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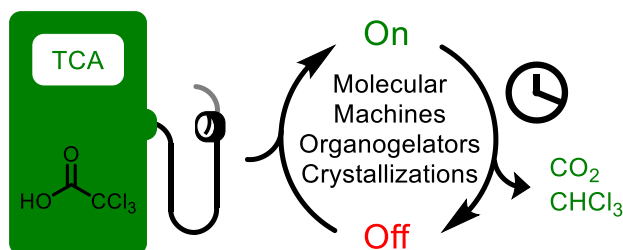
# Out of equilibrium chemical systems fueled by trichloroacetic acid

Enzo Olivieri,<sup>a</sup> Adrien Quintard<sup>b\*</sup>

<sup>a</sup> Ludwig-Maximilians-Universität München, Department Chemie, 81377 München, Germany.

<sup>b</sup> Univ. Grenoble Alpes, CNRS, DCM, 38000 Grenoble, France.

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**ABSTRACT:** Dissipative systems are based on the supply of energy to a system by fuel pulses, and dissipation of this energy through the fuel decomposition, resulting in repetition of a given physical or biological function. Such out of equilibrium processes are at the heart of all living organisms and in the last decade, researchers have attempted to transpose these principles to purely synthetic systems. However, upon fuel decomposition, the resulting waste generated tend to accumulate in the system rapidly inhibiting the machinery after few cycles of fuel pulses. In order to solve this issue, trichloroacetic acid (TCA) has appeared as a fuel of choice to reversibly change the acidity of a system, liberating volatile chloroform and CO<sub>2</sub> upon fuel decomposition. In this perspective, we present the advantages of this fuel and the successful applications ranging from conformational switches, rotary motors, temporal control over crystallization or smart materials.

## INTRODUCTION

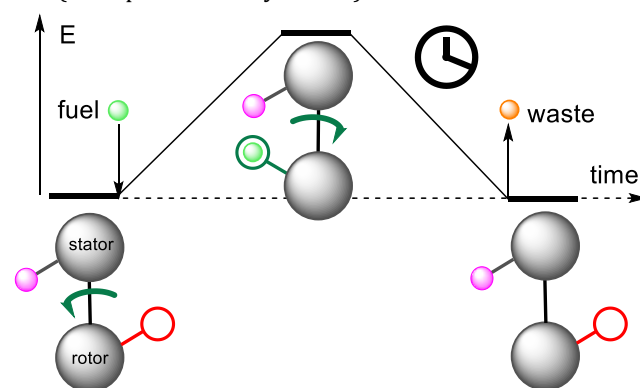
After billions of years of evolution, Nature has increased living systems complexity to a level enabling the wide variety of observed natural functions. These biological processes are based on dynamic changes in the chemical systems. Dissipating the energy taken from different fuels such as light or ATP, these systems can evolve over time out of equilibrium. It was only recently that chemists attempted to dissipate the energy from chemical fuels to create new synthetic systems with temporal control also known as chemically fueled dissipative systems.<sup>1-3</sup>

A dissipative system can be considered as a system evolving through chemical modifications over time after an energy input (fuel addition). This fuel triggers a change in the system (molecular motion, conformation, gelation, ...) by chemical transformations, while the fuel energy dissipation enables the system to return to a resting state without any other stimulus requirement. Three different pathways are known to generate dissipative systems: autonomous fueling, oscillating reactions, and fuel pulses.<sup>4-9</sup> In fuel pulses methodology, the system can only go through one complete cycle upon the addition of a fuel, while in autonomous fueled systems, the presence of the fuel induces several cycles (as in a car engine).

The fuel pulse process can be described by the simplified energy diagram of a theoretical rotary switch presented in Figure 1. From an initial thermodynamically more stable state, the fuel (energy input) reacts with the switch, inducing a change in the conformation (here a rotation) to the higher in energy state. Dissipation of the chemical energy through another chemical reaction liberating a waste, triggers the return to the initial state of the switch over time.

Until recently, molecular switches were operated in a sequential manner, with at least two sequential inputs from the operator to promote the complete cycle. Applying a dissipative strategy enables a spontaneous evolution of the chemical system over time after a fuel pulse.

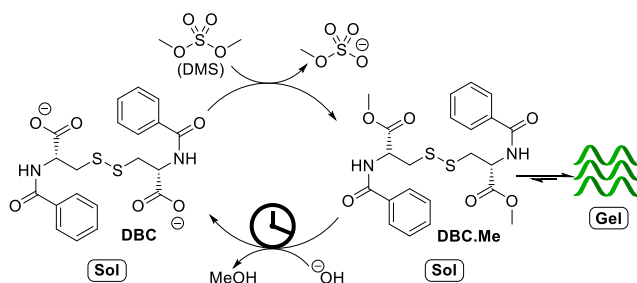
**Figure 1.** Principle of a fuel pulsed dissipative chemical system (example of a rotary switch).



