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Excitonic Dynamics of Chlorophyll Molecules in Chitosan Hydrogel Scaffold

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Biomimetic photo harvesting architecture are being realized as an alternative of existing solar conversion systems. This fact leads us to the successful realization of non-coherent electron hopping [hopping rate 4.28 $nsec^{-1}$] through excitonically coupled Chlorophyll-a (Chl-a) molecules within chitosan hydrogel matrix via TCSPC (Time Correlated Single Photon Count) and fluorescence anisotropy measurements. Chl-a molecules remain stable within hydrogel matrix up to 3 months as evident from UV-Vis spectroscopy. The mono-exponential decay parameter with 78 picoseconds time scale, high initial anisotropy data [0.33] and with reduced TCSPC lifetime [1.311 $nsec^{-1}$] of 23° in plane aligned Chl-a macrocycles, indicate that hopping excitonic cascade is prominent among chlorophyll molecules. It can be postulated from Raman Spectra that they form highly co-ordinated closely packed structure via water molecules within chitosan hydrogel due to 6th co-ordination through central Mg of porphyrin macrocycle. All these data predict that this chlorophyll-chitosan hydrogel can be an active component in artificial light harvesting systems.

† Abbreviations & Symbols used:
Chl-a: Chlorophyll-a molecules, CScl: Chlorophyll-a entrapped chitosan hydrogel, TCSPC: Time correlated Single Photon Count, Anisotropy: Fluorescence anisotropy, UV-Vis: Ultraviolet-Visible, ns: nanoseconds, ps: picoseconds, LHC II: light harvesting complex II.

Introduction

Light harvesting by natural photosystem relies on the process of moving electronic excitation energy (which is stored fleetingly by molecules in excited states) through networks of perfectly aligned light-absorbing molecules (chromophores) to a target chromophore in 10–100 picosecond timescale. The highly packed chromophores of light-harvesting antenna enables it to attain a substantially (~100 fold) increased cross-section for light absorption and energy transfer at a rate of near unit quantum efficiency[1, 2]. This means coupling between transition densities of photon absorbing molecules can provide a framework to design artificial light harvesting systems. Flow of energy over long distances is possible within such systems, providing a microscopic "energy grid" to regulate solar energy conversion.

The current trend in the design of light harvesting assembly relies on biocompatible hydrogels. Hydrogels, capable of encapsulating biomolecules and consisting of 98% water are good alternatives of volatile and environmentally problematic organic solvents. Thus they can serve as "quasi" liquid medium to fabricate materials for biomimetic photodevices[3, 4, 5]. Koo H. Jun (2011) has used Chlorophyll and Photosystem II, embedded in aqueous gel media to construct biomimetic solar cell[6]. In this work we aimed to evaluate the mechanism of excitonic migration through non-covalent self-assembled packing of Chl-a-supramolecular assembly in chitosan hydrogel scaffold which can be used as a candidate material for an artificial light harvesting system.

Experimental:

Materials & Method:

Chl-a was extracted from fresh spinach leaves using standard column chromatography technique[7]. 0.2 gm chitosan was dissolved in 14 ml 1% acetic acid solution and stirred for 8 hours to obtain a viscous homogeneous solution.1 ml of 1% glutaraldehyde solution was drop-wise added to it as a cross-linker[8] and was left for almost1hour.After adjusting pH of the hydrogel to ~6.5, it was cast on a glass petri and kept in a vacuum desiccator for nearly 48 hours to evaporate. The as prepared membrane was then soaked in Chl-a (in ethanol) for 5 hours which results in successful entrapment of molecules inside the hydrogel matrix. The outer surface of hydrogel membrane was washed with bi-distilled water, wiped carefully with blotting paper and blow-dried before performing any characterization. The whole experiment was carried out at room temperature, i.e, 30-35°C. Schematic representation of synthesis and encapsulation is shown in Fig. 1.

