

Perspective

Space and Time Crystal Engineering in Developing Futuristic Chemical Technology

Pathik Sahoo^{1,2,3,*}  and Subrata Ghosh^{4,5} 

- ¹ International Center for Materials Nanoarchitectonics, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Ibaraki, Japan
- ² Foundation of Physics Research Center (FoPRC), 87053 Celico, CS, Italy
- ³ International Institute of Invincible Rhythms, Churat Nala Road, Chakrail, Bhattakufer, Shimla 171006, Himachal Pradesh, India
- ⁴ Chemical Science & Technology Division, CSIR-North East Institute of Science & Technology, Jorhat 785006, Assam, India; ocsgin@gmail.com
- ⁵ Academy of Scientific & Innovative Research, Ghaziabad 201002, Uttar Pradesh, India
- * Correspondence: 2c.pathik@gmail.com

Abstract: In the coming years, multipurpose catalysts for delivering different products under the same chemical condition will be required for developing smart devices for industrial or household use. In order to design such multipurpose devices with two or more specific roles, we need to incorporate a few independent but externally controllable catalytically active centers. Through space crystal engineering, such an externally controllable multipurpose MOF-based photocatalyst could be designed. In a chemical system, a few mutually independent secondary reaction cycles nested within the principal reaction cycle can be activated externally to yield different competitive products. Each reaction cycle can be converted into a time crystal, where the time consuming each reaction step could be converted as an event and all the reaction steps or events could be connected by a circle to build a time crystal. For fractal reaction cycles, a time polycrystal can be generated. By activating a certain fractal event based nested time crystal branch, we can select one of the desired competitive products according to our needs. This viewpoint intends to bring together the ideas of (spatial) crystal engineering and time crystal engineering in order to make use of the time–space arrangement in reaction–catalysis systems and introduce new aspects to futuristic chemical engineering technology.

Keywords: crystal engineering; time crystal engineering; competitive reactions; multipurpose catalysis; chemical technology; nested reaction cycles; fractal cyclic pathway



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1. Introduction

Biological reaction cycles [1,2] with fractal pathways [3] are omnipresent, where catalytic cyclic events can be found inside a host catalytic cycle. These fractal patterns often generate a particular product among few competitive deliverables as per the biological requirements. For example, the transcription factors (TF) are the DNA sequence-specific protein molecules that control the genetic information from a DNA to messenger RNA (mRNA) through the transcription rate. The phenotype or metabolic activity can be expressed differently by dynamically altering the transcriptome through modifying a TF [4], in controlling gene expression. Tanaka and his co-workers [5] cloned two orthologous genes, CpAG1 (AB548889) and CpAG2 (AB548890) of *Cyclamen persicum* (cyclamen), are expressed primarily by stamen and carpel, respectively. Cyclamen flowers blossom with five petals, but expressing a chimeric repressor results in converting five stamens to petals. Finally, cyclamen blossoms with 10 petals.

By perturbing a fractal reaction cycle a little, but in a controlled way, one can end up the reaction with different product [6] or different fractal structures [7]. In a catalytic cycle, all the reaction steps can be considered as an event, which takes some time. Once

such time-consuming events are connected through arrows in constructing a circle, we can represent a cyclic reaction in the form of a clock. By perturbing a single event purposefully, we can tune some other clock event and tune the final product. This concept, the time crystal engineering, can be employed in nested catalytic cycles to engineer the time of the deliverable products. The events inside the clocks or time crystals get repeated against both time and space [8].

However, to design such a multipurpose catalyst for carrying out chemical reactions, one needs to design the catalyst in such a way that, the same catalyst can be used for different purposes under similar conditions, except for one or two controllable parameters. We already have demonstrated how metal organic frameworks (MOFs) crystals play a crucial role in designing heterogeneous catalysts [9] for their various designed active reaction centers, precise voids inside the lattices, photo harvesting centers, tunable band gaps and robust spatial frameworks [10]. In a crystal lattice system, only spatial repetition generates spatial crystal. No time repetition is needed here, as crystal lattice does not behave as a time depending repetitive event.