The complexity of the different functions obtained through such technologies enables chemists to design chemical systems close to Nature's bio machinery or alternatives possessing purely artificial properties. These processes have been applied for example to trigger the motion in different molecular machines, design switchable catalysts or for temporary self-assemblies in smart materials.<sup>4-22</sup>

As a typical example, these properties were used by van Esch and Boekhoven to switch reversibly a solution (sol) to a gel (Scheme 1).<sup>5,23</sup> In this fueled chemical system, a bis-carboxylate (DBC), in solution under basic pH, reacts upon the addition of dimethyl sulfate (DMS) as chemical fuel. The esterification reaction generates the diester (DBC.Me). This diester self-assembles, forming a transient strong gel. In parallel, concomitant ester hydrolysis by hydroxide anions present at the onset, regenerates after few hours the initial bis-carboxylate, regenerating the solution.

**Scheme 1.** Example of a sol-gel-sol dissipative system by van Esch and Boekhoven fueled by DMS.



Different fuels have been applied to trigger other types of dissipative systems notably such materials possessing a temporal control.<sup>1-3</sup> In theory, these dissipative processes are described as similar to a catalytic cycle with a return to the initial state upon fuel consumption. In reality, at the microscopic level, the final state is most of the time totally different from the initial one. Indeed, as exemplified in the sol-gel-sol system of Scheme 1, a co-fuel, here hydroxide anions, present at the onset is often reacting with the chemical fuel. The chemical reaction generates waste accumulating in the system (here methanol and sulfate anions), while the concentration in co-fuel decreases over time. As a result, the chemical composition of the system at the end of a cycle is different. Less co-fuel is present to promote the desired energy dissipation and waste accumulates potentially inhibiting the system through undesired interactions. Macroscopically, this means that the system's properties (such as gelation ability), can also be lost after few fuel pulses. Technical solutions such as the use of selective membranes or syneresis can enable waste removal but still require external operations to proceed.<sup>21-22</sup>

In order to obtain fully operative dissipative systems, avoiding the detrimental requirement for a co-fuel and subsequent waste accumulation, the solution consists in implementing new fuels based on alternative organic reactions. Ideally, the fuel would be consumed through a catalytic transformation liberating volatile gazes directly eliminated from the system during energy dissipation.

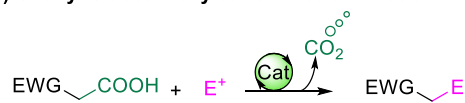
### TRICHLOROACETIC ACID AS CHEMICAL FUEL FOR CONFORMATIONAL SWITCHES

Carboxylic acids possessing adjacent electron-withdrawing groups have for long been known for their propensity to decarboxylate relatively easily.<sup>24-25</sup> These properties have

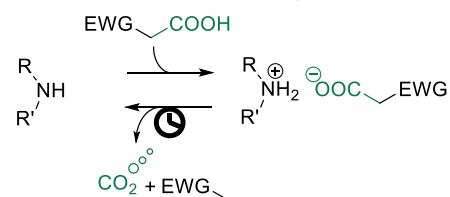
been applied with success in catalyzed transformation to introduce different functionalities while generating one equivalent of gaseous CO<sub>2</sub> as single waste (Scheme 2.a).<sup>26-35</sup> Taking advantage of these attributes, one can envisage a temporary protonation of basic functions such as primary or secondary amines (Scheme 2.b).<sup>36</sup> After formation of the ammonium ion, the time-controlled catalyzed trichloroacetate decarboxylation generates a transient chloroform anion, protonated rapidly by the ammonium salt thus triggering the return to the neutral amine. Of interest, the kinetic of decarboxylation can easily be tuned at will through different parameters, including change in the solvent,<sup>24</sup> basic catalyst nature and loading or amount of fuel used.

**Scheme 2.** Principle of activation of organic molecules by decarboxylation of activated acids.

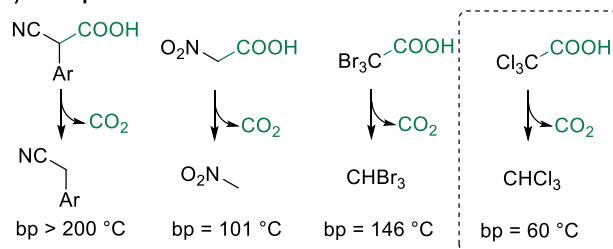
#### a) Catalytic decarboxylative functionalization:



#### b) Transposition to dissipative systems:



#### c) Examples of acids used:



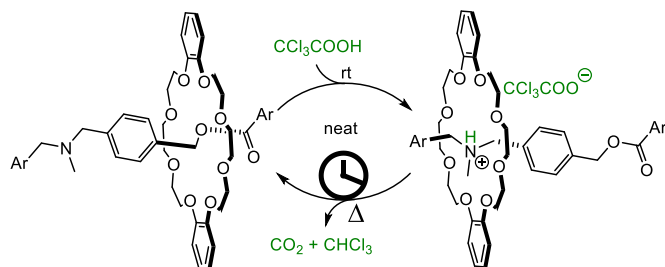
In this context, since 2016, the group of Di Stefano and later the one of Schmittl have applied different 2-cyano-2-arylpropanoic acids to fuel different dissipative systems such as catenanes switches (Scheme 2.c).<sup>37-45</sup> Such acids are interesting given the modularity of the aromatic group influencing the kinetic of decarboxylation, but generating 2-aryl-acetonitriles as accumulating side-product, a non-volatile waste non-removable from the system. The use of nitroacetic acid in water nicely complements these acids and provides nitromethane as waste. However, its relatively high boiling point precludes direct waste elimination.<sup>46-47</sup> Similarly, in 2022, tribromoacetic acid generating non-volatile bromoform was used as dissipative fuel by Badjić.<sup>48</sup>

Complementary to these acids, the use of widely available trichloroacetic acid (TCA) has been recognized as a method of choice to fuel dissipative systems while generating CO<sub>2</sub> and volatile chloroform as single waste upon trichloroacetate anion decarboxylation (Scheme 2.c). Given its unique properties, it has been used with success to fuel different types of fuel-pulsed dissipative systems that will be discussed in detail herein.