Sample Characterization:

For checking stability of Chl-a molecules inside the chitosan hydrogel scaffold, UV-Vis spectra of the samples were done at different time intervals using LAMBDA 35 UV-VIS Spectrometer (Perkin-Elmer). Fourier transformed infrared spectra were measured using IR Prestige 21, Shimazdu spectrometer (resolution 4 cm^{-1}). Resonance Raman scattering spectra were obtained using a Trivista 555 spectrograph of Princeton Instruments at an excitation wavelength 413.1 nm from Kr ion laser (Innovative SBRC-DBW-K) at low wattage. Resolution of the resonance Raman instrument is 0.5 cm^{-1} with grating number 900/mm. Time dependent emission and fluorescence anisotropy measurements were carried out using HORIBA JOBIN YVON IBH, JY-IBH 5000M setup. All synthesis and characterization were done at room temperature (30-35°C). The spectroscopic data were normalized for better comparison.

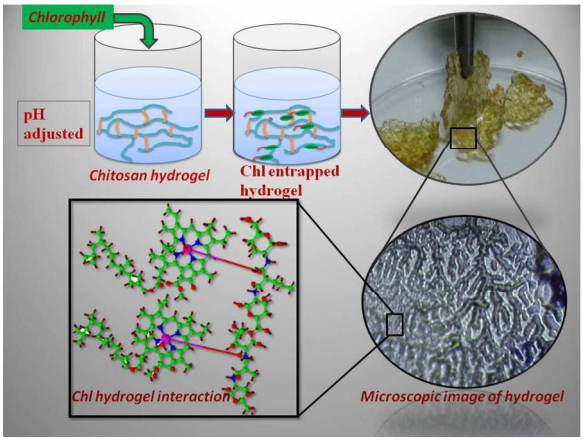

Fig.1. Schematic representation of Chl-a entrapped chitosan hydrogel synthesis along with microscopic image of the hydrogel and probable interaction between hydrogel-Chl-a.

Results and Discussion:

Absorption properties:

Significant inhomogeneous broadening in electronic transition spectra of entrapped Chl-a suggest Chl-a/matrix interaction in chitosan hydrogel scaffold[9] (Fig.2.). Besides intermolecular coupling, pigment-protein interactions also play a role in the amount of delocalization of the excitation in photosystem II[10, 11]. Mukamel et. al. (1989) has shown that differences in electronic transition energies occur due to environmental effect on molecules bound at various sites[12] (different site energies). Pigment-environment interactions also vary for individual pigments (static disorder) which leads to inhomogeneous broadening of absorption bands. The exciton-phonon interactions give rise to additional homogeneous broadening[11]. Increase in broadening of absorbance spectra decreases the extent of delocalization of the excitation[13]. In Chl-a induced chitosan hydrogel, the broadening effects are

much larger (as evident from absorption spectra) which limit the exciton delocalization length. Thus energy transfer by incoherent hopping becomes more prominent at the expense of excitation delocalization decay, which is further highlighted via TCSPC and anisotropy data which is further supported by inhomogeneously broad absorption of entrapped pigment extended up to 900nm, related with different electronic charged delocalization as a result of insight inhomogeneity. This absorption spectrum remains almost same for at least 90 days (Fig.2.)

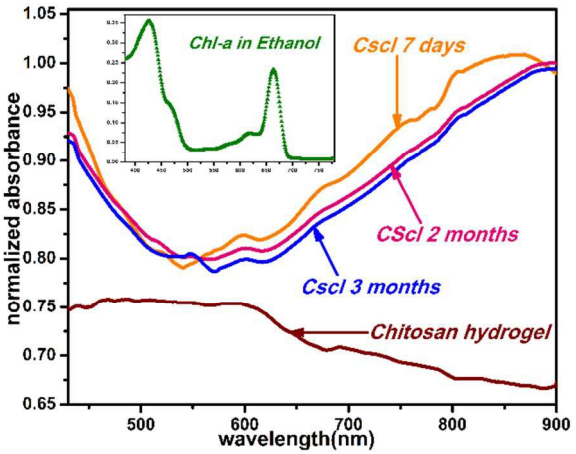

Fig 2. Absorbance spectra of *CScl* taken at different time intervals and of Chl-a in ethanol solvent (inset). Broad absorbance up to 900 nm region is attributed to matrix-Chl-a interaction. This figure also shows stabilization of Chl-a molecules within the matrix.

