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Topology and energy transport in networks of interacting photosynthetic complexes

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Abstract. We take inspiration from light-harvesting networks present in purple bacteria and simulate an incoherent dissipative energy transfer process on more general and abstract networks, considering both regular structures (Cayley trees and hyperbranched fractals) and randomly-generated ones. We focus on the two primary light harvesting complexes of purple bacteria, i.e. the LH1 and LH2, and we use network-theoretical centrality measures in order to select different LH1 arrangements. We show that different choices cause significant differences in the transport efficiencies, and that for regular networks centrality measures allow to identify arrangements that ensure transport efficiencies which are better than those obtained with a random disposition of the complexes. The optimal arrangements strongly depend on the dissipative nature of the dynamics and on the topological properties of the networks considered, and depending on the latter they are achieved by using global vs. local centrality measures. Finally, we compare the networks considered with the real biological networks and find that while the latter have in general better performances, the former with optimal arrangements can mimic the real networks' behaviour for a specific range of transport parameters. These results show that the use of network-theoretical concepts can be crucial for the characterization and design of efficient artificial energy transport networks.

1. Introduction

The process of energy transfer in the photosynthetic membranes of light harvesting bacteria is currently undergoing intense experimental and theoretical investigation. Although research on energy transfer in photosynthesis has a very long history [1], the refinement of experimental techniques in the last decade has dramatically enlarged the range of possible observations at the molecular level [2], thus boosting new interest in the field. Recent progress in this context includes new experimental results aimed at characterizing on one hand the structure of light harvesting systems in other biological systems [3] and on the other hand the presence and relevance of quantum effects in the energy transport process [9, 10]. These results are of fundamental interest both from the biological point of view and from the physical one since they allow to shed light on the mechanisms at the basis of energy transfer processes that take place within disordered systems surrounded by complex environments. Owing to the long course of natural selection, these processes are likely to be optimally efficient. Therefore, a more complete understanding of their features has a potential technological impact in providing useful benchmarks on how to engineer artificial light-harvesting systems.

By virtue of X-ray crystallography and AF microscopy, the structure of photosynthetic membranes of purple bacteria has been described with high precision [2]; moreover the main dynamical parameters governing the exciton dynamics have been measured or calculated [4], and a peculiar capability of the bacteria to adapt their membrane's structure to growth conditions has been revealed [5]. In these systems the basic actors in the energy transfer process are two kinds of molecular complexes, called the LH1 and the LH2. The latter play the role of antennas, capturing the incoming photons and funneling the resulting excitations to the former, that also act as antennas and furthermore contain the reaction centers (RCs) where charge separation is eventually induced [6]. Theoretical models of the process based on classical, Markovian master equations have already been proposed [7, 8]. However, a comprehensive study of the relevance of the *topology* of LH1 and LH2 arrangement for the efficient energy transfer has yet to be developed. This may be very important for applications: current techniques like nanoimprint lithography already allow to form regular patterns of light harvesting complexes [12] and future developments in this direction might allow to arrange them according to more complex designs.

The aim of the present work is to relate the dynamics and the topology in systems that can mimic the complex incoherent dissipative transport process modeled for photosynthetic membranes formed by antennas (LH2) and cores (LH1). We therefore take inspiration from the real biological networks and transpose the energy transport model [7, 8] on more general and abstract networks, focusing on the topology of LH1/LH2 arrangement. We investigate both well-known regular structures (Cayley trees and regular hyperbranched fractals) [14, 15, 16], and randomly-generated structures. Regular structures are more controllable (their topology depends just on a few parameters) and more suitable to single out the relevant topological factors affecting the dynamics. On the other hand, random networks allow to take into account irregular topologies with different degrees of disorder. In order to characterize the networks' nodes we consider different network-theoretical centrality measures, selected among the most common measures used in the description of dynamical processes on complex networks, and use them as a guide to choose different arrangements of the LH1 and LH2 on the network.

Our analysis shows that the networks analyzed display in general a high sensitivity of

the efficiency of the energy transport with respect to the choice of the antenna/core arrangements. In particular, the use of centrality measures allows to highlight how specific arrangements can ensure a better/worse efficiency with respect to the random arrangement. While the type of arrangement which is more appropriate depends on the specific geometric properties of the networks (e.g. average distance between nodes), our results show how the network-theoretical concepts applied can guide the analysis and the design of artificial networks supporting energy transport processes. The efficiencies obtained for the best arrangements are then compared with those of real biological networks with the same number of nodes and with those obtainable by applying an optimization algorithm. Our analysis shows that in general, real networks, depending on the values of the parameters, have comparable or better efficiencies than the artificial ones, while the optimization procedure allows for significantly better performances only for the kind of random networks considered.

This work is structured as follows: in Sec. 2 we introduce the basic notions on light-harvesting membranes and we review the light harvesting membrane model used in the paper. In Sec. 3 we introduce the types of networks and the main network-theoretical tools used in this work. In Sec. 4 we discuss our main results on the relation between network topology and efficiency. Sec. 5 closes the paper with some final remarks.

2. Energy transfer in purple bacteria

The first step of the photosynthetic process of purple bacteria takes place in intracytoplasmic photosynthetic membranes, where electromagnetic energy (photons) is captured and transformed into electronic molecular excitations, and eventually exploited to reduce quinone to quinol [6].

The whole process is based on two different kinds of pigment-protein complexes called LH1 and LH2 which grow in the membranes. The LH2 (which have a ring shape with octameric symmetry and contain 16 B-850 and 8 B-800 bacteriochlorophylls) play the role of antennas, absorbing incoming photons and transferring the resulting electronic excitation to the LH1. The LH1 complexes (which have a ring shape with 16-fold symmetry and contain 32 B-875 bacteriochlorophylls) are also effective in absorbing light, at a different wavelength, and they contain the reaction centers (RC) where the excitation is absorbed by a special pair of chlorophylls, inducing ionization of the pair, i.e. charge separation. Electrons freed in the process are then captured by quinone and cause the subsequent reduction of quinone to quinol, together with protons available in the cytoplasm [6]. Excitations are initially created on one complex via photon absorption and can hop to neighboring complexes through a Förster resonance mechanism.

The membrane structure is known in great detail, since AFM techniques have provided high-resolution images of the membranes of *Rsp. photometricum* [5] (for pictures and for a simplified depiction in terms of the constituent complexes see [5, 7]); LH2 complexes are always more abundant than LH1 ones: however, the $s = N_{LH2}/N_{LH1}$ ratio, also called stoichiometry, varies depending on the environmental conditions. Light-harvesting membranes show a remarkable ability to adapt to the intensity of the incoming light: bacteria grown under low light intensity (LLI, $\sim 10W/m^2$) conditions have a stoichiometry $s_{LLI} \approx 7 - 9$, while those grown under high light intensity (HLI, $\sim 100W/m^2$) conditions have a stoichiometry of $s_{HLI} \approx 3.5 - 5$. As for the network geometry, the membranes have a planar structure where complexes are densely packed, and the cores (LH1+ RC) are surrounded by LH2 complexes (5-7 on average) [5].