## TRICHLOROACETIC ACID-FUELED MOLECULAR SWITCHES AND MOTORS

In 2012, the group of Takata was the first to take advantage of the properties of trichloroacetic acid to fuel a conformational molecular switch.<sup>49</sup> It was found that a rotaxane shuttle could switch between two distinct positions depending on the charge of the amine function (Scheme 3). At the neutral state, the crown ether is located on the side of the rotaxane possessing an ester stopper. Upon addition of TCA, the amine is protonated and the crown ether moves to this end of the rotaxane to stabilize the cationic charge of the ammonium ion. Trichloroacetate decarboxylation liberates CO<sub>2</sub> and chloroform and the crown ether shuttle can return to the initial position. While demonstrating the potential of TCA as fuel, in this initial report, the ammonium salt was found to be quite stable and required a subsequent heating above 100°C for an efficient decarboxylation. As a result, this system is based on two different successive stimuli (TCA and heat) and energy arising from TCA pulses is not spontaneously dissipated. Despite this issue, at least four cycles could be performed through successive TCA addition and thermally initiated decarboxylation. In 2016, the same authors extended this strategy to other rotaxanes containing other stoppers such as urethane or nitrile N-oxide functions.<sup>50</sup>

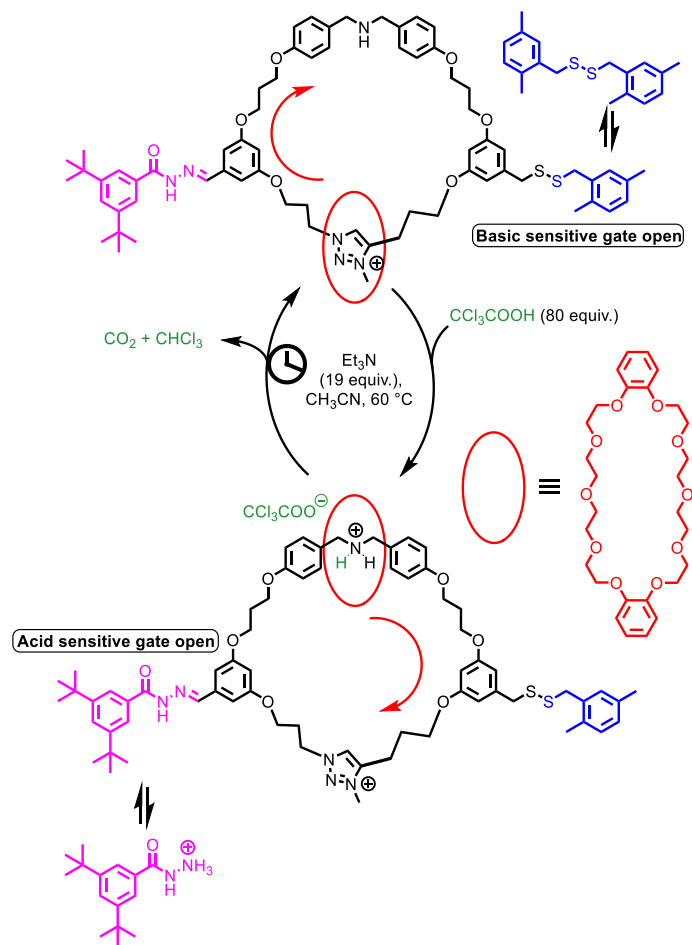
**Scheme 3.** First application of TCA for a stepwise molecular switch.



In 2017, the group of Leigh, took advantage of TCA properties to develop a complex unidirectional rotating motor (Scheme 4).<sup>9</sup> Based on a catenane core, this conformational rotating motor is fueled by successive pulses of TCA, each of them inducing a 180° rotation. This rotary motor consists in two potential stations for the crown ether, locked by two orthogonal basic or acid-sensitive gates. At the resting state (basic conditions), the crown-ether is stabilizing the triazolium positive charge and the disulfide gate can be opened. When adding a pulse of TCA, the secondary amine is protonated and the disulfide gate closes while on the opposite side, the acid-labile hydrazone gate opens. The crown ether can cross this gate and move to stabilize the generated ammonium ion. Upon triethylamine induced trichloroacetate decarboxylation, a basic solution is regenerated after all fuel consumption, the disulfide gate can re-open to let the crown ether go back to the resting state. As a result of this sequential gate opening, the crown ether performs a 180°

