

## Supporting Information

### **Dissimilar chemobrionic growth in copper silicate chemical gardens in the absence or presence of light**

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## **A. Experimental Section**

### **Preparation of the Materials**

#### **Preparation of the 1M sodium silicate solution**

1M sodium silicate solution was prepared by following procedure.

To find out the initial molar concentration of the sodium silicate i.e., 3.871 M, we utilize the parameters as described below:

Density of the original solution is 1.35 g/mL and percentage assay is 35%.

The equation we use to convert the percentage concentration to molarity:

$$\text{Molarity} = (\text{Percentage concentration} * \text{Density}) / (\text{Molar mass} * 100)$$

$$\text{i.e., } 35 * 1350 / 122.06 * 100$$

$$\text{Molarity} = 3.871 \text{ M.}$$

For preparing 1M sodium silicate solution we use  $M_1V_1=M_2V_2$  leading to

$$V_2=M_1V_1 / M_2$$

$$V_2=1 * 100 / 3.871$$

$$V_2=25.83 \text{ ml required for making solution.}$$

#### **Preparation of the copper silicate chemical gardens**

To prepare the copper silicate chemical gardens in the initial set of experiments where copper sulphate powders were utilized, accurately weighed analytical grade copper sulphate pentahydrate was pulverized in a clean mortar with a neat pestle and the powder was placed at the bottom of a 25 ml Borosil glass beaker. 1M sodium silicate solutions were prepared previously using sodium silicate solution (27-35% assay with initial concentration of 3.871M) and Milli-Q water. 25 ml of this 1M sodium silicate solution was gradually added down via the side of the glass beaker. Without shaking, this mixture was kept in the dark viz. in a dark cabinet undisturbed. As well as, a similar set of glass beaker with the copper sulphate powder and the carefully added sodium silicate solution was kept under the regular laboratory light conditions. After a few seconds, bluish needle-like vertical structures appeared in the glass beakers (both light and dark). And, after a few minutes, vertical hollow tubes emerged fully grown in both the light and dark reactions. Leaving the reaction vessels for some more time resulted in either no new noticeable vertical tube-like structures or no further growth in the existing structures. This represented cease of the growth in both the dark and light cases.

In the next set of experiments, growth of copper silicate chemical gardens was carried out using pellets prepared from copper sulphate pentahydrate and then by adding sodium silicate

solution separately under both the light and dark conditions. To prepare proper pellets to be utilized in these systematic growth experiments, copper sulphate pentahydrate analytical grade powder was pulverized in an agate mortar with a clean pestle to homogenize the solid. Grounded  $\text{CuSO}_4$  was pressed using a cell at 4 tonnes pressure over 3 minutes to obtain pellets of 10 mm diameter. Again, same 1M sodium silicate solution was prepared using sodium silicate solution (27-35% assay) and Milli-Q water.

The pellet was well placed at the bottom of a 25 ml of Borosil glass beaker. 25 ml of the 1M sodium silicate solution was slowly added down the side of the glass beaker. After a few hours, bluish needle-like vertical structures appeared in the glass beakers (both light and dark). Copper sulphate pellets were used to prepare three sets of tube height measurements for light and dark grown copper silicate chemical gardens. Using ImageJ software, one tube was chosen from each set, and the tube heights were measured and recorded along with the time. Plots of height versus time were also made.

All the experiments were carried out at room temperature. The structures were then collected with utmost care and they were oven-dried at  $110^\circ\text{C}$  for 10 minutes. After that, they were utilized for characterization. During the characterization, samples were not kept in dark conditions.

### **Preparation of the cobalt silicate chemical garden**

To prepare the cobalt silicate chemical gardens in the initial set of experiments where cobalt chloride powders were utilized, accurately weighed analytical grade cobalt chloride hexahydrate was pulverized in a clean mortar with a neat pestle and the powder was placed at the bottom of a 25 ml Borosil glass beaker. 1M sodium silicate solutions were prepared previously using sodium silicate solution (27-35% assay with initial concentration of 3.871M) and Milli-Q water. 12 ml of this 1M sodium silicate solution was gradually added down via the side of the glass beaker. Without shaking, this mixture was kept in the dark viz. in a dark cabinet undisturbed. As well as, a similar set of glass beaker with the cobalt chloride powder and the carefully added sodium silicate solution was kept under the regular laboratory light conditions. After a few seconds, dark-bluish needle-like vertical structures appeared in the glass beakers (both light and dark). And, after a few minutes, vertical hollow tubes emerged fully grown in both the light and dark reactions. Leaving the reaction vessels for some more time resulted in either no new noticeable vertical tube-like structures or no further growth in the existing structures. This represented cease of the growth in both the dark and light cases.

### **Preparation of the magnesium silicate chemical garden**

To prepare the magnesium silicate chemical gardens in the initial set of experiments where magnesium chloride powders were utilized, accurately weighed analytical grade magnesium chloride hexahydrate was pulverized in a clean mortar with a neat pestle and the powder was placed at the bottom of a 25 ml Borosil glass beaker. 1M sodium silicate solutions were prepared previously using sodium silicate solution (27-35% assay with initial concentration

of 3.871M) and Milli-Q water. 12 ml of this 1M sodium silicate solution was gradually added down via the side of the glass beaker. Without shaking, this mixture was kept in the dark viz. in a dark cabinet undisturbed. As well as, a similar set of glass beaker with the magnesium chloride powder and the carefully added sodium silicate solution was kept under the regular laboratory light conditions. After a few seconds, whitish needle-like vertical structures appeared in the glass beakers (both light and dark). And, after a few minutes, vertical hollow tubes emerged fully grown in both the light and dark reactions. Leaving the reaction vessels for some more time resulted in either no new noticeable vertical tube-like structures or no further growth in the existing structures. This represented cease of the growth in both the dark and light cases.