There is evidence of core-core clustering, i.e. two cores tend to be found in close contact or separated by an LH2 at most. The membranes have an approximately repetitive pattern; it was shown that if one isolates a minimal area with fixed s , its behavior does not significantly differ from that of the larger membrane [7]. A crucial feature of the energy transport process is the fact that when an excitation leads to charge separation within a RC, the latter features a “busy” time interval during which quinol is produced, removed and then a new quinone becomes available; therefore the RC is “closed” for a time interval t_{block} , called recycling time, during which it cannot exploit incoming excitations. So at any time only some of the RCs are available for turning the excitation into a useful charge separation. The number of available RCs decreases with increasing t_{block} and the transport process passes from the active regime in which all RCs are open to the saturated regime in which all RCs are closed. The global dynamics results from a non-trivial interplay of excitation transport to the cores and RC cycling.

The problem of modeling energy transfer processes in biological and artificial systems has been thoroughly studied in the past decades, and models of the excitation transport dynamics in light-harvesting complexes have been developed in order to take into account both incoherent and coherent phenomena [11]. Here we focus on a simple classical Markovian model developed in [7, 8] where the dynamics can be reproduced and analysed either with a Master equation approach, or with random walk simulations. Results obtained by either procedure show excellent agreement.

The membrane is modeled as a network of $M = 2N_{LH1} + N_{LH2}$ sites, where links are defined by proximity (only adjacent sites are connected). The N_{LH1} RC sites have a single link with the surrounding LH1. The process of energy transfer involves three steps: a) a photon is absorbed at a rate R , exciting some LH (1 or 2) b) the excitation hops from one site to a neighboring site with typical (measured) time $t_{X \rightarrow Y}$ that depends on the specific complexes X, Y until it either dissipates (with typical dissipation time t_{diss}) or leads to charge separation in a RC (with typical time t_{cs}) c) after charge separation has occurred, the RC remains in a closed state for time t_{block} and becomes a quencher for excitations, increasing its dissipation rate ($t_{diss}^{RC} \ll t_{diss}$). The rate of photon capture depends on the LH1 and LH2 cross sections at the relevant incident light wavelength: the total cross section is $\sigma = \sigma_1 N_{LH1} + \sigma_2 N_{LH2}$, with $\sigma_1 = 67.29 \text{ \AA}^2$ and $\sigma_2 = 116 \text{ \AA}^2$. We have that $\sigma = N[\sigma_1 + \frac{(\sigma_2 - \sigma_1)}{1+1/s}]$ where $N = N_{LH1} + N_{LH2}$. Since $\sigma_2 - \sigma_1 > 0$, if the number of components N is fixed, then the higher the stoichiometric ratio $s = \frac{N_{LH2}}{N_{LH1}}$, the higher the total cross section. The rate of photon capture is $R = I\sigma/h\nu$, with I the light intensity at the relevant wavelength. In Table 1 and 2 we report the values of the relevant dynamical parameters of the LLI- and HLI- adapted membranes [4, 7, 8] composed by $N = N_{LH1} + N_{LH2} \sim 180$ sites.

Table 1

	I	N_{LH2}/N_{LH1}	σ	R^{-1}	t_{diss}	t_{diss}^{RC}	t_{cs}
HLI	100 W/m^2	4.64	$\approx 12 \text{ \AA}^2$	0.02 ms	1 ns	30 ps	3 ps
LLI	10 W/m^2	7	$\approx 14 \text{ \AA}^2$	0.16 ms	1 ns	30 ps	3 ps

The transfer times from complex $X \rightarrow Y$ are also taken from [7]:

Table 2

$t_{LH1 \rightarrow LH1}$	$t_{LH2 \rightarrow LH2}$	$t_{LH1 \rightarrow LH2}$	$t_{LH2 \rightarrow LH1}$	$t_{LH1 \rightarrow RC}$	$t_{RC \rightarrow LH1}$
20 ps	10 ps	3.3 ps	15.5 ps	25 ps	8 ps

The timescales for energy capture, excitation lifetime and RC reopening are roughly $R^{-1} \sim 10^{-1} - 10^{-2} \text{ ms}$, $t_{diss} = k_{diss}^{-1} \sim 1 \text{ ns}$, $t_{block} \sim 1 \text{ ms}$ respectively. The recycling time t_{block} can differ significantly depending on the specific kind of bacterium analyzed ($1 - 30 \text{ ms}$). Since $t_{diss} \gg R^{-1}$ simultaneous occurrence of two excitations in the network is very unlikely, therefore the system can be modeled as if a single excitation were present in the network at each time t . Moreover, for any fixed t_{block} the number of closed RC rapidly reaches its average value and it fluctuates around it during the lifetime of a single excitation. Each excitation sees an effective fraction of closed RCs corresponding to a given average value [7]. Due to the separation of timescales, the single excitation transfer and trapping can be described in terms of the random migration of a single excitation in a membrane with an effective fraction of closed RC.

This allows for a Master equation treatment of both active (all RCs open) and saturated (most RCs closed) photosynthesis. More precisely, the process is governed by different probability rates and thus can be modeled by a (Markovian) Master Equation (ME), $\frac{dp_m}{dt} = \sum_n K_{mn} p_n$, whose solution is $|p(t)\rangle = e^{Kt}|p(0)\rangle$ (the N -dimensional vector $|p\rangle$ is composed by the probabilities $\{p_n\}$ for the excitations of being in site n). The transfer matrix K can be written as [7]:

$$\begin{aligned} K_{mn} &= W_{mn} - \delta_{mn} \left(\sum_l W_{ln} + \delta_{n,RC^o} k_{cs} \right) - \\ &= -\delta_{mn} (k_{diss}(1 - \delta_{n,RC^c}) + k_{diss}^* \delta_{n,RC^c}) \end{aligned} \quad (1)$$

where: the excitation transfer rates W_{mn} are taken as the inverse of the excitation transfer times given in Table 2, $k_{diss} = t_{diss}^{-1}$, $k_{diss}^* = t_{RC^c}^{-1}$, $k_{cs} = t_{cs}^{-1}$. In the ME approach, the effect of the recycling time of RCs can be taken into account by keeping N_{block} RCs closed, where N_{block} is determined as the average number of RCs closed at time t in a fixed illumination condition. For each value of N_{block} , one randomly chooses the initial position of the excitation in the network, and evaluates some relevant functionals (efficiency, excitation lifetime, etc.: see below). The procedure is repeated a high number of times and one finally determines the average of the functionals for a given N_{block} . ‡.