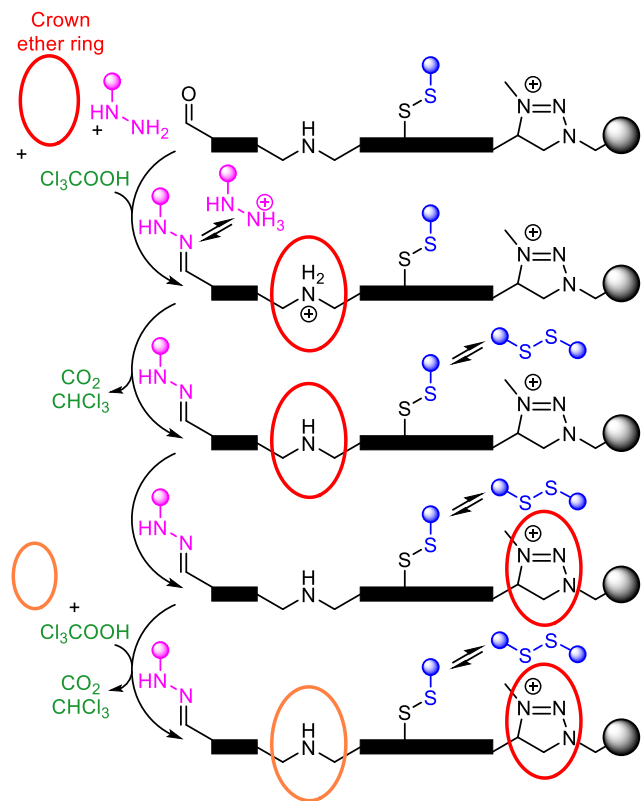
unidirectional rotation upon each cycle initiated by a pulse of TCA. In order to promote the opening of the acid-sensitive gate at an appropriate rate, use of a large excess of TCA is needed (80 equiv.). To counterbalance this, a 19-fold excess of triethylamine is required to consume all the fuel at a convenient rate.

**Scheme 4.** TCA fueled rotary motor by Leigh and co-workers.



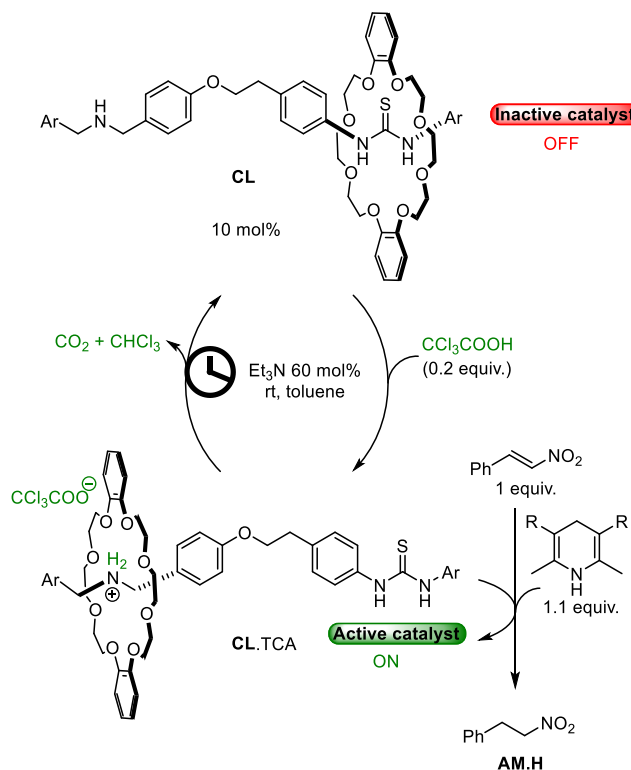
Recently, the team of Leigh further extended this principle to a system where pulses of trichloroacetic acid acting as a fuel trigger the pumping of crown ethers to functionalized polystyrene beads (Scheme 5).<sup>51</sup> In this system, dissipation of the energy enables to thread sequentially crown ether rings upon an axle, with a final state distinct from the initial one. This proceeds through sequential opening of the acidity sensitive hydrazone or disulfide gates upon the presence or not of TCA. Regeneration of the free axle (initial state), is only achievable through another set of chemical reactions.

**Scheme 5.** Successive threading of crown ether rings in a rotaxane through TCA pulses.



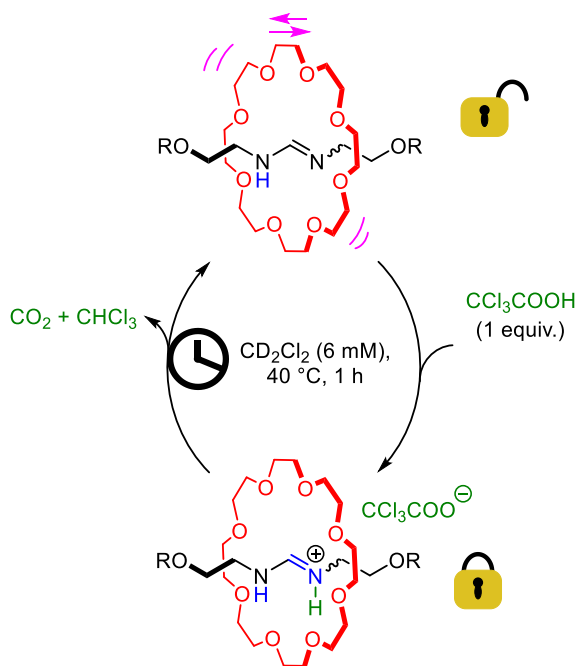
Taking advantage of the formation of charged species and the differences in stabilization by a crown ether, another rotaxane conformational switch was applied by the same group as a time-controlled catalyst (Scheme 6).<sup>52</sup> At the resting state, the crown ether is stable around the thiourea and the catalyst is inactive (OFF). Through the addition of a pulse of TCA, the secondary amine gets protonated forming an ammonium ion. The crown ether shuttles to this position liberating the thiourea, active catalyst (ON) for the Michael addition of an hydride from an Hantzsch ester to nitrostyrene. The addition of an additional basic amine accelerates the rate of trichloroacetate decarboxylation, enabling upon completion, a return to the initial state, shutting-off the catalyst activity. Altogether, the catalytic activity of the rotaxane can be controlled at will, even if a small background reaction is observed at the OFF state. TCA pulses can trigger a transient formation of the active catalyst, back inactivated through trichloroacetate decarboxylation.