### **Preparation of the nickel silicate chemical garden**

To prepare the nickel silicate chemical gardens in the initial set of experiments where nickel chloride powders were utilized, accurately weighed analytical grade nickel sulphate hexahydrate was pulverized in a clean mortar with a neat pestle and the powder was placed at the bottom of a 25 ml Borosil glass beaker. 1M sodium silicate solutions were prepared previously using sodium silicate solution (27-35% assay with initial concentration of 3.871M) and Milli-Q water. 12 ml of this 1M sodium silicate solution was gradually added down via the side of the glass beaker. Without shaking, this mixture was kept in the dark viz. in a dark cabinet undisturbed. As well as, a similar set of glass beaker with the nickel chloride powder and the carefully added sodium silicate solution was kept under the regular laboratory light conditions. After a few seconds, greenish needle-like vertical structures appeared in the glass beakers (both light and dark). And, after a few minutes, vertical hollow tubes emerged fully grown in both the light and dark reactions. Leaving the reaction vessels for some more time resulted in either no new noticeable vertical tube-like structures or no further growth in the existing structures. This represented cease of the growth in both the dark and light cases.

### **Preparation of the ferrous silicate chemical garden**

To prepare the ferrous silicate chemical gardens in the initial set of experiments where ferrous chloride powders were utilized, accurately weighed analytical grade ferrous chloride tetra hydrate was pulverized in a clean mortar with a neat pestle and the powder was placed at the bottom of a 25 ml Borosil glass beaker. 1M sodium silicate solutions were prepared previously using sodium silicate solution (27-35% assay with initial concentration of 3.871M) and Milli-Q water. 12 ml of this 1M sodium silicate solution was gradually added down via the side of the glass beaker. Without shaking, this mixture was kept in the dark viz. in a dark cabinet undisturbed. As well as, a similar set of glass beaker with the ferrous chloride powder and the carefully added sodium silicate solution was kept under the regular laboratory light conditions. After a few seconds, dark greyish black needle-like vertical structures appeared in the glass beakers (both light and dark). And, after a few minutes, vertical hollow tubes emerged fully grown in both the light and dark reactions. Leaving the reaction vessels for some more time resulted in either no new noticeable vertical tube-like

structures or no further growth in the existing structures. This represented cease of the growth in both the dark and light cases.

### **Preparation of the ferric silicate chemical garden**

To prepare the ferric silicate chemical gardens in the initial set of experiments where ferric chloride powders were utilized, accurately weighed analytical grade ferric chloride hexahydrate was pulverized in a clean mortar with a neat pestle and the powder was placed at the bottom of a 25 ml Borosil glass beaker. 1M sodium silicate solutions were prepared previously using sodium silicate solution (27-35% assay with initial concentration of 3.871M) and Milli-Q water. 12 ml of this 1M sodium silicate solution was gradually added down via the side of the glass beaker. Without shaking, this mixture was kept in the dark viz. in a dark cabinet undisturbed. As well as, a similar set of glass beaker with the ferric chloride powder and the carefully added sodium silicate solution was kept under the regular laboratory light conditions. After a few seconds, brownish needle-like vertical structures appeared in the glass beakers (both light and dark). And, after a few minutes, vertical hollow tubes emerged fully grown in both the light and dark reactions. Leaving the reaction vessels for some more time resulted in either no new noticeable vertical tube-like structures or no further growth in the existing structures. This represented cease of the growth in both the dark and light cases.

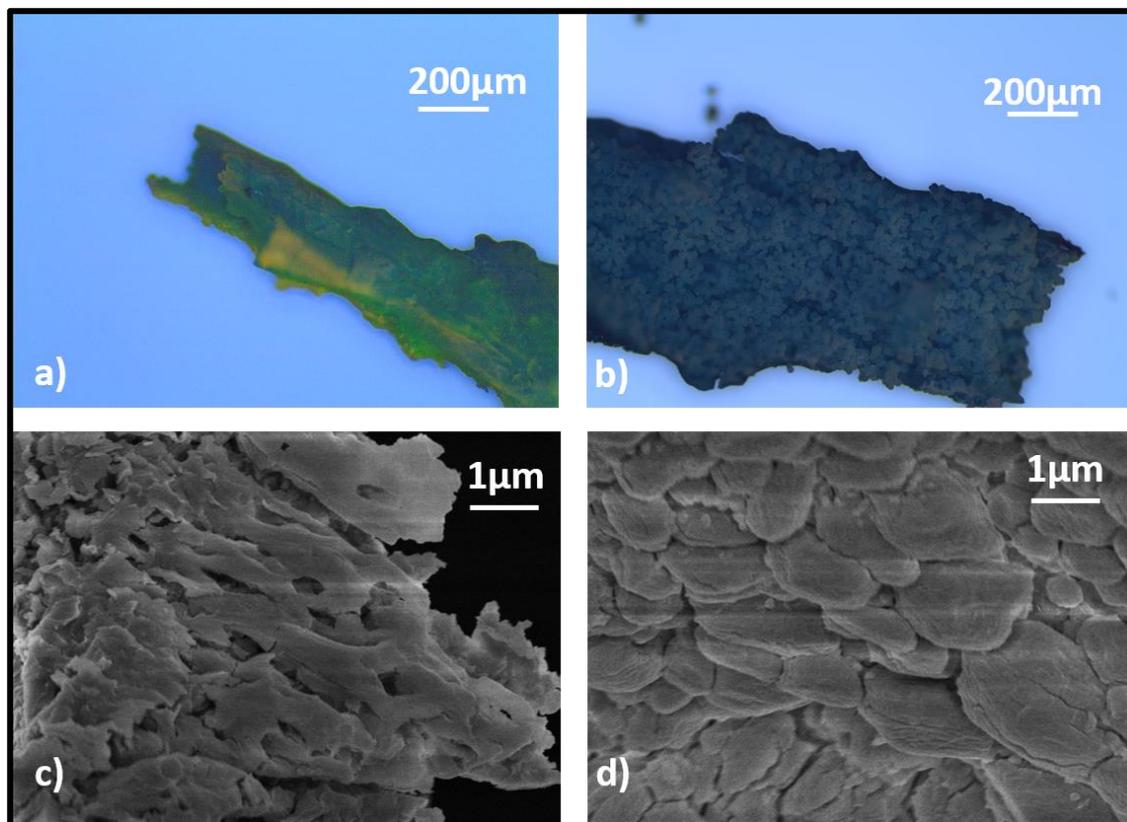
### **Characterization of the Materials**