Alternatively to the ME approach one can implement a random walk simulation: (single) excitations are created at random times $\{t_i\}$, which are determined in advance by using a Poissonian distribution, in sites chosen at random§; the created excitations follow a random walk, and the probability of jumping from a site j in a given time step δt is given by $p_{jump}^j(\delta t) = K_j \delta t$ with

$$K_j = \sum_{i \neq j} W_{ij} + k_{diss}(1 - \delta_{j,RC^c}) + k_{diss}^* \delta_{j,RC^c} + k_{cs} \delta_{j,RC^o} \quad (2)$$

(thus remaining on the same site or jumping to a neighboring one according to different probabilities) until they dissipate or lead to charge separation in a RC. When charge

‡ The exact relation between N_{block} and t_{block} is obtained by $t_{block} = \frac{h\nu \cdot N_{block}}{\eta(N_{block}) \cdot I \cdot \sigma}$ where $\eta(N_{block})$ is the quantum yield of the process (see below) when N_{block} RC are closed

§ LH1 with probability $p_1 = \frac{N_1 \sigma_1}{N_1 \sigma_1 + N_2 \sigma_2}$ and analogously for LH2

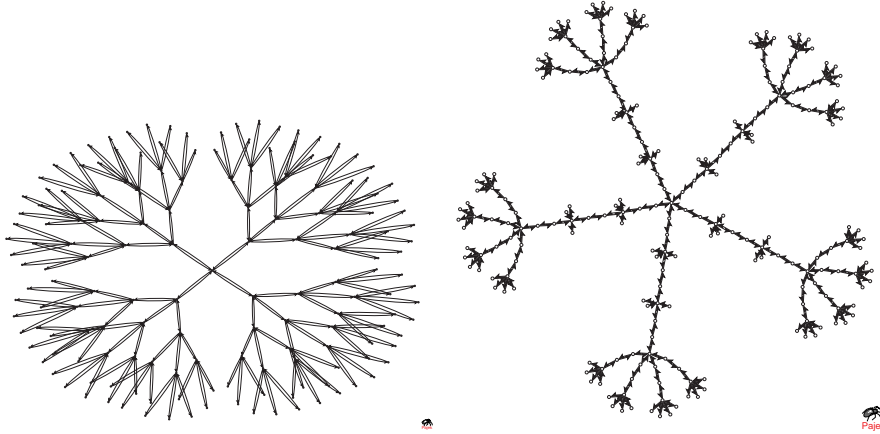


Figure 1: (Left) 4-th generation 4-Cayley tree (Right) 3-rd generation RHF with $f = 5$.

separation occurs, the RC closes and remains closed for time t_{block} in the simulation. The simulation covers a long time of $\sim 1s$, so that the histories of 10^5 excitations are simulated [13].

The optimality and robustness of energy transfer are characterized by performance measures: the most relevant is the measure of efficiency of the transport process η i.e, the probability that an excitation lead to a charge separation starting from any complex.

In the ME approach, this quantity can be obtained from the inverse transfer matrix K^{-1} . Indeed we have $\eta = \int_0^\infty \omega_{cs}(t)dt$ where $\omega_{cs}(t)$ is the probability of an excitation causing charge separation at time t and is given by $\omega_{cs} = k_{cs} \sum_{n \in RC} p_n(t) = k_{cs} \sum_{n \in RC} \langle n | e^{Kt} | p(0) \rangle$ where $|n\rangle$ is the probability vector corresponding to probability 1 of being in site n . Therefore $\eta = -k_{cs} \sum_{n \in RC} \langle n | K^{-1} | p(0) \rangle$.

In the random walk approach we evaluate the ratio $\eta = N_{cs}/N_{abs}$ where N_{cs} is the number of photons that are used for charge separation in RCs and N_{abs} the total number of photons absorbed by the network.

3. Biologically-inspired networks and network-theoretical tools

3.1. Selected networks

Our main aim is to address the role of topology in the dynamics of biologically inspired light-harvesting membranes. The very structure of light-harvesting membranes allows to regard them as complex networks, where the LH1, LH2 and RC play the role of nodes. Therefore we will make use of the proper tools developed in complex networks theory in order to build different regular and randomly-generated structures and simulate on them the energy transport dynamics described above.

We start by introducing the particular networks we will focus on: *i*) Cayley trees (CT) *ii*) regular hyperbranched fractals (RHF) and *iii*) randomly-decimated hexagonal networks (RN). As for CTs and RHF, they are well-known regular structures which have been considered in models of energy transport [14, 15, 16]. A possible natural way to

generate planar networks that could be seen as possible realizations of light-harvesting networks is to consider for example randomly-decimated hexagonal networks (RN). These are obtained according to the following prescription: we consider a hexagonal lattice of N_{tot} sites and remove m randomly-chosen links such that the connectedness of the network is preserved. For different values of m we repeat the procedure $N = 100$ times in order to obtain different ensembles of RNs.

As for the Cayley trees (CT), they are constructed as follows. The n -th generation d -Cayley tree (see fig. 1) is a tree of n levels in which all vertices on the interior have degree d , while vertices on the outermost layer have degree 1.

The RHF instead are constructed as follows. A first generation (RHF) (as shown in fig. 1) of functionality f is a star graph consisting of a central vertex connected through f edges to f surface vertices. To construct a second generation RHF, f copies of the first generation RHF are connected to the core first generation RHF through a single leaf-leaf edge. This procedure is repeated n times for an n -th generation RHF.

In this work, we shall always consider the following network topologies:

- real HLI and LLI networks [17] (note that LLI and HLI networks have a different topology)
- RNs: from the initial network of 256 sites and 768 links, $m = 193$ or $m = 321$ links are removed, so that the mean degree becomes ~ 4 or ~ 3 .
- CTs with $d = 4, n = 4$
- RHF with $f = 5, n = 3$

3.2. Network-theoretical centrality measures

We now introduce the basic network-theoretical tools used in the following analysis. Our aim is to quantify how the transport efficiency is affected by different arrangements of the cores on a given network.

An important effort in the development of the theory of complex networks has been devoted to the assessment of the “relevance” of nodes within a network, i.e. to the study of *centrality measures* [18]. A huge variety of such measures has been proposed in the literature: the usefulness of a given measure depends strongly on the specific problem at hand, since the latter determines which nodes are more “important” from case to case.

Two large families of centrality measures are the set of degree-like and the set of betweenness-like centrality measures. Degree-like measures are essentially based on counting the number of paths emanating from the node. Different measures are obtained considering different path lengths and different kinds of paths (edge- or node-disjoint, geodesic, etc.). The simplest of such measures is the *degree*(DEG) [19]: the degree k of a node is simply the number of nodes to which it is connected (i.e. the number of paths of length 1 emanating from the node). Betweenness-like measures instead are based on counting the number of paths that pass through a given node. Again, different measures are obtained considering different path lengths and different kinds of paths. The most common of such measures is the *shortest path betweenness centrality*(SPB) [20], which counts the number of shortest paths through the node (notice that the shortest path is not uniquely defined, but in general there are many different paths of minimal length between two nodes). The shortest path betweenness centrality of node k is defined as $B_k = \sum_{ij} \frac{g_{ijk}}{g_{ij}}$ where g_{ij} is the total number of

shortest paths from node i to node j and where g_{ijk} is the total number of shortest paths from node i to node j passing through node k . The fastest known algorithm [22] allows to compute it for all nodes in the network in $O(N^2 \log N)$ steps where N is the total number of nodes.

While the degree is a local measure of node centrality, depending only on the structure of the network in the immediate neighbourhood of a given node, the shortest-path betweenness is a global measure of node centrality, since it takes into account the structure of the whole network. In the following, we will systematically characterize the nodes with the above described local (DEG) and global (SPB) centrality measures in order to determine the arrangements of the RCs in the given networks.

4. Energy transport on biologically inspired networks

We now outline the setting and the main steps of our numerical analysis and we describe the functionals that will allow for a thorough characterization of the exciton dynamics on the selected networks and of its efficiency.