Infra-red spectroscopy results:

The absorbance spectra result is supported by FTIR transmittance data and Raman Spectra (Fig.3).FTIR spectra of CScl shows shift in pyrrole ring vibration peak (841 cm^{-1} to 864 cm^{-1}) along with ester carbonyl bond vibration peak (1735 cm^{-1} to 1852 cm^{-1}) to higher energy region, showing some interaction is present between closely packed Chl-a molecules as well as Chl-a/chitosan matrix. Absence of any significant carbonyl peak may be because vibration of hydrogen bonded carbonyl is highly restricted inside hydrogel media[further supported by anisotropy data].The presence of pyrrole ring vibrations in FTIR[864 cm^{-1}] and Raman spectra [1350cm^{-1}](Fig.3.B.) also support the formation of Chl-a entrapped chitosan hydrogel[14, 15,16]. The 16 member ring vibration in Raman spectroscopy around 1500-1650cm^{-1} region is sensitive to Mg-N coordination state, which is further related to altered macro-cyclic symmetry. In resonance Raman spectra of Chl-a in polar solvent the C=O stretching Raman lines remain in the region 1668-1702 cm^{-1} and the frequency is independent of the solvent dielectric constant as the dipole moment does not coincide necessarily with the Mg--O coordination. The dipole moment of the environment effects the C=O Raman frequency state. In contrast no specific C=O bond vibration signal is found in CScl spectrum where chlorophyll molecules are mostly in aqueous environment. This may be accounted for decreased frequency of carbonyl Raman vibration while compared to other peak due to the presence of long range electronic push-pull interaction between peripheral C=O groups via water molecules similar to those systems having regular arrangements of hydrated chlorophyll aggregates[17]. This regular arrangements is also evident from mono exponential anisotropic decay. The dipole moment of water molecules in hydrogel matrix in the axial position points towards the central mg atom because of local pseudo C_{2v} symmetry[18, 19] around the oxygen atom. Some portion of negative charge is donated to the Mg atom and the amount of charges increases. The electronic charge is transferred through the macrocycle to the peripheral C=O group which results in increase C=O resonance structure decreasing the value of C=O stretching force constant and intensity decreases. In addition the macrocycle breathing vibration which is very closely related to Mg coordination shifted from 1645 cm^{-1} in hydrogen bonded and 5th coordinated chlorophyll in ethanolic solvent to 1590 cm^{-1}.in aqueous environment indicates that there is a possibility of the presence of 6^{th} coordinated Mg in Chlorophyll macrocycle, which may arise through the interaction with water molecule in hydrogel environment or through nitrogen in chitosan matrix. Thus it can be predicted that Chl-a molecules may be interactive with chitosan hydrogen scaffold through 6th coordination like photosystem II rather than isolated monomeric form[20, 21].

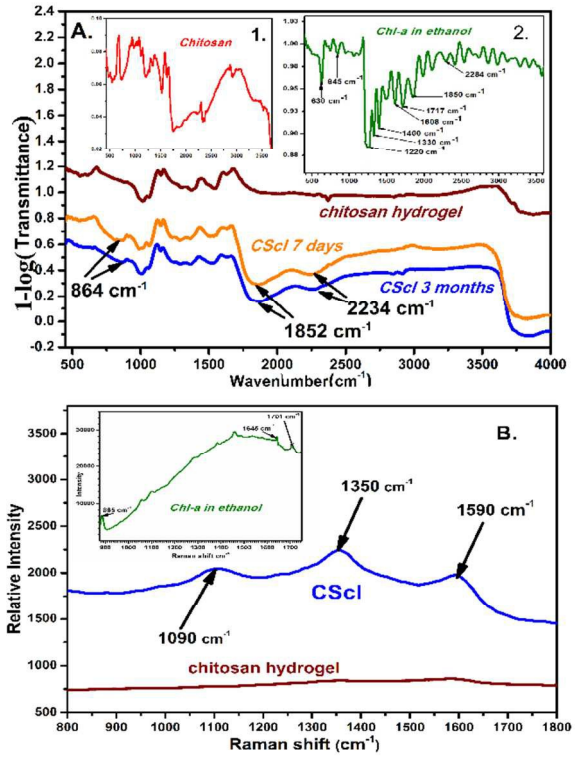

Fig. 3.A. FTIR transmittance spectra of all samples at different time intervals, **B.** Resonance Raman spectra of *CScl.* In Fig. 3.A. inset 1 and 2 are infrared spectra of bare chitosan polymer & Chl-a in ethanol respectively. The IR and Raman spectra shows successful formation of Chl-a entrapped chitosan hydrogel. Shifts in IR as well as Raman spectra depicts there may be Chl-a matrix interaction via water molecules and coordinated central Mg atom.