OLYMPUS BX3M-KMA-S Optical microscope was employed to obtain optical microscopic images of the samples. Zeiss ULTRA-55 FE-SEM (Field Emission-Scanning Electron Microscope) was used to obtain scanning electron microscopic images of the samples. Powder X-ray diffraction (PXRD) patterns were obtained using a Bruker D8 DISCOVER target diffractometer with Cu K $\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ) radiation. The detection of crystalline phases presented in the prepared materials was accomplished by comparing XRD patterns with JCPDS files. PERKIN-ELMER (Spectrum Two) Spectrometer was employed to obtain FTIR (Fourier Transform Infra-Red) data from  $4000 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$  wavenumber range with a sweeping rate of  $4 \text{ cm}^{-1}$ . Solid state UV/Visible spectroscopic analysis was performed using Jasco UV. Cyclic voltametry analysis was performed using Metrohm Autolab B.V.

### **Cyclic voltammetry experiments**

Eppendorf vials were filled with 700  $\mu\text{L}$  of NMP solution, and 10 mg samples of light and dark grown copper silicate were added separately to the vials. PVDF (poly-1,1-difluoroethene) was employed as a binder, with 1 mg applied to each vial. Following that, the contents in the vials were sonicated for 1 hour before being deposited onto the surface of glassy carbon electrode (GCE). A three-electrode cell arrangement was employed to measure the cyclic voltammogram, with GCE serving as the working electrode, silver-silver chloride Ag/AgCl serving as the reference electrode, and platinum wire serving as the counter electrode. The start and stop potentials were kept at 0 volts throughout the experiment. The upper vertex and lower vertex potentials were kept at 1 and -1 volt respectively. Scan rate was kept at 0.1 volt.

## B. Supporting Information Figures



**Figure S1.** a) Optical microscopic image of the as obtained vertical structure collected from the light reaction vessel. b) Optical microscopic image of the as obtained vertical structure collected from the dark reaction vessel. c) SEM images of the vertical structures obtained from the light condition and d) SEM images of the vertical structures obtained from the dark condition.

a)	SET 1 (Height) (cm)	SET 2 (Height) (cm)	SET 3 (Height) (cm)	TIME (Min.)	b)	SET 1 (Height) (cm)	SET 2 (Height) (cm)	SET 3 (Height) (cm)	TIME (Min.)
	0.144	0.201	0.134	0		0.289	0.249	0.277	0
	0.169	0.376	0.189	10		0.363	0.377	0.465	10
	0.338	0.665	0.258	20		0.462	0.466	0.443	15
	0.647	0.684	0.433	30		0.629	0.588	0.576	25
	1.198	0.724	0.601	35		0.693	0.687	0.62	30
	1.266	0.91	0.703	55		0.867	0.631	0.789	45
	1.384	1.086	0.778	60		0.959	0.798	0.731	60
	1.395	1.25	1.833	65		1.244	0.997	0.985	90
	1.587	1.647	1.601	70		1.156	1.141	1.03	95
	2.037	1.911	2.101	85		1.355	1.487	1.496	105
						1.37	1.595	1.522	125

**Figure S2.** a) represents tube height Vs time data sets for three selected tubes from the light reactions and b) represents the tube height Vs time data sets for three selected tubes from the dark reactions.

**Figure S2** above represents the tube height data each for light and dark grown copper silicate chemical gardens with respective time intervals.