We start by evaluating the DEG, SPB of all nodes for each network considered (CT, RHF, RN). A full characterization of the network in terms of these measures is presented in the Appendix. We obtain different possible arrangements of the cores (LH1+ RC) in the network as follows. The nodes of a given network that are occupied by LH1 are selected with the following three criteria:

- randomly
- nodes with maximal SPB, or DEG
- nodes with minimal SPB, or DEG

and then a single RC node is added to the network, with a single link to the corresponding LH1. While other choices are possible, these are the basic and natural ones that can allow to test how the transport efficiency can be affected by different arrangements of the RCs on a given network. If a given criterion does not allow to univocally identify the core position on the network we randomize the corresponding possible choices.

As already mentioned, we have chosen two possible settings: for the High Light Intensity (HLI) we use the value of intensity $I_H = 100 \text{ W/m}^2$ and correspondingly the stoichiometric ratio $N_{LH2}/N_{LH1} = 4.64$; for the Low Light Intensity (LLI) we use the value of intensity $I_H = 10 \text{ W/m}^2$ and correspondingly the stoichiometric ratio $N_{LH2}/N_{LH1} = 7.04$. The values of all the relevant parameters [7] are reported in Tab. 1 and 2.

For each network topology and for each choice of LH1 arrangement, we simulate the random walk dynamics with t_{block} varying over a large range of values ($10^{-3} \text{ ms} - 10^3 \text{ ms}$) and we evaluate the following quantities, considered as functions of the recycling time t_{block} : the efficiency η , the average lifetime $\langle \tau \rangle_{cs}$, the average maximal distance $\langle d \rangle_{cs}$ (i.e. the distance, in steps, between the initial site of the exciton and the most distant site it reaches during its random walk) and the average exploration parameter $\langle x \rangle_{cs}$ (number of different sites visited by the exciton/total number of sites) of the excitations that are used by RCs for charge separation, the average fraction of closed RCs $\langle n_{RC}^c \rangle = \langle N_{RC}^c / N_{RC} \rangle$. The results of the random walk dynamics have been compared with the ones obtained in the master equation approach and the two methods show perfect agreement.

4.1. Characterization of the dynamics under different LH1 arrangements

We now show how the functionals η , $\langle \tau \rangle_{cs}$, $\langle d \rangle_{cs}$, $\langle x \rangle_{cs}$, $\langle n_{RC}^c \rangle$ are of use in characterizing the dynamics and its relation with the topology of LH1/RC arrangement in CTs. Analogous considerations also hold for the remaining network topologies (RN, RHF). In particular, the analysis of the dynamics will be essential in understanding the behavior of the *sensitivity* of the network to different LH1/RC arrangements.

As a first general comment, we note that the dynamics is characterized by three important time scales, given by the absorption rate R^{-1} , the typical dissipation time t_{diss} and the recycling time t_{block} . In particular there are two distinct regimes: the high efficiency regime, that is characterized by $t_{block} < R^{-1} \ll t_{diss}$, i.e. the recycling time is smaller than the absorption rate; the low efficiency regime, characterized by $R^{-1} < t_{block} \ll t_{diss}$, i.e. the recycling time is greater than the absorption rate. The transition between the two regimes occurs at $R^{-1} \approx t_{block}$.

In fig. 2 (left panel) we show η for CTs in HLI and LLI for all different LH1 arrangements. Since $R_{HLI}^{-1} \approx 10^{-1} R_{LLI}^{-1}$ the transition between the two regimes occurs in HLI networks earlier than in LLI ones.

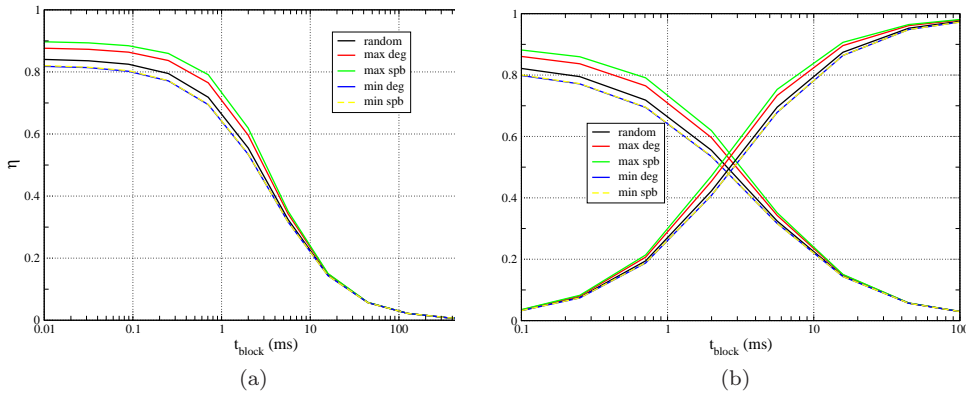


Figure 2: (Left) efficiency for Cayley trees at LLI (Right) efficiency and n_{RC}^c for Cayley trees at LLI.

When $t_{block} > R^{-1}$ each absorbed photon sees a network which is not only characterized by the stoichiometric ratio but also by the number of closed RC. The higher this number, the higher the efficiency: for any fixed t_{block} more efficient LH1/RC arrangements have a larger fraction of closed RC (RC get occupied sooner for efficient configurations). In fig. 2 (right panel) both η and n_{RC}^c are plotted together for the different LH1/RC arrangements, and this fact is apparent: indeed, the ordering of the efficiency curves is the same as the RC-closure curves.

As more RCs get occupied, it becomes more difficult for excitons to reach open RCs. This is mirrored by the behavior of τ_{cs} , plotted in fig. ???. We can see that τ_{cs} remains essentially constant in the high efficiency region ($t_{block} < R^{-1}$), then suddenly increases in the transition region ($t_{block} \sim R^{-1}$): now excitons take more time to yield charge separation, since they spend more time in searching for an open RC. A maximum τ_{cs} is reached when $\sim 90\%$ of the RC are closed. Thereafter, it becomes improbable for excitons to reach an open RC, even if they explore the network for a

longer time: unless one of the very few open RCs is found in the vicinity of the initial excitation site, the exciton is dispersed before reaching any RC. This qualitatively explains the slight decrease of τ_{cs} which then appears.

In general, the higher value of the stoichiometric ratio s , and therefore the smaller number of RCs, and the higher average values of τ_{cs} ; indeed, in the active photosynthesis regime one has that $\tau_{cs} \in [80ps, 120ps]$ for HLI while for LLI $\tau_{cs} \in [90ps, 180ps]$.

We now discuss the behavior of $\langle d \rangle_{cs}$ and $\langle x \rangle_{cs}$: $\langle d \rangle_{cs}$ is a measure of how far the exciton travels starting from the initial site, while $\langle x \rangle_{cs}$ measures how many nodes of the network the single exciton is able to visit in its path. We notice that $\langle d \rangle_{cs}$ and $\langle x \rangle_{cs}$ show the same behavior of τ_{cs} : they remain constant in the high efficiency region, then they rise in the transition region, reaching a maximum as $n_{RC}^c \sim 0.9$ and finally undergo a slight decrease, see fig. ?? . The plots of $\langle x \rangle_{cs}$ in Fig. ?? (panels c and f) show that the absorbed excitons do not explore the whole network, but only a relatively small portion of it. Indeed, only 5 – 10% of all sites are visited by the excitons that are captured by RCs; the maximum exploration is in the transition region and the values are similar for LLI and HLI networks.