These MOF-based photocatalysts with multiple reaction centers should be designed in such a way that, the reaction centers can be activated by different light frequencies, and in the same chemical solution, they can generate different products. In order to make the catalytic cycles nested, the intermediates, products or by product, should be used for carrying out different photocatalytic reaction cycles. These secondary cycles will not be dependent on each other, so that. By activating one particular reaction center in a photocatalyst, one specific secondary reaction cycle could be activated. Even so, by using the intermediates or products of the secondary cycle, a tertiary cycle can also be constructed. In such a nested cyclic architecture, one primary circle, one selective secondary circle over the selected primary circle, and its one selective tertiary reaction circle over the secondary circle and so on can be geometrically assigned as a fractal reaction cycle.

Previously, by considering a single reaction step in a catalytic cycle as an event, we have demonstrated that the repetitive events can be connected to form a clocking topology in construction of the time crystal. Like a spatial crystal lattice, where unit cells are getting repeated over a single axis, the events in a time crystal are getting repeated over the time [11].

In the case of homogeneous reactions, the reaction happens in the same chemical reaction, but in the case of heterogeneous reactions, it may not happen in the same place. In particular, in the biological system, different chemical steps can happen in different places, e.g., photosynthesis (*vide infra*).

2. Crystal Engineering in Designing MOF Based Catalyst

Symmetry breaking in a Hamiltonian system is fundamental in modern physics to attribute the concepts like superconductors, cosmology, (anti)ferromagnets, high-energy physics or Bose–Einstein condensates. Likewise, the breaking of spatial translation symmetry generates crystal while changing the phase from liquid to solid state. The predictability behind the proposed supramolecular 3D arrangement and robustness in spatial architecture encourages the supramolecular chemists in designing or engineering the crystal. From our previous works, we have seen that designing any supramolecular materials like supramolecular gels [12–15], pharmaceutical co-crystals [16] or metal–organic frameworks (MOFs) [17] by crystal engineering approach always need to have a quest of certain supramolecular synthons with the desired property and related functional groups at the molecular backbones. Therein, supramolecular synthons build the desired 1D, 2D or 3D architecture and the functional group introduces the additional supramolecular property. In designing a MOF, chemists focus on designing bi-dented or multi-dented ligands, selection of appropriate cations, anions. Solvents and crystallization techniques often play a crucial role in forming the crystal lattice.

2.1. Supramolecular Role

To design a MOF as a photocatalyst, some salient features will be discussed here briefly. Irradiating a metal center by photon ($h\nu$) with similar to higher than the bandgap will eject an electron (e) to a conduction band (CB), creating a positive hole (h^+) simultaneously on the valence band (VB). All these charged centers for participating in photochemical reactions get shifted toward catalytic sites. Therein, the electron reduces, and the hole oxidizes the adsorbed reaction species. In this process, basically, the electrons are localized at the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) with a 3 eV energy difference. It makes an energy mismatch between a metal center and its corresponding ligand.

The density functional theory (DFT) calculation plays a crucial role while designing MOF to make a semiconducting system in designing a photocatalyst. All the photocatalyst needs to have a specific bandgap, but an overlapping bandgap energy level in two catalysts with the same catalytic centers can produce the multipurpose catalysts (Figure 1) [18,19].