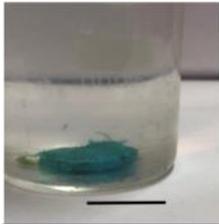
# Pellet Light Set 1



3 hours



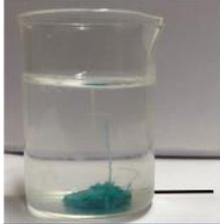
3 hours/ 10 mins



3 hours/15 mins



3 hours/20 mins



3 hours/30 mins



4 hours/ 30 mins



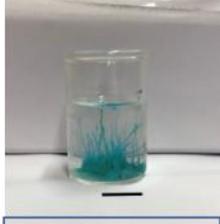
4 hours/ 35 mins



4 hours/ 40 mins



4 hours/ 45 mins



5 hours

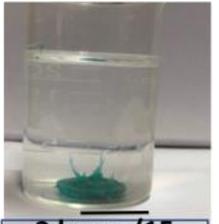
# Pellet Light Set 2



3 hours



3 hours/ 10 mins



3 hours/15 mins



3 hours/20 mins



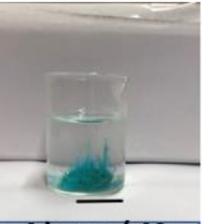
3 hours/30 mins



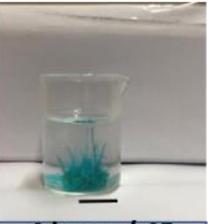
4 hours/ 30 mins



4 hours/ 35 mins



4 hours/ 40 mins

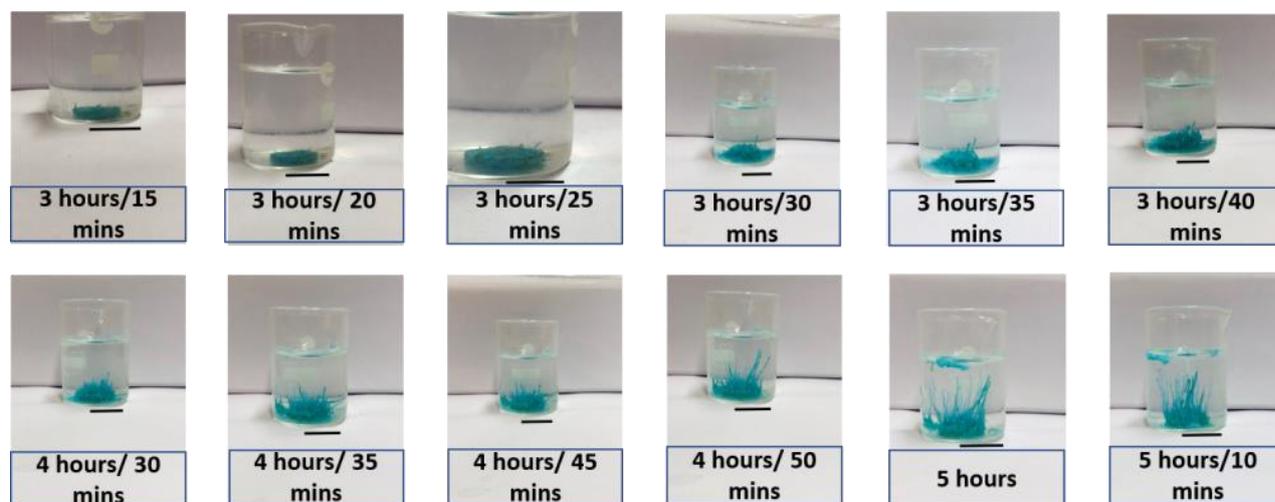


4 hours/ 45 mins



5 hours

### Pellet Light Set 3



**Figure S3.** Time lapse images of the reaction vessels kept under light condition for pellet reactions (sets 1, 2, 3). Scale bar for each set's images is (—=1.5 cm.)