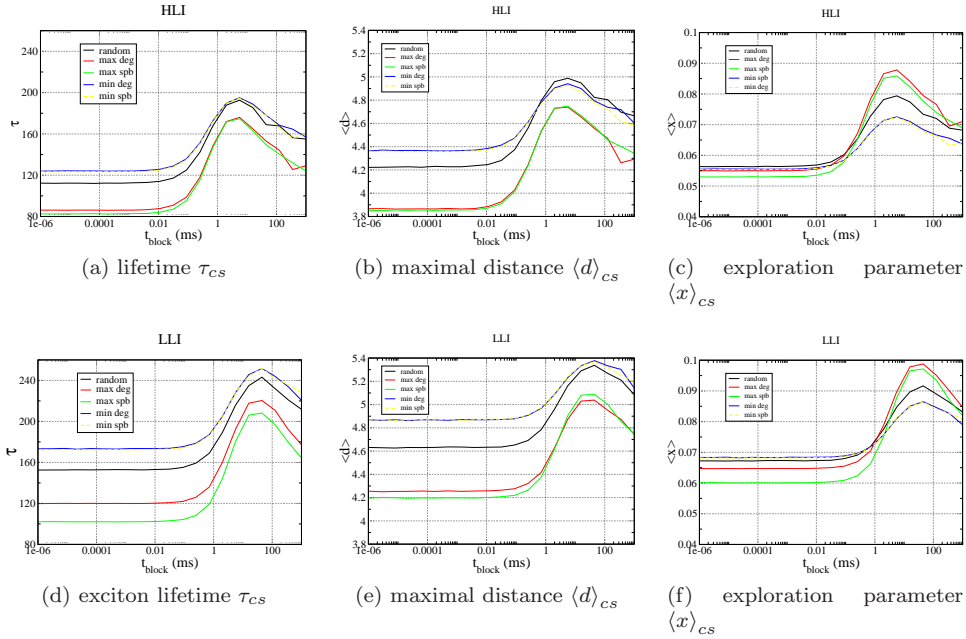


Figure 3: Cayley trees: lifetimes τ_{cs} , mean maximal distances $\langle d \rangle_{cs}$, exploration parameter $\langle x \rangle_{cs}$ of absorbed excitons as a function of the recycling time t_{block} for HLI (top) and LLI (bottom).

As for the maximal average distance traveled by the excitons, the ordering of the $\langle d \rangle_{cs}$ curves is reversed with respect to the efficiency curves: the higher the efficiency, the smaller the region explored by the exciton in order to be captured by a RC. This is reasonable since for efficient configurations excitons should find an open RC in the vicinity of the initial site and reach it in the shortest time. On the contrary, when

many RCs are closed excitons are expected to travel further away from their initial site in order to find an open RC. Indeed $\langle d \rangle_{cs}$ grows in the transition region while the ordering remains the same.

As expected, significant differences can be found when comparing HLI and LLI networks. In general $\langle d \rangle_{cs}$ and $\langle x \rangle_{cs}$ are higher for LLI networks, for all RC arrangements: the smaller the RC density, the greater the portion of the network explored on average by the excitons and the higher the sensitivity of the networks to the different RCs arrangements.

In the case of the Cayley tree the criterion that gives the highest efficiency is the maximal SPB, which requires to have the LH1/RCs clustered around the root of the network on its adjacent sites. If we focus on the LLI case we can see that in the active photosynthesis region the distance $\langle d \rangle_{cs} \approx 4.2$ is comparable with the average distance between two nodes of the network which is of 6.4 steps and the diameter which is 8, while the exploration parameter is relatively small. This means that the exciton does not explore every branch of the tree, but is nevertheless able to move from the periphery to the center of the tree and vice-versa. Therefore, it can take advantage of the global character of the centrality of the nodes occupied by the LH1/RCs. This is confirmed by evaluating the linear correlation coefficient between the betweenness of each node and the average time spent on it, which we find to be approximately 0.7 in all regions. We finally notice that both for LLI and HLI structures the maximal SPB criterion allows to obtain a significant improvement with respect to the random arrangement, thus indicating that the chosen network theoretical tools represent a useful guiding principle for the identification of the most efficient configurations.

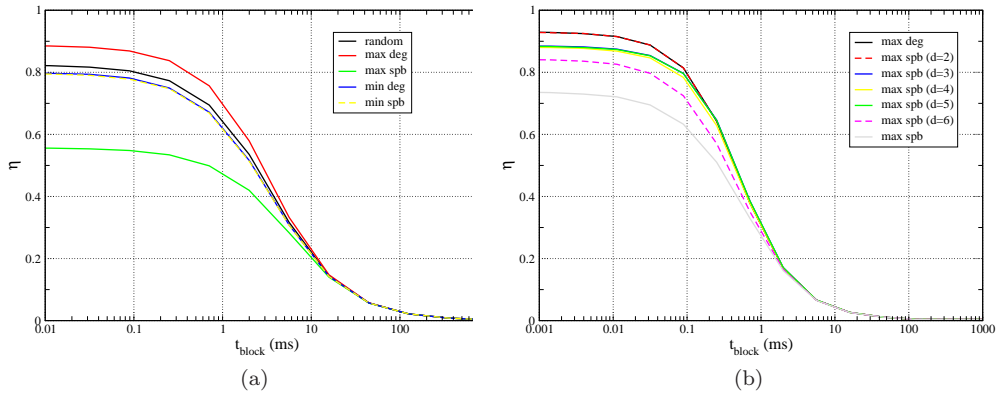


Figure 4: RHF trees: (Left) efficiency curves at LLI (Right) efficiency curves for arrangements based on $SPB(d)$ at HLI.

We now pass to analyze the behavior of the RHF networks. In Fig. 4 (left panel) we show the efficiency η for the various LH1 arrangements for the LLI case. The behavior of the other functionals with t_{block} is analogous to the one described for the CTs. However there is an important difference in that the range of the various functionals is much higher for the RHF, showing that these networks are much more sensitive to the choice of the LH1 arrangement; for example, in the active photosynthesis regime $\tau_{cs} \in [100ps, 375ps]$ for LLI while for HLI $\tau_{cs} \in [70ps, 240ps]$. The criterion that allows for a maximal efficiency in this case is the maximal degree, i.e.

a local measure of centrality of the nodes, and again this criterion allows for efficiencies which are significantly higher than those corresponding to a random placement of the LH1s.