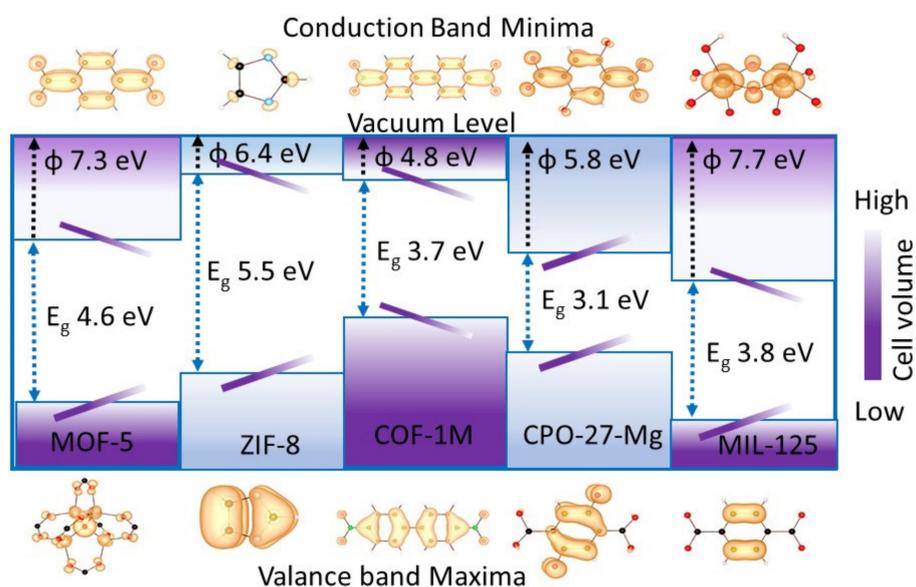


Figure 1. DFT-HSE06 calculated valence band and conduction band energy levels of five MOFs (ref [19]).

2.2. Designing Ligands

The ligands play several roles, e.g., as a light harvesting antenna, bridging the cationic nodes as linkers, creating supramolecular voids, conducting electrons and holes and finally, tuning bandgaps in the crystal lattice. If the ligand has a property of molecular motor and harvest energy to change the redox state of the metal center, then the result in a catalyst could be multipurpose, as by using their change of redox state the same catalyst structures can promote one or more parallel reactions sequentially or simultaneously in the same beaker [20]. Thus, it is possible to create many more time crystals, which may reduce the reaction time and cost.

When the function groups donate electrons to its π electron conjugation in suppressing the bandgap, the ligand acts as an antenna. The methyl group with its +I effect donates electrons poorly and decreases the bandgap from 3.57 to 3.5 eV with similar efficiency of $-Cl$ (3P electron). However, functional groups such as $-OH$ (2.8 eV) and $-NH_2$ (2.6 eV) can donate 2P electrons strongly to reduce the bandgaps [21]. The binding functionalities in the ligand—the anchors—control the charge transferring to the catalytic sites and provide frame stability. For example, $-COOH$ anchors sustain higher electron density and transfer electrons faster than $-PO_3H_2$ [22].

2.3. Secondary Building Unit

Secondary building units (SBUs) are the metal cluster ions that are bonded through non-metal atoms and act as catalytic centers in photocatalytic reactions [23]. This also helps to tune the bandgap in MOFs. By changing the metals or changing the bridging nonmetals, one can tune the bandgap here. For example, moving from O to Te, the bandgap can be shifted from 1.7 to 3.6 eV [24].

2.4. Decorating MOFs with Nanoparticles

The MOFs with poor efficiency in electron or hole generation and charge separation need to be decorated with additional catalytic centers to promote the photocatalytic efficiency. Several spinels or metal oxides are basically used as the decorative nanoparticles for this purpose [9,25,26]. Metal sulphide nanoparticles, precisely MoS₂, CdS are used for decorating MOF in photocatalytic hydrogen evolution reactions [27]. Metal nanoparticles such as silver nanoparticles [28], Pt nanoparticles, combined nanoparticles [29] or silver iodide [30] are often used for decorating MOFs. Now, if we want to design a multipurpose catalyst, we can consider decorating the nanoparticles on MOFs with specific but different photocatalytic activities. Sometimes, multiwalled carbon nanotubes [31] or graphene [32] are also used for coating MOF for various photocatalytic reactions.