**Scheme 6.** TCA fueled time-controlled rotaxane catalyst.



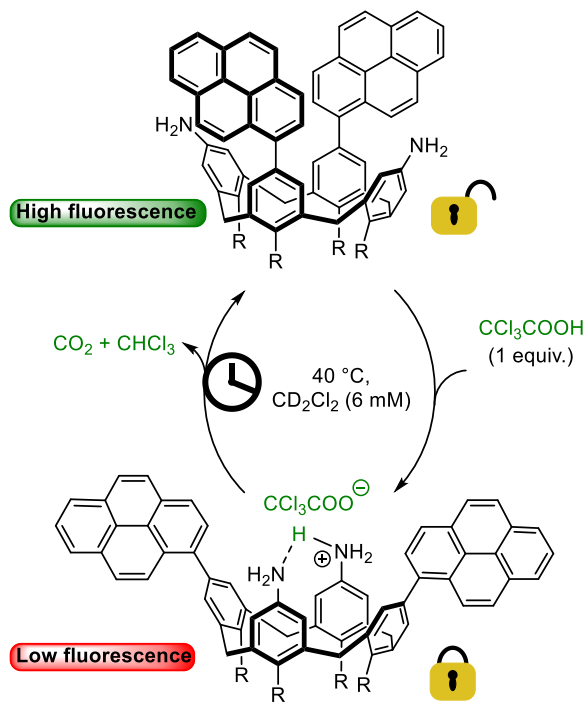
In 2021, the group of von Delius further took advantage of TCA properties to fuel a new type of rotaxane conformational switch based on an amidine architecture (Scheme 7).<sup>53</sup> At the neutral state, the rotaxane thread consists in this particular amidine surrounded by a crown ether ring. The stabilization between the ring and the thread being weak, a fast interconversion between *E,Z*- and *E,E*-isomers of the amidine is observed. Upon TCA addition, an amidinium is generated, strongly stabilized by the crown-ether ring through electrostatic interactions. This stabilization slows down the interconversion between the two isomers until all TCA is consumed through the amidine catalyzed decarboxylation operative at 40°C and not requiring any external base. Successive TCA additions enable to switch reversibly from a relatively conformationally flexible rotaxane to a rigid one. It must be pointed out that the relatively moderate extent of the conformational freedom makes it difficult to monitor and is only noticeable through a small splitting of the benzylic, aromatic, and tert-butyl protons in <sup>1</sup>H NMR.

**Scheme 7.** TCA fueled control of a rotaxane conformational dynamic.



Aside from rotaxanes, in 2022, the group of Baldini and Di Stefano reported a TCA-fueled time-controlled fluorescent switch based on different conformations of a calixarene platform (Scheme 8).<sup>54</sup>

**Scheme 8.** TCA fueled time-controlled calixarene conformational switch with different fluorescences.

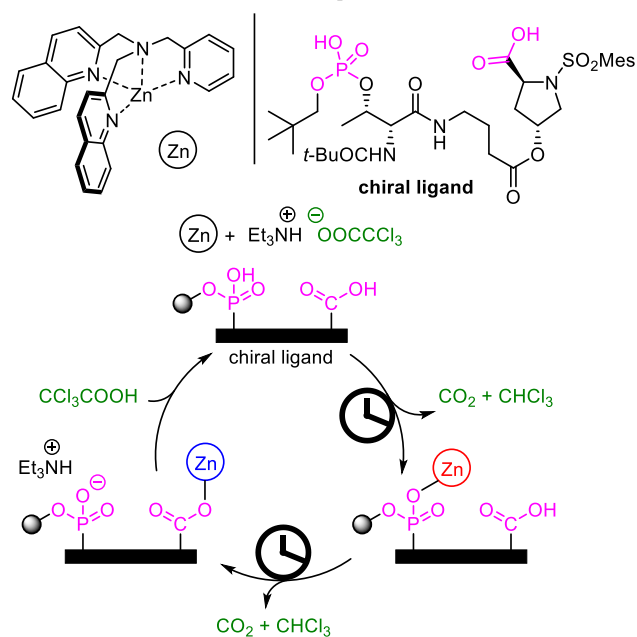


At the neutral state, a calix[4]arene possessing two primary amines and two pyrenes substituents on the upper rim, shows a strong fluorescence through  $\pi$ - $\pi$  interaction of

