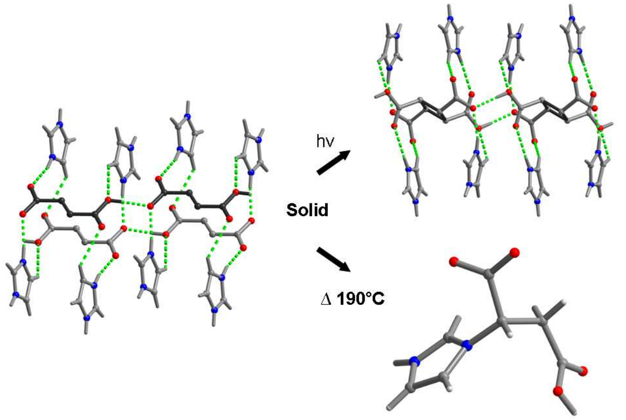
Graphical Abstract



A example of double reactivity in the solid state is achieved from a ionic array directed by charge-assisted hydrogen bonds