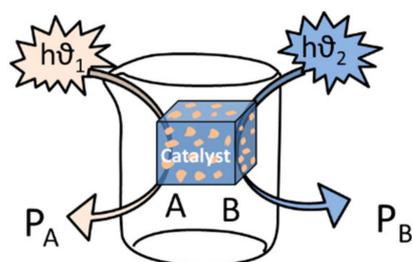
3. Designing Multipurpose Catalyst

A movement started more than a decade ago in engineering a catalyst with a multipurpose role [33]. A common trend is going on by accommodating different catalytically active nanoparticles in the same composite [34] or the same catalyst material under different reaction conditions to develop a multipurpose catalyst [35–37].

It is a little challenging to incorporate two different reaction centers, where they can catalyze two different reactions in the same reaction medium. The primary knowledge for selecting reaction specific catalytic centers, light-harvesting antennas, tuning bandgap for reaction centers are essential but not sufficient conditions in designing such multipurpose MOFs.

By using the same reaction conditions, sometimes a few competitive reactions can be carried out simultaneously. Often these reactions are uncontrollable and compete with each other. For example, controlling water oxidation [38,39] and CO₂ reduction often becomes a challenge, as these compete with hydrogen evolution reactions. As CO₂ is a stable molecule (bond enthalpy: +805 kJ/mol), the reduction reaction of CO₂ is an uphill process ($\Delta G^0 > 0$). It requires significant energy, but by irradiating the catalyst by photon, the electron jumps from the valence band to the conduction band and reduce the molecule.

A catalyst with two active sites with different two absorption bands can be used for two different light tuned reactions. Incorporating two such sites in the same MOF driven catalyst cannot be easy without theoretically designing it before. Herein, bridging ligands will influence both the bandgap energy levels of catalytic centers. Bipyridyl metal complex formation on a ligand backbone in a mixed ligand complex can be a probable solution but, to avoid such mutual influence of catalytic centers, the nanoparticle-based catalyst could be doped over the MOF, where two activation energy levels of two components can influence differently the reaction medium to obtain the light controllable different products (Scheme 1).

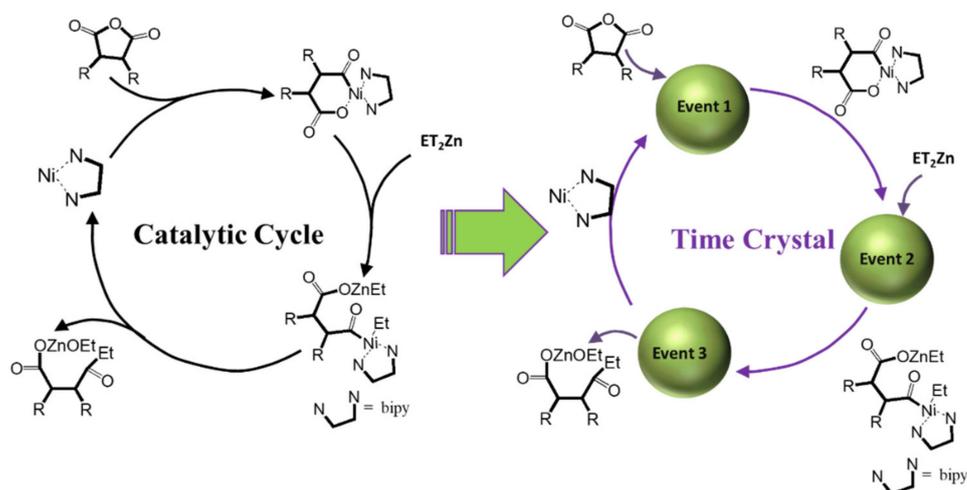


Scheme 1. A multipurpose catalyst with two different catalytic sites developed by nanoparticle coated MOF, which can selectively react with either reagent A or B for producing P_A or P_B .