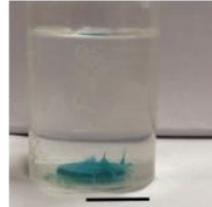
## Pellet Dark Set 1



2 hours



2 hours/ 10 mins



2 hours/15 mins



2 hours/30 mins



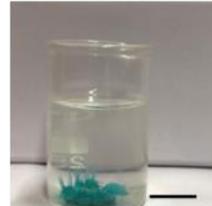
3 hours



3 hours/ 30 mins



3 hours/ 35 mins



4 hours

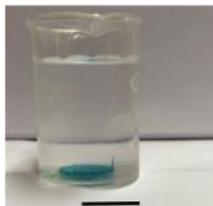


4 hours/ 25 mins



5 hours

## Pellet Dark Set 2



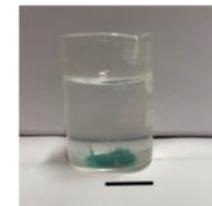
3 hours



3 hours/ 10 mins



3 hours/15 mins



3 hours/20 mins



3 hours/30 mins



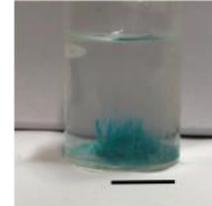
4 hours/ 30 mins



4 hours/ 35 mins



4 hours/ 40 mins

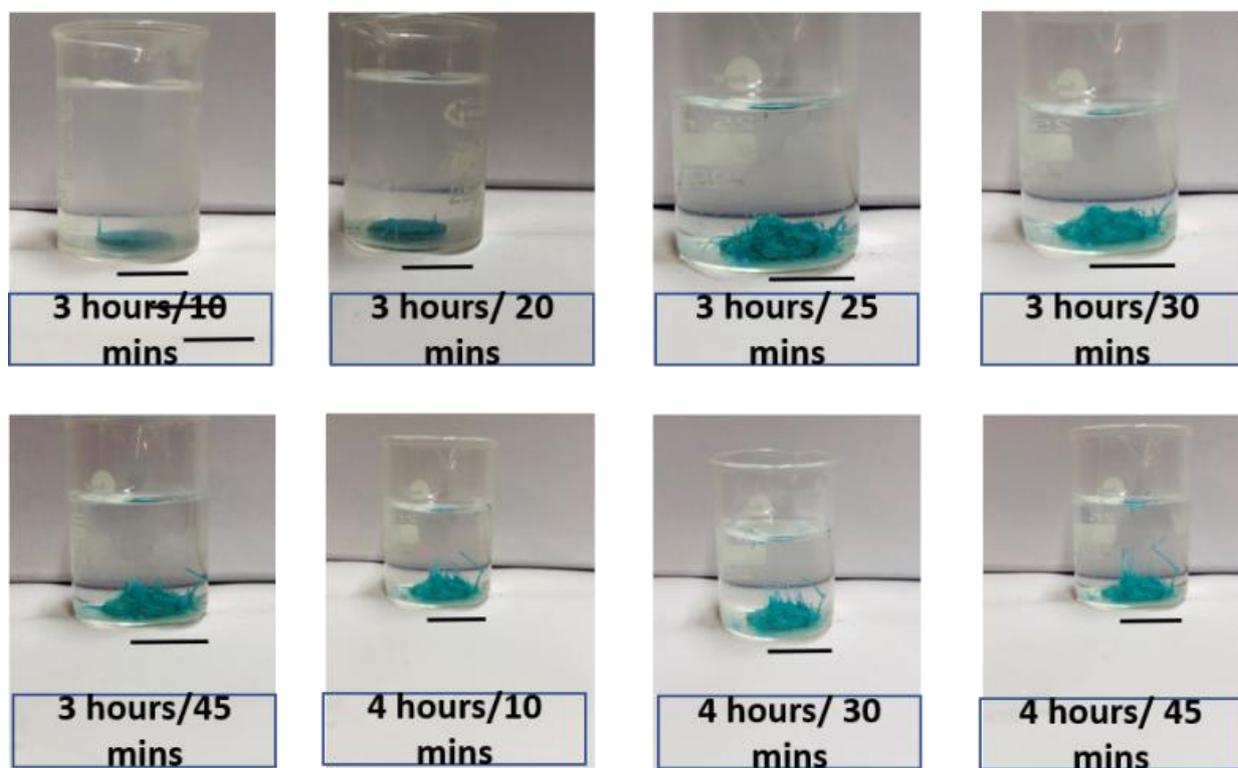


4 hours/ 45 mins

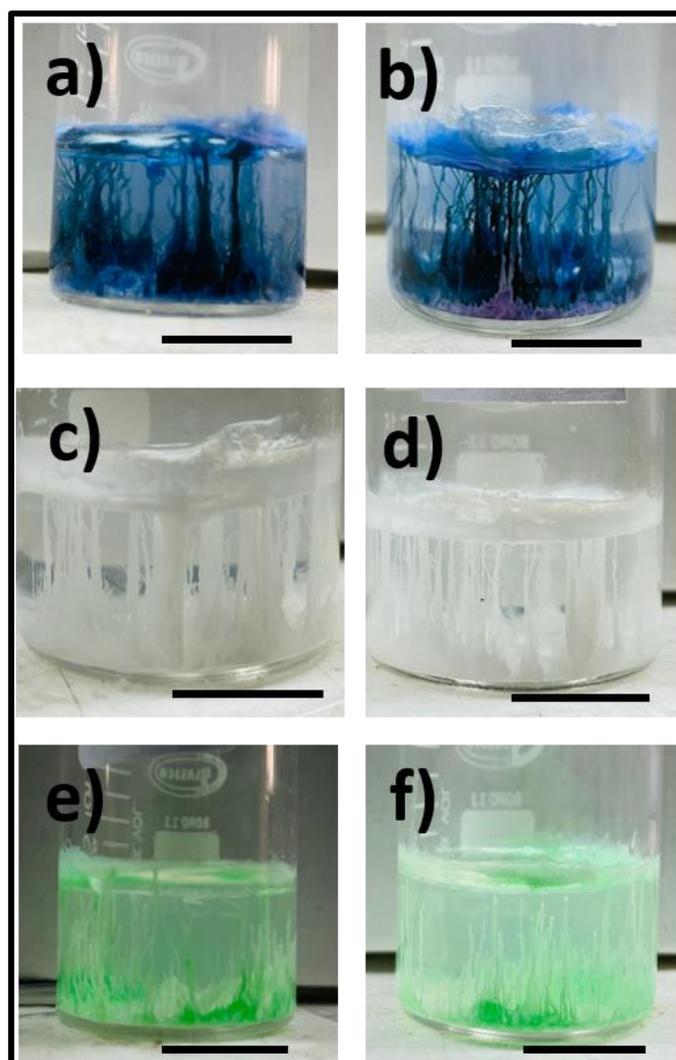


5 hours

## Pellet Dark Set 3

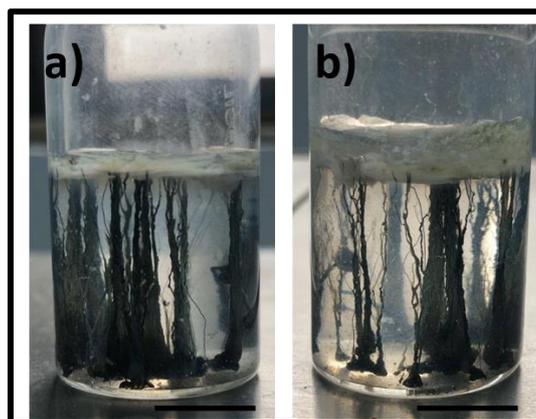


**Figure S4.** Time lapse images of the reaction vessels kept under dark conditions for pellet reactions (sets 1, 2, 3). Scale bar for each set's images is (—=1.5 cm.)



**Figure S5.** Camera images of the reaction vessels kept under light and dark conditions for different metal ion containing chemical gardens such as a) light, b) dark cobalt silicate chemical garden. c) light, d) dark magnesium silicate chemical garden. e) light, f) dark nickel silicate chemical garden. Scale bar for Figure S5 a), b), c), d), e), f) is (—=1.5 cm.)