the pyrene units (excimer emission). From this stable fluorescent adduct, the addition of trichloroacetic acid leads to an important change in the conformation of the calixarene. To accommodate the interaction between the two amines sharing a proton from the added TCA, the two pyrene units are forced apart quenching the excimer emission, considerably decreasing the fluorescence of the system. Upon trichloroacetate decarboxylation, a return to the initial neutral amine is observed restoring the strong fluorescence. As in other systems, the rate dependence of the return to the initial state is proportional to the amount of TCA added and can be easily tuned. The system can be operated over four successive cycles upon TCA pulses without a strong loss in the fluorescent properties. Here, once again, no exogenous base is required for the trichloroacetate decarboxylation solely catalyzed by the primary amines.

In 2022, the group of Clayden applied TCA to fuel a dissipative chiroptical switch based on a zinc cation bearing a bis(2-quinolylmethyl)-(2-pyridylmethyl)amine (BQPA) ligand (Scheme 9).<sup>55</sup> The zinc cation could adopt three different states depending on its coordination with an external chiral ligand. The absence of coordination with the chiral ligand induce a near to 0 circular dichroism (CD) signal. Upon coordination with the phosphate binding site of the ligand a strong CD negative signal is obtained while coordination with the carboxylate gives a strong positive signal. The addition of TCA pulses triggers the evolution of the system through the three different ligation states resulting in successive distinct chiroptical signals. Trichloroacetate decarboxylation kinetic is easily tunable by adjusting the temperature or adding water to slow down TCA decarboxylation rate.

**Scheme 9.** TCA fueled Zinc chiroptical switch.

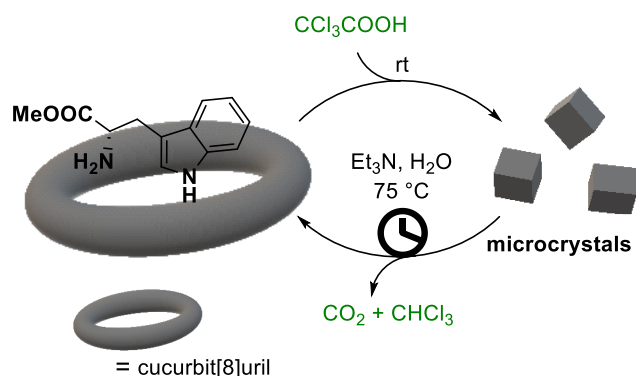


### TRICHLOROACETIC ACID FUELED CRYSTALLIZATION

Aside from these molecular switches, TCA can be used for the temporary crystallization of amines. For example, in

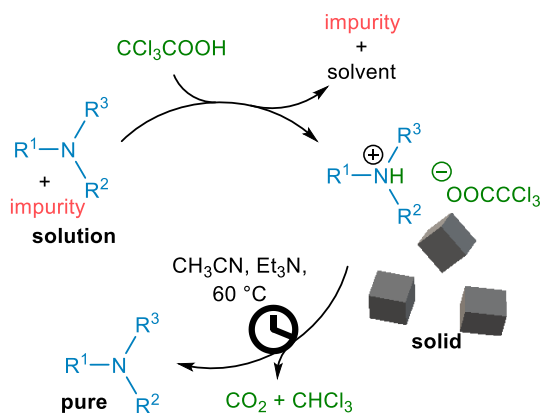
2019, Mukhopadhyay and Baek reported a dissipative host-guest system generating in a temporary manner a suspension of microcrystals (Scheme 10).<sup>56</sup> At the resting state, cucurbit[8]uril [CB8] and tryptophan form a host-guest insertion complex. When adding TCA, the tryptophane is protonated leading to the crystallization of the host-guest system generating microcrystals suspension. In the presence of additional triethylamine and heating at 75 °C, the trichloroacetate is decarboxylated dissolving back the microcrystals. The volatility of the waste generated avoids the degradation of the system over the cycles and up to 18 cycles can be performed efficiently. The high temperature required for the good operation of the system is attributed to the use of water as the solvent, considerably decreasing the rate of trichloroacetate decarboxylation which takes one day under those conditions. This is a general challenge associated with the reactivity of TCA in water, considerably limiting its applicability.

**Scheme 10.** Temporary crystallization of a host-guest system based on a cucurbituril [CB8].



Taking advantage of the difference in solubility between neutral and protonated amines, recently, our group reported a new method for the purification of amines (Scheme 11).<sup>57</sup>

**Scheme 11.** Amine purification through the temporary formation of a solid ammonium salt.



From a neutral amine containing impurities, this approach is based on a temporary formation of a solid ammonium trichloroacetate salt enabling the removal of the soluble impurities with the solvent. As an alternative to