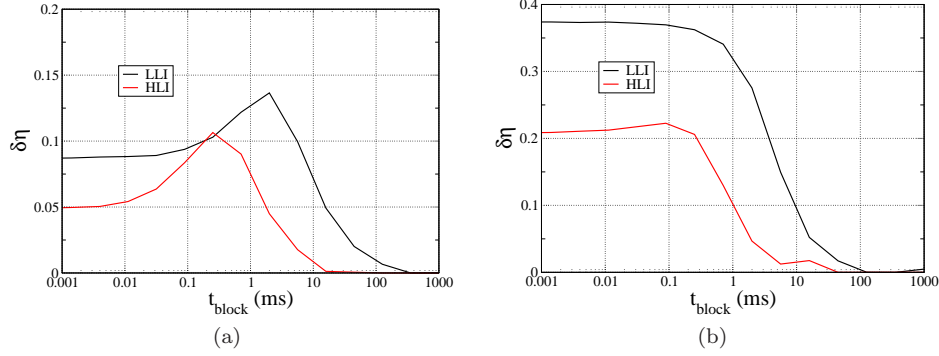
On the other hand, the least efficient criterion is the global criterion given by the maximal SPB. The latter requires the placement of the LH1s on the central nodes clustered around the root of the network; the RCs are now too far apart from the outer nodes of the network, where most of the excitons are captured. Furthermore, the values of $\langle d \rangle_{cs}$, which range between 4 and 6 for the LLI case in the active photosynthesis region, are in general small if compared to the average distance between the nodes of the network (16.68 steps). For the above reasons the resulting efficiency is considerably low (60% in the active photosynthesis region), and the dynamics does not exploit the global centrality of the nodes with max SPB. In the same way as above, this is confirmed by the linear correlation coefficient between the betweenness of each node and the average time spent on it which is now negative and equal to -0.5 in the active photosynthesis region.

This result suggests that for networks with high values of the average distance between nodes and in presence of a dissipative dynamics that does not allow for high values of $\langle d \rangle_{cs}$, in order to find optimal LH1/RC arrangements, one should in general consider topological measures able to characterize the centrality of the various nodes with respect to the local surrounding network. In order to test this idea we introduce a class of centrality measures that can be obtained by the following prescription: for each node, one can fix a distance d and consider the subnetwork of nodes whose distance from the given node is $\leq d$. One then evaluates the shortest path betweenness of the given node in the subnetwork. We shall denote such “d-local” centrality measure as $SPB(d)$. Notice that a similar measure, called local betweenness centrality has been used in the context of search on complex networks [23]. Let us consider RHF and compare the results obtained with the LH1 arrangement based on global SPB and that based on $SPB(d)$ for various values of d . In Fig. 4(right panel) we clearly see, that while the global SPB induces a very inefficient arrangement, the local $SPB(d)$ measures progressively induce more efficient arrangements as d decreases and an increasingly local structure of the network is considered [24]. While this precise hierarchy is specific to the RHF, it is also a good qualitative example of how local, rather than global centrality measures may be more appropriate for dissipative dynamics that take place on networks with large average distance between sites.

4.2. Comparison of different networks topologies and arrangement criteria

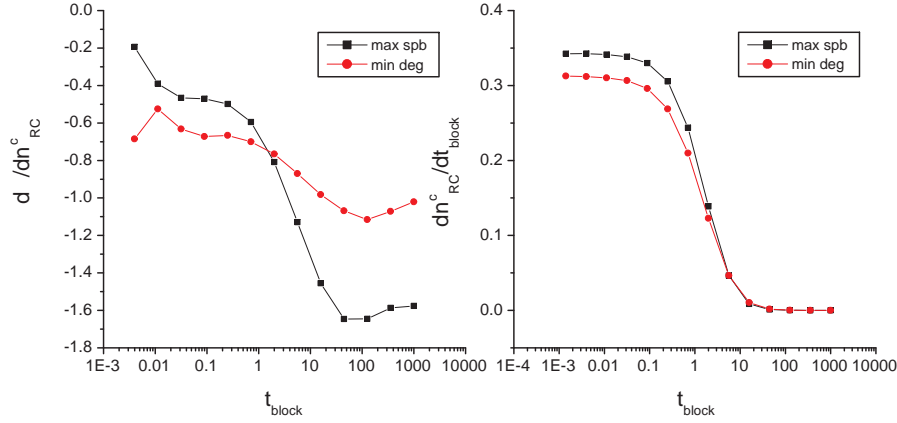
In our previous considerations, we have noticed that different LH1/RC arrangements cause significant differences in efficiencies, lifetimes and all other functionals. In the following, we shall concentrate on η which is by far the most important parameter - being one of the main goals of biological and/or artificial optimization. In particular, the basic feature we want to study is the *sensitivity of the efficiency* of a given network with respect to the choice of the LH1s/RCs arrangement. In order to quantify this sensitivity we introduce the functional $\delta\eta = |\eta_M - \eta_m|/\eta_M$ where, for any fixed values of t_{block} , η_M (η_m) is the maximal (minimal) efficiency that will correspond to the RCs arrangement giving the highest (lowest) efficiency for that given t_{block} .

In fig. 5 the sensitivities of CTs and RHF are shown as a function of t_{block} . A first important feature is that the LLI networks are in general more sensitive than the


 Figure 5: $\delta\eta$ vs t_{block} for the Cayley trees (left) and RHF (right).

HLI ones. As already anticipated this difference is related to a general feature: the sensitivity of a network grows when the number of RCs decreases and therefore, when the stoichiometric ratio becomes very high, the definition of criteria for choosing RCs arrangements becomes crucial in order to have efficient energy transport.

As for CTs the sensitivity has some initial value (5–9%) in the high efficiency regime, it grows to a maximum ($\approx 12–14\%$) approximately when $t_{\text{block}} = \bar{t} \approx 2R^{-1}$ and then falls off to zero when $t_{\text{block}} \gg R^{-1}$. It is therefore in the transition regime that in general the energy transport is most affected by the choice of RCs arrangement.


 Figure 6: Relation between $\Delta\eta$ and n_{RC}^ϵ for Cayley trees at LLI, $\dot{n}_{\text{RC}}^\epsilon$ (left), $d\eta/dn_{\text{RC}}^\epsilon$ (right).

This feature is rooted in the ability of most efficient configurations to ensure high value of efficiency and at the same time a higher resilience to RCs closure. In order to clarify this point we focus on the absolute sensitivity $\Delta\eta = \eta_M - \eta_m$ (here M = maximum SPB, m = minimum degree), which mirrors the behavior of $\delta\eta$ and on its derivative with respect to the recycling time t_{block} ; in the following we define $d\eta/dt_{block} \doteq \dot{\eta}$. In the initial part of the transition region ($t_{block} < \bar{t}$) we have that $\dot{\eta}_m < \dot{\eta}_M < 0$, i.e. the efficiency for the best LH1/RC arrangement (M) *decreases less* than that of the least efficient one (m) and therefore $\Delta\dot{\eta} > 0$. The derivative of the efficiency with respect to t_{block} can be decomposed in the product of two contributions $\dot{\eta} = \dot{n}_{RC}^c \, d\eta/dn_{RC}^c$ where n_{RC}^c is the number of RCs closed for a given arrangement. Since for all t_{block} one has $\dot{n}_{RC,M}^c > \dot{n}_{RC,m}^c > 0$, the enhancement of the absolute sensitivity must be traced back to the variation of the efficiency with respect to the number of closed RCs; indeed for $t_{block} < \bar{t}$ we have $d\eta_m/dn_{RC}^c < d\eta_M/dn_{RC}^c < 0$. This relation shows that, at least in the first part of the transition region (\bar{t} corresponds to $n_{RC}^c \sim 50\%$) the maximum SPB configuration is not only the most efficient but it is also more resilient to RCs closure. This feature no longer holds for $t > \bar{t}$ and therefore when $n_{RC}^c \gtrsim 50\%$ the sensitivity starts to decrease: $0 > d\eta_m/dn_{RC}^c > d\eta_M/dn_{RC}^c$ and $\Delta\dot{\eta} < 0$. This analysis also holds in general for RNs.