Fluorescence properties:

To elucidate the inter-molecular excitonic migration or excited-state interaction through stacked Chl-a molecules entrapped within chitosan matrix the time-resolved fluorescence decays of CScl have been evaluated [Fig. 4.A]. The signature of different excitonically interactive species, evident from 600nm and broad inhomogeneous absorption cross section quite similar to photosystem I is supported by TCSPC data. The fluorescence decay time (τ) values with tri-exponentially fitted decay curves [Table 1] arise due to the increased conformational heterogeneity within the system as evident from UV-Vis data [Fig.2.]. The decay time of all three components are faster than monomeric counterpart which implies most of the Chl-a molecules are participated to form closely co-ordinated molecular assembly with each other within hydrogel matrix. This fact is also evident from low quantum yield calculated from equation (2). The emitting dipole strength (1.09 D^2) is much closer to monomeric Chl-a[10] implying an excitonic interaction which leads to redistribution of dipole strength over the different transitions. Because of inhomogeneous broadening and differences in the site energies, this effect is relatively small; which means, there is no strong delocalization.

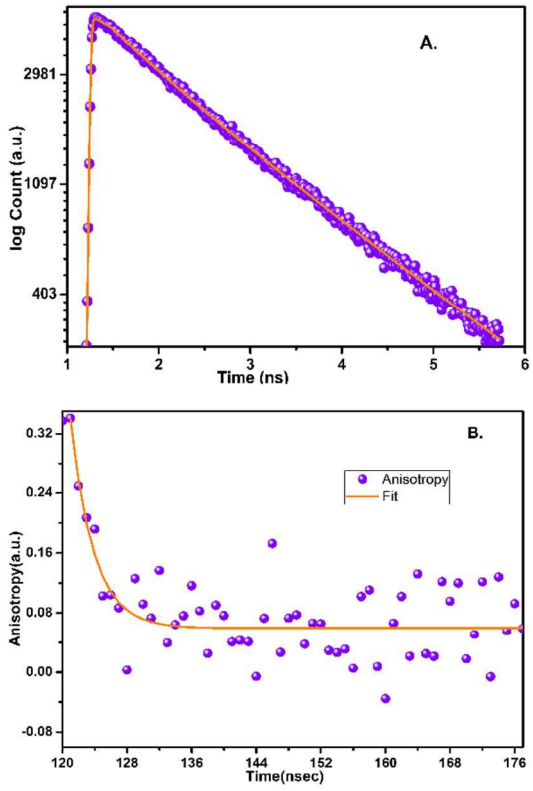

Fig.4.A. Time correlated fluorescence emission spectra, **B.** Fluorescence anisotropy of *CScl*. Short excited state lifetime and high initial fluorescence anisotropy value predicts excitonic hopping is taking place among the Chl-a molecules.

The transition to the lowest state has a dipole strength close to that of monomeric Chl-a and there are no indications of presence of strong delocalization. Therefore, it seems justified to view the energy migration as a process where the excitation hops from one pigment compartment to another, like in LHCII[22], with the hopping transfer rate 4.28 $nsec^{-1}$ [calculated from eq.5]. Although we can't exclude the probability of fluorescence quenching via amino group of matrix chitosan like some amino acid does in light harvesting complex II. The calculated low quantum yield [eq. 2] leading to reduced radiative decay rate can be attributed to highly coupled pigments in hydrogel where non-radiative rate is higher due to hopping [Table1].

Associate fluorescence anisotropy data could be fitted into monomeric decay curve with 78 pico-seconds decay time. For anisotropy measurements, a polarizer was placed before the sample. The analyzer was rotated by 90° at regular intervals and the parallel ($I_{\parallel}(t)$) and perpendicular ($I_{\perp}(t)$) components for the fluorescence decay were collected for equal times, alternatively. Then, r(t) was calculated using the formula29

$$r(t) = \frac{I_{\square}(t) - GI_{\perp}(t)}{I_{\square}(t) + 2GI_{\perp}(t)}$$

The G value of the setup is 0.70.