4. Time Crystal Engineering in Selecting One of the Competitive Products

A spontaneous symmetry translational symmetry breaking in time creates a spacetime crystal or in short, 'time crystal' [40,41]. The structure of time is not a one dimensional system, but like a clock, gets repeated over time and space simultaneously [8,42]. In the case of a spatial crystal (such as a sugar cube), the unit cell gets repeated in space through the x , y and z axes. As the total energy is conserved, the time crystal never performs any mechanical work by using thermal energy. Time crystals are present in biological systems, such as neurons [43,44], brains [45,46], microtubules [47] etc.

To draw a time crystal for the cyclic reactions, first, we need to consider all the single reactions inside the reaction cycle as a single event. These single events are time-consuming and are connected to the next event by some reagents, catalysts or by transition states. As all the reactions inside a cycle consume different times, thus the spatial event size inside the time clock would be different; a bigger sphere will always represent the larger time frame in conducting the event (Scheme 2). If in a reaction system, several nested reaction cycles form a fractal geometry, then a certain fractal branch can be activated to produce certain reaction products, by deactivating other fractal pathways.



Scheme 2. Conversion of a catalytic cycle to a time crystal cycle. Catalytic cycles never concern the time, associated with the reaction and connects the intermediates, transition states by arrows to draw a circle. On contrary, the time crystals connect the time consuming various events, where the chemical reactions are happening to construct a clock topology-based time crystal model [48].

4.1. Time Crystals in Nested Catalytic Cycles

When one of the side products in a catalytic cycle drives another catalytic cycle in the same reaction condition, two nested cycles run simultaneously. Herein, one advantage is, just by adding the reagent or catalyst for the second reaction we can decide if the secondary product is needed or not. The number of nested reaction cycles could be higher

than two as well [11]. While converting the cycles in the time crystal, the cycle with the highest time consumption would appear as a bigger clock. In the biological system, several simultaneous catalytic cycles are running and by perturbing or triggering a certain reaction cycle, the product associated with different cycles could be controlled. Each catalytic cycle from the nested catalytic cycle forms time crystals and gets integrated over the primary or host time crystal to form the poly time crystal.

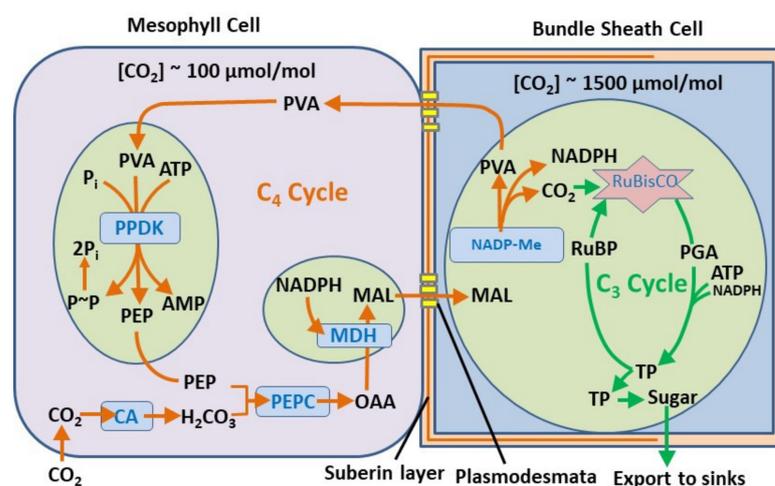
4.2. Time Breathing in Tuning the Reaction Rate

As the size of the time crystal always represents the reaction time schematically, the higher time consumption will make the cycle bigger and vice versa. Just by making the reaction faster or slower, the radius of the time crystal could be increased or decreased accordingly. As each event in a time crystal is time-consuming, by changing the reaction parameters, we can also increase or decrease the 3D spherical event size in the time crystal.