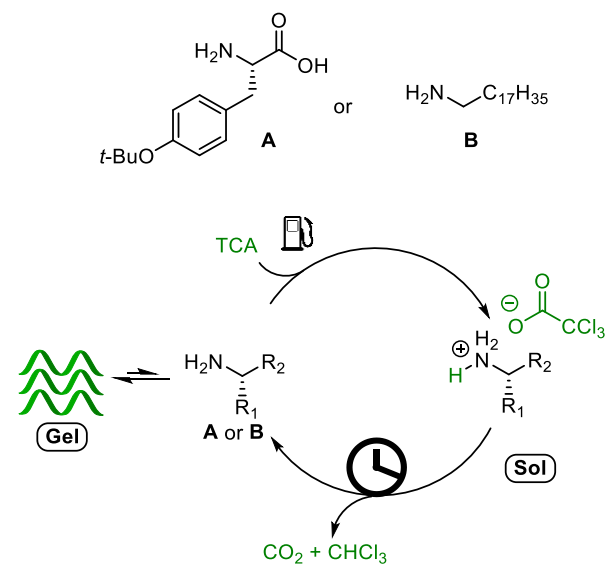
processes requiring multiple operations for amine purification, this strategy avoids all operations and waste associated with liquid-liquid separation for the return to the desired neutral amine through the decarboxylation of the trichloroacetate anion. The decarboxylation could occur spontaneously upon heating but it was found more practical and swifter in the presence of CH<sub>3</sub>CN and Et<sub>3</sub>N under vacuum, directly removing all these volatile reagents as well as the generated chloroform. This procedure could be applied to a broad range of amines, showcasing the interest of applying a temporary crystallization/precipitation processes through the use of TCA.

## TEMPORAL CONTROL OVER MATERIALS

As depicted in the introduction, development of chemically fueled dissipative organogels is a highly attractive research area where numerous groups have developed a broad array of different organogelators or fueling strategies. However, as already mentioned, the chemical waste resulting from fuel consumption results in huge limitations for the reliability of these smart materials notably for application over multiple cycles. In order to overcome these limitations, our group has taken advantage of TCA's properties to fuel material formation/deformation. The overall strategy relies on the change in acidity of the system depending on TCA presence and was applied to complementary gel-sol-gel or sol-gel-sol processes.

In 2022, we reported the use of *O*-tert-Butyl-L-tyrosine (A) or octadecylamine (B) in a TCA fueled gel-sol-gel cycle (Scheme 12).<sup>58</sup> Both molecules were previously used as low molecular weight organogelators for polar aprotic solvents like DMF or DMSO.<sup>59-60</sup> It was found that in the absence of TCA, both neutral amines could form resistant gels using as low as 1 wt% of A. TCA addition triggers the instantaneous protonation of the amines. The resulting ammonium salts are soluble in the organic solvents, leading to the destruction of the gel fibers. From the obtained clear solutions, the amines catalyze the trichloroacetate decarboxylation, consuming all fuel until a critical concentration in neutral organogelator is reached, where a rapid gelation is observed. The gel-sol-gel process can easily be controlled through the fuel concentration or by changing the solvent, resulting in cycles ranging from through 3-4 minutes to hours. Interestingly, the overall cycle can be easily monitored through the incorporation of acid-sensitive color indicators, moving from the yellow solution in the presence of TCA to green for the neutral organogel (Scheme 12). Of importance, gel-sol-gel cycles can be reproduced by another fuel pulse of TCA. Given the absence of waste accumulation, this provides highly reliable systems, where 15 consecutive gel-sol-gel cycles could be induced through the different fuel pulses.

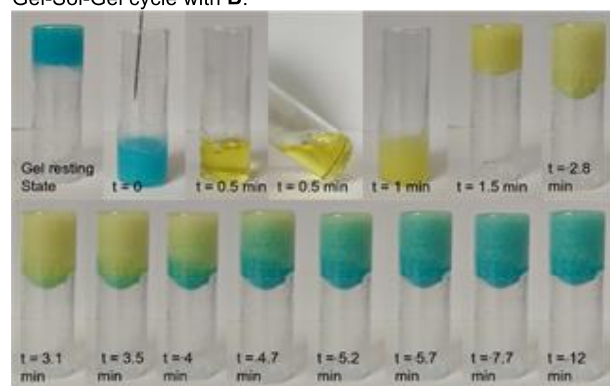
**Scheme 12.** Fuel-pulsed dissipative gel-sol-gel systems. Pictures adapted with permission from *ACS Applied Materials & Interfaces*, **2022**, *14*, 24720-24728. Copyright 2022 American Chemical Society



Gel-Sol-Gel cycle with A:



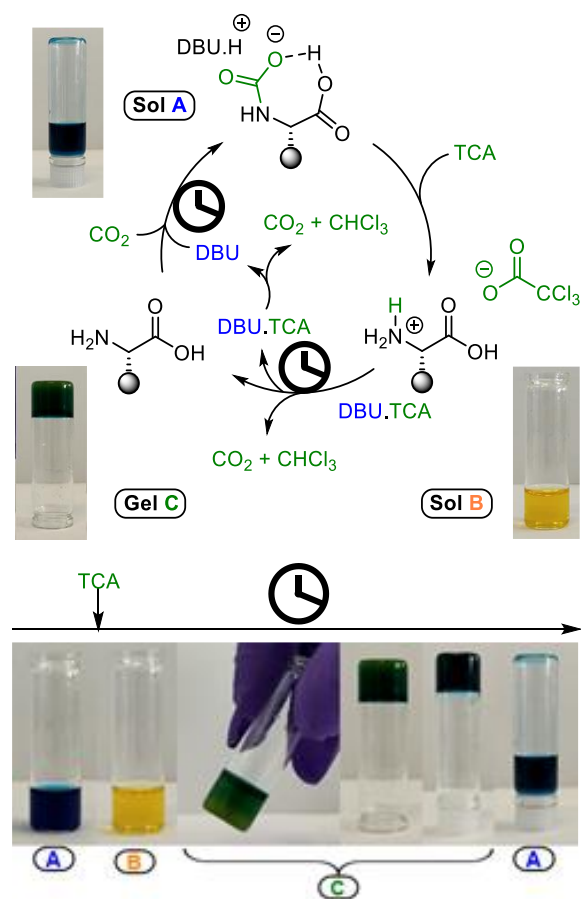
Gel-Sol-Gel cycle with B:



Complementary to the gel-sol-gel system, we reported in 2021 the use of TCA to generate a sol-gel-sol system using O-tert-Butyl-L-tyrosine (A) as organogelator.<sup>61</sup> Inspired by the above-mentioned gel-sol-gel mechanism, the idea to obtain the complementary sol-gel-sol cycle was to take advantage of the addition to the system of a strong base. Adding 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (Scheme 13), an additional state (Sol A) is added to this cycle (anionic solution of the amino-acid). As a consequence, upon TCA addition, the initial solution instantaneously evolves to sol B containing the protonated forms of both amines. Upon amine catalyzed partial trichloroacetate decarboxylation, the less basic amino-acid is released first, providing the transient gel C. Upon final decarboxylation of the remaining trichloroacetate, the strong base is released again, leading

to the destruction of the gel. This process is involving the trapping of one equivalent of  $\text{CO}_2$  through the formation of carbamate solution A. Once again, the time dependence of all intermediate states can easily be controlled through TCA and DBU concentrations. Monitoring of the sol-gel-sol process through addition of acid-sensitive color indicators could enable an easy visualization of the chemical cycle (Scheme 13). The absence of decomposition of the system by undesired waste accumulation enabled to perform up to 25 consecutive sol-gel-sol cycles without loss of the material properties.

**Scheme 13.** Fuel-pulsed dissipative sol-gel-sol systems. Pictures adapted with permission from *J. Am. Chem. Soc.* **2021**, *143*, 12650–12657. Copyright 2021 American Chemical Society



Interestingly, the dissipative processes developed enabled to envisage a broad array of innovative applications for these materials. Aside from the reversible and temporary molding of different objects of great stiffness, the use of the enantiopure O-tert-Butyl-L-tyrosine also gave rise to chiroptical switching materials, of interest for logic gates devices or data storage.<sup>62</sup> In the gel-sol-gel process, the two states of the system provided two distinct Electronic Circular Dichroism (ECD) signals (negative for the gel and positive for the cationic solution). In the presence of DBU, the system shows three distinct states in ECD (-1, 0, 1) corresponding to the three-state depicted in Scheme 13. The resting state solution A possesses a close to zero ECD signal,

TCA addition induces the transition through a new solution B with a positive signal and gel formation C leads to a negative signal (green).

Finally, these materials have also been applied to make flexible and easily recyclable electrical welds with temporal control, showcasing all the possibilities such new type of materials possess.

## CONCLUSION

In the last years, TCA has become the most convenient fuel for fuel-pulsed dissipative systems. Beside its availability, TCA is the most attractive in terms of waste management and control over fuel-consumption kinetics. It has been now well established that trichloroacetate decarboxylation rate can be finely tuned by modifying the nature of a catalytic base or changing the solvent enabling a strong time-control over the systems developed. A rapid decarboxylation is observed in strong polar aprotic solvents (DMSO or DMF), while decreasing the polarity considerably reduces decarboxylation rate. Decarboxylation in protic solvents and water is even more challenging. In addition, using water, non-miscible chloroform is generated which should push researchers to develop alternative fuels for such solvents which is capital for example for bio-based applications.

Aside from the time-control over fuel-consumption, the great interest of TCA lies in waste management. Indeed, in sharp contrast with other fuels, the liberation of volatile CO<sub>2</sub> and chloroform avoids the problems classically associated with waste accumulation in dissipative systems. As a consequence, it has been described that up to 25 consecutive TCA fuel pulses could be used to induce consecutive cycles.

As a result of all the above-listed advantages, TCA has been applied in a great diversity of systems. For example, it could serve as the fuel for a unidirectional motor, promote different conformational switches, enable temporary crystallization or trigger complex sol-gel-sol cycles. Given the complexity of the chemical and physical answers and the temporal control resulting from a simple stimulus, the discovery of other TCA fuel-pulsed technologies should considerably expand in the next years.

## Data Availability Statement

The data underlying this study are available in the published article.

## AUTHOR INFORMATION

### Corresponding Author

Adrien Quintard, Univ. Grenoble Alpes, CNRS, DCM, 38000 Grenoble, France.

Email: [adrien.quintard@univ-grenoble-alpes.fr](mailto:adrien.quintard@univ-grenoble-alpes.fr)

### Author

Enzo Olivieri, Ludwig-Maximilians-Universität München, Department Chemie, 81377 München, Germany.

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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