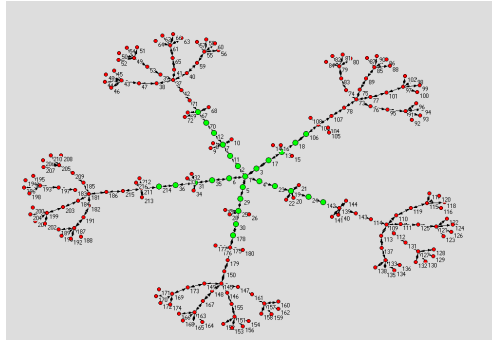


Figure 7: RHF at LLI: image for LH1 in points of max SPB.

As for the sensitivity of RHF, we first notice that the initial sensitivities are very high: 21% in the HLI case and 37% in the LLI case. This is an important indication that the analysis of the topology of RCs arrangements becomes crucial in order to maximize the transport efficiency for such kind of networks. As for the enhancement of the sensitivity in the transition region we see that this is practically absent both in the HLI and LLI case. This is due to a lower resilience to RCs closure in the case of the best arrangement (maximal DEG) and also has an impact on the overall performance of RHF. Indeed a direct comparison shows that the most efficient configuration for RHF is much less resilient than for CT, i.e. $|d\eta_M/dn_{RC}^c|_{RHF} < |d\eta_M/dn_{RC}^c|_{CT}$ and this causes the RHF to be the network with the worst performance in the transition region (see also fig. 10 where artificial networks' performances are compared with those of the real biological networks).

4.3. Random networks

We now pass to examine the random networks generated according to the procedure described in Sec. 3. In Fig. 8 we show the efficiency curves for the LLI networks with

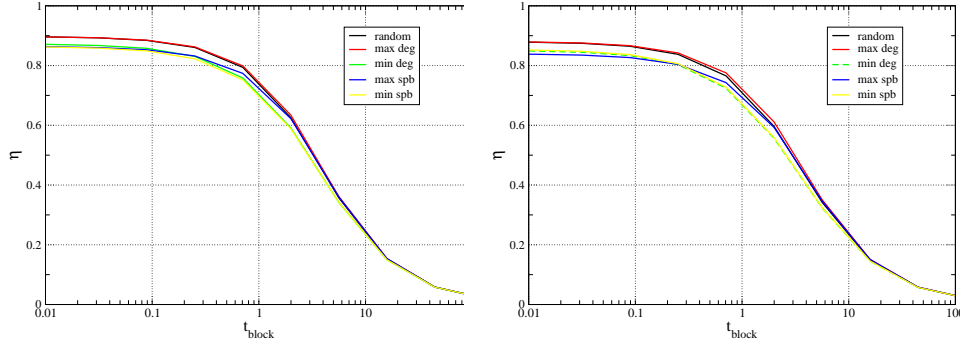


Figure 8: efficiency for random networks at LLI: (Left) $m = 193$ (Right) $m = 321$.

$m = 193, 321$ links eliminated (mean DEG= 3, 4 respectively). The efficiency η , as well as the other functionals, follow the same behavior of the previously examined cases. In particular the average maximal distance traveled in this case is $\langle d \rangle_{cs} \in [5.8, 6.5]$, which has to be compared with the average distance between pairs of sites which is ≈ 11 . As a result, the criterion that gives the best efficiency is a local one i.e., the maximal DEG. The LLI networks are more sensitive to changes in the LH1 arrangements than the HLI ones, and the sensitivity $\delta\eta$ (see Fig. 9) is between 5 – 10%. In general the efficiency decreases when the number of links suppressed grows, and this is due to the fact the progressive elimination of links results in a global lower connectivity of the networks.

For all values of t_{block} the efficiency corresponding to the best topological criterion is comparable or only slightly better with respect to that obtained with a random arrangement of the LH1. However, the data on the sensitivity show that upon selecting different LH1 arrangements for the examined RNs one can sensibly vary η , in particular

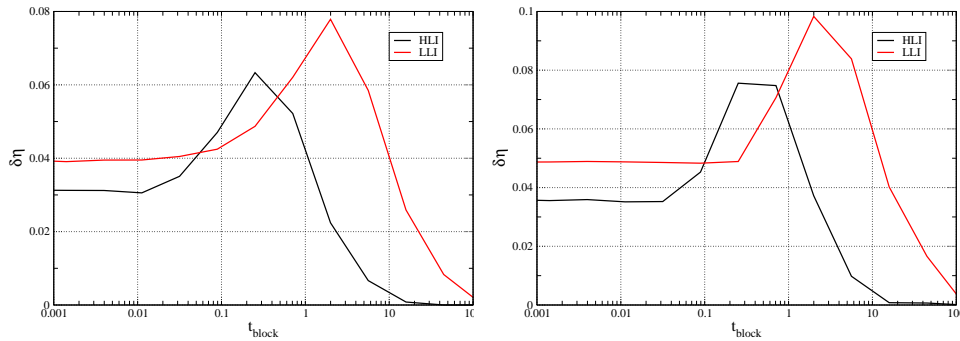


Figure 9: sensitivity for random networks (Left) $m = 193$ (Right) $m = 321$.

4.4. Comparison with real networks and optimized arrangements

We now consider the performances of LH1/RC arrangements based on centrality measures for all network topologies considered (CT, RHF and RNs) and compare them with the efficiency of the real, biological networks [17] with a similar number of nodes

and with the results obtained with a numerical optimization method. To this aim in fig. 10 and 11 we plot $\delta_x = (\eta_x - \eta_M)/\eta_M$ where $x = \{\text{real, optimized}\}$ and η_M is the efficiency for the best arrangement of a given network. A first relevant message of these plots is that the real biological networks are optimal both at LLI and HLI, in the sense that they have an equal or better performance than all other network topologies considered, and the main differences arise in the first part of the transition region. The optimality of real networks has to be related to their higher degree of connectivity with respect to the other networks analyzed. In particular they have a higher value of the average degree ($\langle k \rangle \sim 5.75$ for both HLI and LLI), and smaller values of the average distance between pairs of nodes (5.1 for HLI and 4.7 for LLI) and these features allow the excitons to explore greater parts of the network in search for an open RC; indeed, while for such networks $\langle d \rangle_{cs} \in [5.5, 7]$ is comparable or slightly higher than in the other cases, the exploration parameter reaches sensibly higher values: $\langle x_{cs} \rangle \in [0.16 - 0.29]$ for HLI and $\langle x_{cs} \rangle \in [0.17 - 0.28]$ for LLI, where the minimum corresponds to the active photosynthesis region and the maximum to the transition one.

Despite their lower connectivity, however, there are pairs of artificial network topologies and RCs arrangements that allow for efficiencies that are comparable with those of the real networks at least in the high efficiency region; this in particular is true for Cayley trees for LLI conditions with LH1/RC disposed in nodes of maximal SPB and RHF for HLI conditions and LH1/RC disposed in nodes of maximal degree. As for the RNs, those that better approximate the efficiency of the real ones are those with a higher degree of connectivity ($m = 193$).