To tune, the reaction rate, reaction temperature, pressure, or catalyst triggering light frequency can be changed. This process can tune the size of the clock diameter. However, a periodicity in repetitive increasing and decreasing will introduce the time breathing in the reaction system. Le Chatelier's principle could be even employed in time breathing. For nested reaction cycles, the cycles may show some different breathing properties.

4.3. Time Crystal Engineering in Nature

Photosynthesis in the plant kingdom occurs in C_3 or C_4 pathways. The C_3 pathway produces 3 carbon-based first intermediate, phosphoglyceric acid, whereas the C_4 pathway produces 4 carbon-based first intermediate oxaloacetate and gets further reduced to malate (Scheme 3). Only 3% of plants follow the C_4 pathway, which allows plant photosynthesis in drought and high-temperature environments. For example, sugarcane, maize, and pearl millet follow the C_4 pathway. In a drought, the temperature becomes high and RuBisCO can discriminate CO_2 and O_2 poorly. At higher temperatures, the solubility of CO_2 becomes low and its concentration decreases in the chloroplast. The C_4 cycle in mesophyll cell (with full of chloroplast) increases the CO_2 concentration and activates the C_3 cycle. Similarly, if we can employ a certain product to activate another reaction cycle as required, it can be used in chemical technology. Once a product is produced in a catalytic cycle, it is never thought of to be employed for triggering another reaction cycle for getting a specific product as needed [49].



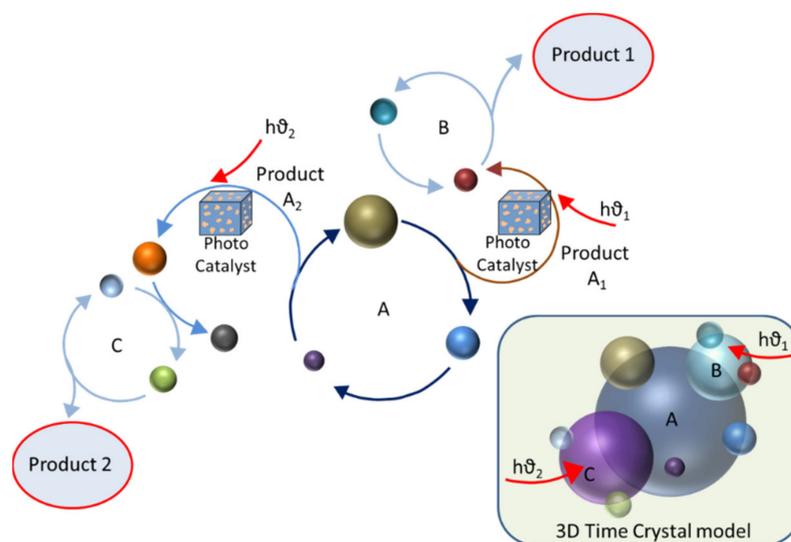
Scheme 3. The C_4 photosynthetic mechanism initiates the C_3 photosynthetic catalytic cycle for the plants at drought land.

In the C_3 system, the atmospheric CO_2 first comes into the mesophyll cell and is reduced by the carbonic anhydrase (CA) enzyme. Then the next enzyme phosphoenolpyruvate carboxylase (PEPC) binds the bicarbonate and phosphoenolpyruvate (PEP, a

3-carbon based compound) to produce oxaloacetate (OAA, a 4-carbon based compound). Oxaloacetate is then further reduced by the enzyme malate dehydrogenase to malate (MAL) and transported to the bundle sheath through the plasmodesmata and reduced further by NADP-malic enzyme into pyruvate under decarboxylation procedure. This process generates CO_2 and the CO_2 gets associated with Rubisco under the C_3 cycle to produce sugars. Then on the other hand, the pyruvate goes back to the mesophyll cell and phosphorylated by pyruvate phosphate dikinase (PPDK) enzyme to regenerate phosphoenolpyruvate (PEP).