For a porphyrin complex in solution the time dependent fluorescence anisotropy $r(t)$ can be written as a product of two independent depolarization processes

$r = r^{ET}(t) r_{T}^{RD}(t)$, where $r^{ET}(t)$ and $r_{T}^{RD}(t)$ represent energy transfer within the complex and rotational diffusion of the complex itself[23]. The rotational dynamics of the molecule is determined by two rotational diffusion coefficients, D_l (out-of-plane rotation about the in-plane axis) and D_{ll} (in-plane rotation about the symmetry axis perpendicular to the plane). In case of a bi-exponential fluorescence anisotropy decay curve, the slower decay component arises from rotational motion of the porphyrin complex which is highly restricted in the present system due to interaction of closely packed chlorophyll-a molecules with the hydrogel scaffold. On the other hand, the faster decay component is attributed to energy transfer. For our system initial anisotropy value (r_o =0.33) implies both absorption and emission dipoles are nearly parallel, and they lie in the plane of the molecule in the 625-630 nm region which is assigned to the Qv (0-0) transition[24, 25]. The initial r_o =0.33 for the excitation to the lowest energy level implies no HOMO-FRET is operating[26, 27]. The composite absorption dipole makes an angle of 23°to the emission dipole. As the initial anisotropy is very high the 78pico-seconds time scale depolarization may be either the effect of individual porphyrin or the faster hopping depolarization within porphyrin cluster[28, 29, 30]. As from UV-Vis absorption we could not find any monomeric signature; this could be attributed to the excited state energy migration through hopping from one pigment compartment to other. The translational diffusion along the surface and the rotational dynamics of the porphyrin is expected to be restricted in highly viscous chitosan hydrogel media[31].

Data analysis:

The average excited state life time was calculated from TCSPC data using the relation

$$\tau_{avg} = \frac{a_1\tau_1^2 + a_2\tau_2^2 + a_3\tau_3^2}{a_1\tau_1 + a_2\tau_2 + a_3\tau_3} \qquad (1)$$

Quantum yield φ of the Chl-a induced hydrogel was calculated taking bare Chl-a in ethanol as a reference using the formula

$$\varphi = \varphi_{ref} \frac{\eta^2}{\eta_{ref}^2} \frac{I}{A} \frac{A_{ref}}{I_{ref}} \qquad (2)$$

Here I and I_{ref} are integrated fluorescence intensity of CScl and bare Chl-a respectively. Quantum yield of monomeric chlorophyll in ethanol is 0.25 and radiative decay rate is 0.05 nsec^{-1} [32]. Similarly A and A_{ref} denote absorbance of the same. η^2 and η^2_{ref} represent refractive indices of the hydrogel and ethanol respectively. From quantum yield and fluorescence lifetime radiative decay rate k_{rad} was calculated using equation (3).

$$k_{rad} = \frac{\varphi}{\tau} \qquad (3)$$

This rate is related to dipole strength μ^2 of emitting state by Einstein formula of spontaneous emission

$$k_{rad} = n\frac{16\pi^3\upsilon^3}{3\varepsilon_0 h_c^3}\left|\mu^2\right| \qquad (4)$$

Here n is refractive index of the solvent, h is Plank's constant, c is speed of light in free space, ε_0 is permittivity of free space. The values of quantum yield, decay rate and dipole strength calculated from these equations are tabulated in Table 2.

The strong dipole strength suggests pigments are highly coupled in terms of excitonic dipolar interaction within chitosan matrix. We further calculated exciton transfer rate through hopping (k_{hopp}) using the relation [32]

$$k_{hopp} = \frac{1}{N\tau} \qquad (5)$$

Here N_c is the number of chromophores taking part in excitonic transfer and τ is the anisotropy decay time calculated form fluorescence anisotropy. The as calculated value of hopping exciton transfer rate is 4.28nsec^{-1}. The effective interaction radius R_0^6 was also calculated by help of the equation[32]

$$R_0^6 = 8.857\times10^{-5}\frac{\kappa^2\phi J}{n^4} \qquad (6)$$

Where J is overlap integral between absorption and emission spectra of chlorophyll doped hydrogel and its value is ~75 × 10^{14} mole^{-1}cm^{-1}nm^4 [Fig. 4]. κ^2 is taken as 2/3 for usually assumed random orientation of fluorophores. ϕ is fluorescence quantum yield of the sample. From this value, distance between two adjacent chlorophyll molecules was calculated using the equation[32]