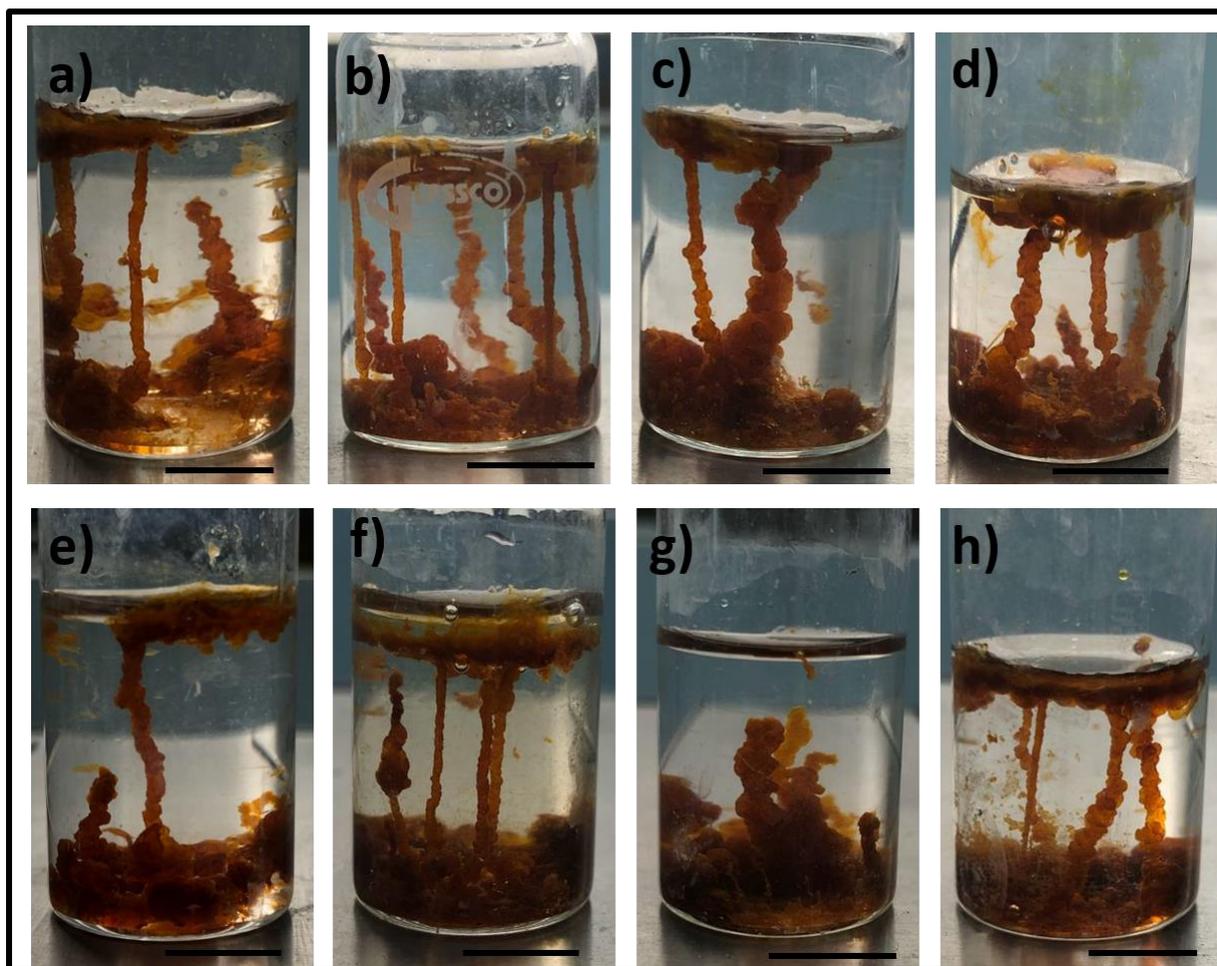
The light and dark induced growth phenomenon was also extended to other previously reported chemical gardens, as shown in the Figure S5 above. In these chemical gardens, no difference in tube height or thickness was observed.



**Figure S6.** Camera images of the reaction vessels kept under light and dark conditions for metal ion containing chemical gardens such as a) light, b) dark Ferrous silicate chemical garden. Scale bar for Figure S6 is (  $\blacksquare$  =1.25 cm.)