5. Future Chemical Engineering

Multitasking efficiency is a requirement for building smart devices in today's materialistic environment. Multipurpose catalysts in a fixed chemical setup with externally controllable specific roles are a current requirement. From the same reaction setup, we can receive the product as per our needs. A multipurpose catalyst can be designed by a crystal engineering approach, where several different reaction centers can be comprised in a MOF. In addition to the inbuilt different reaction centers, we can coat the MOF microparticles with nano-sized metal or metal oxide catalysts (*vide supra*). These different catalytic reaction centers in the same catalyst particle would carry out several nested catalytic reaction cycles (Scheme 4). The main reaction cycle will construct the principal or host circle in the poly time crystal (Scheme 4, inset). The byproducts or the intermediate can be used for carrying out different catalytic reaction cycles, which would construct the guest or secondary time crystal over the principal time crystal. By using two or more such intermediates or byproducts, we can build several secondary time crystals. The secondary time crystals are dependent on each other and as per need, we can activate the particular catalytic reaction centers externally by light frequency to selectively produce the specific product.



Scheme 4. Time crystals A, B and C of three nested catalytic reactions. The different spheres are showing different reaction events, where the size of the sphere are dependent on different reaction times. These events are connected on a clock topology to build the time crystal of that corresponding reaction cycle. Here, the cycles B and C are dependent on cycle A, but mutually independent. The product A_1 could be selected by $h\nu_1$ to activate cycle B, and likewise, product A_2 could be selected to trigger cycle C by irradiating the reaction cycle with $h\nu_2$. Inset: a complete time crystal 3D model of nested catalytic reaction cycles.

5.1. Engineering Technologies

In order to develop such a system, there are two fundamental ways. By crystal engineering we need to design the multipurpose catalyst, workable under same chemical

atmosphere and then we can selectively activate certain fractal reaction cycles to get the specific product.

5.1.1. Crystal Engineering

The catalyst can be excited to the specific energy state by the light with a certain wave range for a monocyclic reaction system. This can selectively produce a certain product by activating one reaction cycle. The catalyst designing part is described here (vide supra), where inside a MOF, two different reaction centers could be incorporated, or the MOF could be decorated by some metal oxide base nanocatalysts. The two different catalytic reaction centers will do two independent reactions by simply changing the wavelength of light.

5.1.2. Time Crystal Engineering

Once a nested cyclic system is found (Scheme 4), in addition to the primary reaction cycle driven product, we can activate some secondary reaction cycles as per our requirements. In Scheme 4, time crystal A is ongoing, where two reaction products (which can be transition states), product A1 and product A2 can be obtained. In this condition, by-product can be used as a trigger to operate time crystal B or time crystal C to selectively get the targeted product 1 or 2 respectively. This activation of the time crystal can be achieved by radiating light of different wavelengths ($\theta 1$ or $\theta 2$). So as per need, in addition to an activated clock A, we can activate either clock B or C to selectively produce product 1 or product 2.

6. Conclusions

Designing multipurpose catalysts for delivering competitive but controllable products under the same chemical condition would be of prime interest in developing smart devices. For developing the photocatalysts, the crystal engineering should be employed to introduce several different reaction centers at the MOF that can carry the different photoreactions in a same solution. Once the catalyst is ready, the different reaction centers can be activated selectively by external different light frequencies to selectively activate its electronic state and activate one of the required catalytic cycles. We can simply extract the right product from a reaction system as per the requirement if a single catalyst can carry a central catalytic cycle, where the intermediates or products of the cycle can also introduce some other nested reaction cycles with full control. These nested reaction cycles are independent of each other, but nested with the principal reaction cycle. After converting the nested catalytic cycles as time crystals, we can plan to tune reaction events to kinetically control the reaction rate and select a specific fractal reaction pathway to get a specific product. The control over the desired product can open up a new aspect of chemical engineering for futuristic use.

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