$$d^6 = \frac{R_0^6}{k_{hopp}\tau_{avg}} \qquad (7)$$

And the value came out to be 39 A^0. From initial anisotropy (0.33) angle between donor and acceptor flourophores was calculated to be ~23^{0}using the formula[33]

$$r_0 = 0.2\left(3\cos\theta - 1\right) \qquad (8)$$

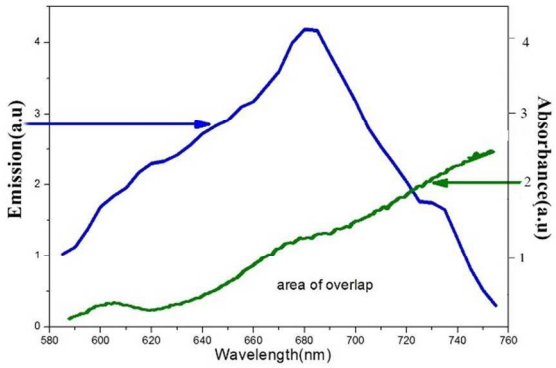

Fig.5. Overlap Integral of Absorbance & Fluorescence emission curves of *CScl.* Value of area under curve was used to calculate values tabulated in Table 1 and 2.

Table 1: TCSPC decay components of *CScl*

Excitation (nm)	Emission(nm)	a_1 (%)	τ_1 ns^{-1}	a_2 (%)	τ_2 ns^{-1}	a_3 (%)	τ_3 ns^{-1}	τ_{avg} ns^{-1}	$\chi 2$
405	675	48.14	0.0118	21.90	0.097	29.96	1.39	1.311	1.102

τ_1, τ_2, τ_3 are lifetimes of three different species and a_1, a_2, a_3 are their relative percentage amplitudes respectively.

Table 2: Calculated values of Dipole strength, decay rates and distance between chlorophyll molecules

Quantum yield	k_{rad}	k_{hopp}	N	d	R_0	$\|\boldsymbol{\mu}^2\|$	r_0	τ	Angle b/w Chl-a molecules
0.22	0.167	4.28	3	39	52	1.09	0.33	78	23 deg

Units of k_{rad} and k_{hopp}: ns^{-1}, unit of d and R_0: A^0, unit of τ:ps

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CONCLUSION:

Lastly it can be concluded that the efficiency of chitosan hydrogel matrix as a novel class of supramolecular template to elucidate excitonic fate among non-covalently adsorbed Chl-a was studied. The results show signature of excitonic hopping or exciton dissipation through matrix amino groups, like protein encapsulated photosystem of natural light harvesting process II. Thus the experimental results support suitable candidature of this hybrid material as photo harvesting component in organic solar cell. The mono-exponential decay parameter with 78 picoseconds time scale and high initial anisotropy data correspond to the perfectly aligned porphyrins [23°angle] which are participating in hopping excitonic dynamic. Therefore, it seems justified to view the energy transfer in this system as a process where the excitation hops from one pigment to another, which can be explained through localized Forster mechanism, like photosystem II and not by a coherent mechanism. This data along with the 1.311 nanoseconds excited state life time of Chl-a entrapped hydrogel can support the fact that the as prepared hybrid material can be used to construct artificial hydrogel devices, in particular solar cells with a high photovoltaic efficiency.

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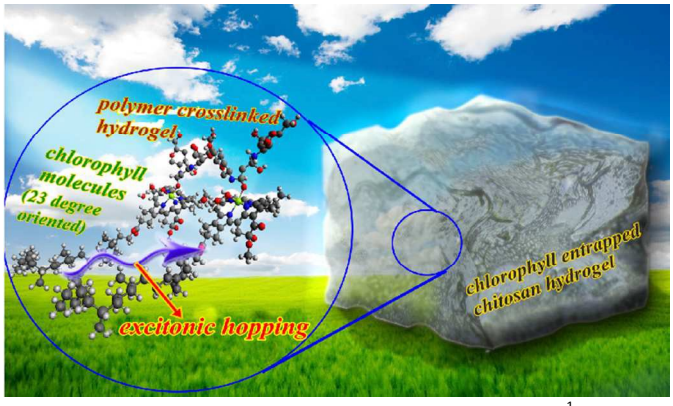

Non-coherent energy hopping [hopping rate 4.28 $nsec^{-1}$] through excitonically coupled 23° aligned Chl-a molecules within chitosan hydrogel matrix, for artificial light harvesting system.