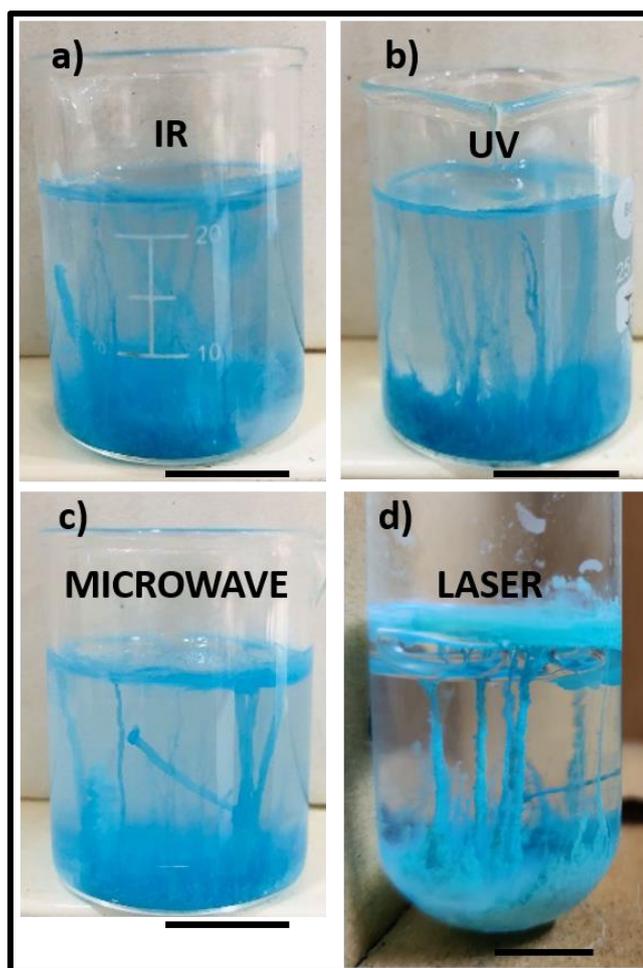
For Iron ( $\text{Fe}^{+2}$ ) based chemical garden light and dark growth phenomena was studied for ferrous silicate chemical garden. As evident from Figure S6, there was no such difference in tube height or number in the ferrous silicate chemical garden.

Because, based on the electrochemical series the standard reduction potential for  $\text{Fe}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Fe}(\text{s})$  is  $E^{\circ} (\text{V}) = -0.44$  volts, it is very difficult for  $\text{Fe}^{+2}$  to get converted into  $\text{Fe}^{+1}$  and so there is no difference in the height or number of tubes grown either in light grown or the dark grown samples.



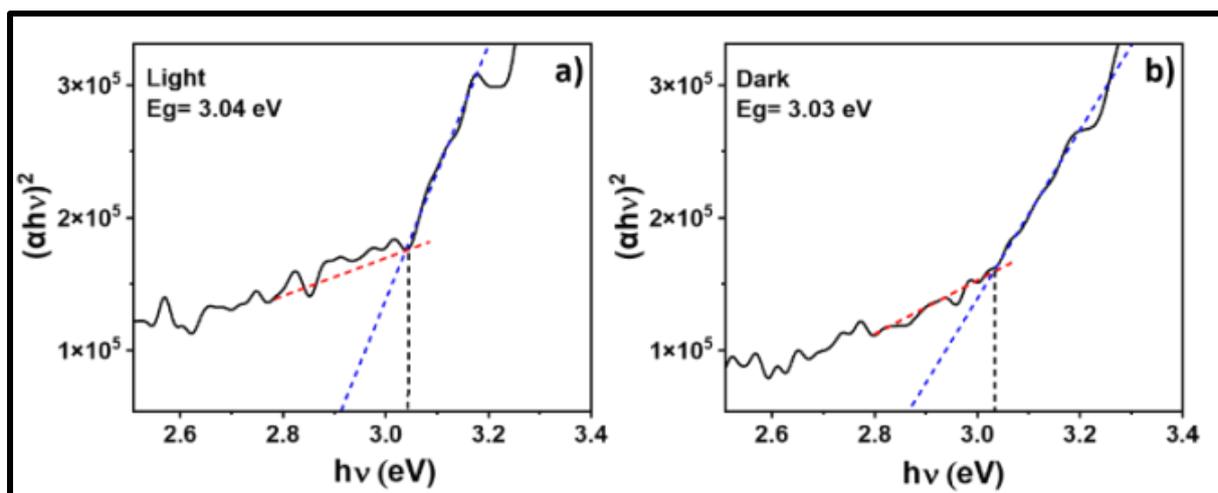
**Figure S7.** Camera images of the reaction vessels kept under light and dark conditions for  $\text{Fe}^{3+}$  ion containing chemical gardens a), b), c), d) under light, and e), f), g), h) under dark. Scale bar for Figure S7 a), b), c), d), e), f), g), h) is ( — = 1.25 cm.)

According to electrochemical series  $\text{Fe}^{3+} + \text{e}^{-} \rightleftharpoons \text{Fe}^{2+}$  is having the standard reduction potential value  $E^{\circ}$  (V) = 0.771 volts. As evident from the Figure S7 above, slight differences in number and height of tubes was observed attributable to the high positive standard reduction potential.



**Figure S8.** Camera images of the reaction vessels kept in a) IR, b) UV, c) Microwave and d) Laser light conditions. Scale bar for Figure S8 a), b), c), is ( — =1.5 cm.) and for Figure S8 d) is ( — =0.65 cm.)

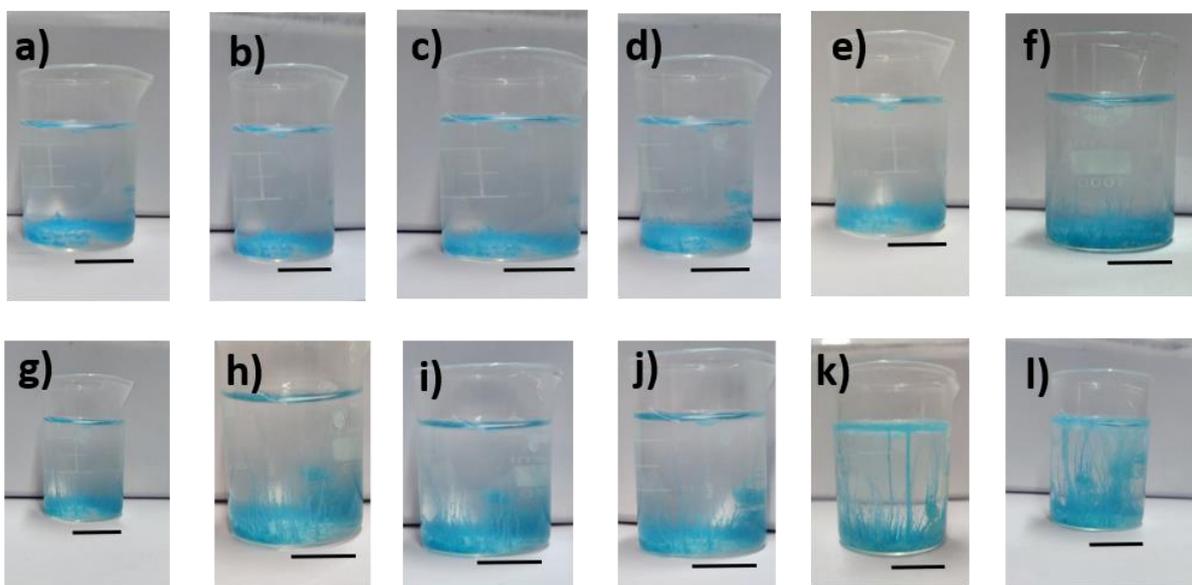
Irradiations were achieved using Murphy Infrared Heat Therapy Lamp having wattage of 150 Watt purchased from Amazon, UV lamp (kept under closed box) having wavelength of 250-400 nm, Raga's Microwave oven at 240 watt and Red Laser source having wavelength of 632 nm. For all the reactions using different light sources, irradiation time was kept fixed i.e., 10 minutes. These were used to confirm whether changing the light conditions had any effect on the growth of the copper silicate chemical gardens or not. The spectral quality of these lights influenced the growth of copper silicate chemical gardens significantly. There was no difference in tube thickness or height, except for the Red Laser light growth. Tube thickness was higher in the laser light condition than in the other light conditions owing to the superior irradiation achieved by the laser because of its monochromatic nature.



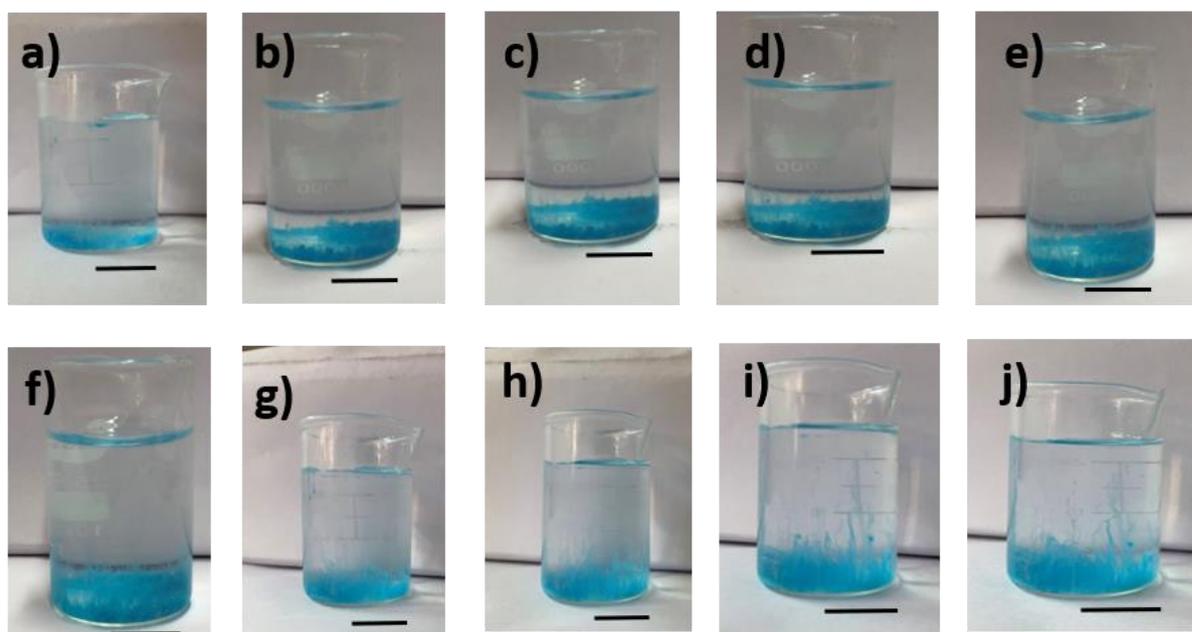
**Figure S9.** Tauc plots of the copper silicate chemical garden grown under light and dark conditions. a) represents Tauc plot for light grown copper silicate chemical garden, and b) represents Tauc plot for dark grown copper silicate chemical garden.

Solid-state UV-visible spectra of copper silicate chemical garden obtained from the light and dark reactions. The direct optical band gap is traditionally measured by extrapolating the linear region of the square of the absorption curve to the abscissa, and a variation of this method, developed by Tauc is utilized.<sup>1</sup> The band gaps ( $E_g$ ) of copper silicate chemical garden grown in light and dark conditions were found to be almost identical 3.04 eV and 3.03 eV values respectively indicating the insulating characteristic of both the light and dark grown samples.

## Powder light set 1



## Powder Dark set 1



**Figure S10.** Time lapse images of the reaction vessels kept under light and dark conditions for powder reactions. Starting from a) 30 seconds there is a time interval of 30 seconds each for this powder set reactions for both light and dark grown sample. Scale bar for each image is (—=1.5 cm.)

## Additional References

- 1 P. Makuła, M. Pacia and W. Macyk, *J. Phys. Chem. Lett.*, 2018, **9**, 6814–6817.