Our analysis of artificial networks allows to identify the optimal pairs (network, arrangement criterion) that insure the realization of high efficient energy transport in all regions: (Cayley trees, max SPB), (RHF, max DEG), (random networks, max DEG). In order to further test the optimality of such arrangements based on centrality measures, we compare their efficiencies with those obtained through an optimization method. For the latter, we have used an optimization algorithm based on simulated annealing [25] to search for the best LH1/RC arrangement. The algorithm uses $1 - \eta$ as a cost function, and evaluates it in the Master equation approach in the limit of no RC closed ($t_{block} \ll R^{-1}$). Starting from a random LH1 arrangement, LH1 and LH2 positions are swapped till a minimum of the cost function is found.

The comparison (see fig. 11) shows that, in particular for regular topologies (CT for HLI and LLI, RHF for HLI) the best LH1/RC arrangements are optimal in that they allow to obtain, in all regions approximately the same efficiencies obtained by numerical optimization. The optimization procedure gives better results in the case of RNs, since of course it allows to select the best arrangement for each element of the ensemble of networks.

5. Conclusions

In our work we have taken inspiration from biological light harvesting networks present in purple bacteria and we have simulated an incoherent dissipative energy transfer model devised for these systems on more general and abstract networks, focusing on the arrangement of the two primary light harvesting complexes, i.e. LH1 and LH2. We have investigated well-known regular structures (Cayley trees and RHF), as well as

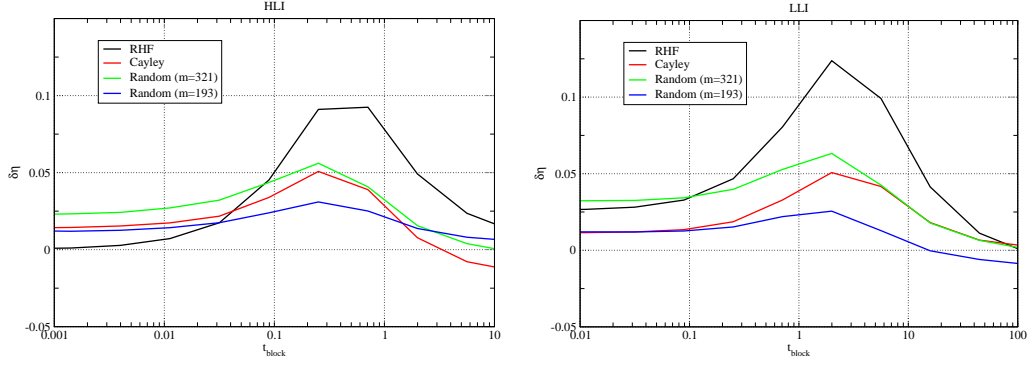


Figure 10: efficiency $\delta\eta$ vs. t_{block} for different networks, HLI (right) LLI (left)

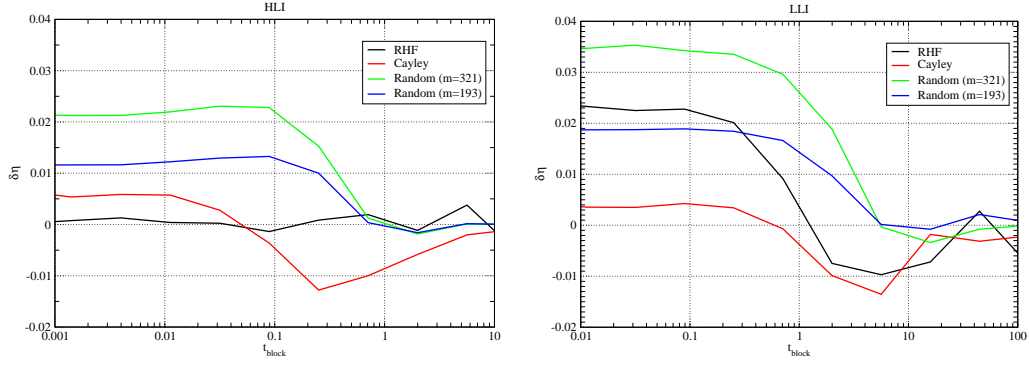


Figure 11: efficiency $\delta\eta_{\text{annealing}}$ vs. t_{block} for different networks, HLI (right) LLI (left).

randomly-generated structures and we have considered different network-theoretical centrality measures in order to select different LH1 and LH2 arrangements.

Depending on the relation between the rate of photon capture and the recycling time of the reaction centers (RC) which are placed in the center of LH1 complexes, one can identify three transport regimes (high-efficiency regime, low-efficiency and the transition regime) characterized by the increasing average number of closed RCs found by an incoming excitation.

Different LH1/RC arrangements yield significant differences in the transport efficiency. The sensitivity of the networks to changes in the topological arrangements of RCs is always higher for structures that have a lower number of LH1/RC complexes (higher stoichiometric ratio). In general, in correspondence of efficient configurations the excitons travel shorter distances in order to find open RCs and the most efficient arrangements allow to have a higher fraction of closed RCs at fixed recycling time. In the transition region, the networks have better performances when the optimal arrangement allows for a higher resilience to RCs closure.

The simple set of network-theory-based principles considered help identifying antennas/core arrangements which ensure transport efficiencies which are better (CTs, RHF) or comparable (random networks) to those obtainable with a random disposition of the LH1/RC. The optimal criteria strongly depend on the dissipative nature

of the dynamics and on the topological properties of the networks considered: global (local) centrality measures give better results for networks with small (large) average distance between the nodes.

Our analysis shows that real biological networks always have in general better performance with respect to the structures considered. Indeed, while in the high efficiency region the performances of real and artificial networks with optimal arrangements are comparable, the main differences appear in the transition region where the behavior of the real networks benefits from their higher level of connectivity that allows the excitations to explore a larger fraction of the overall network in search for an open RC.

The above results show that, while the identification of an optimal criterion for the arrangement of the RCs is in general network- and model-dependent, the use of network-theoretical measures can be crucial for the characterization and design of efficient artificial energy transport networks.

Appendix A. Characterization of the selected networks

We report in the figures below (Fig. A1,A2,A3) the distribution of the network-theoretical measures (DEG, SPB) for the selected networks. Notice that the distributions shown for random RNs (Fig. A3) are an average over $M = 100$ networks with different topology.

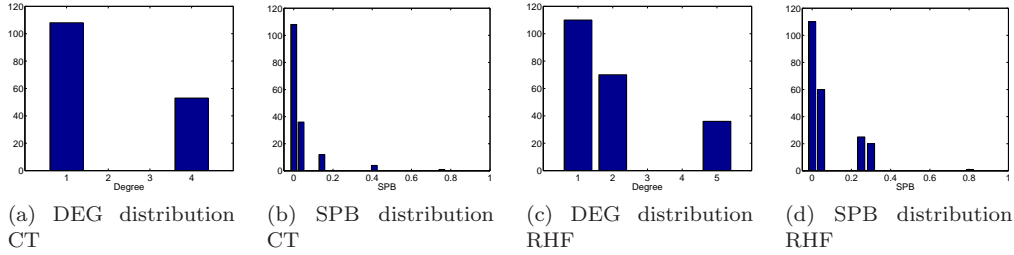


Figure A1: Distributions of DEG, SPB for CTs, $d = 4$, $n = 4$ and for RHF, $f = 5$, $n = 3$

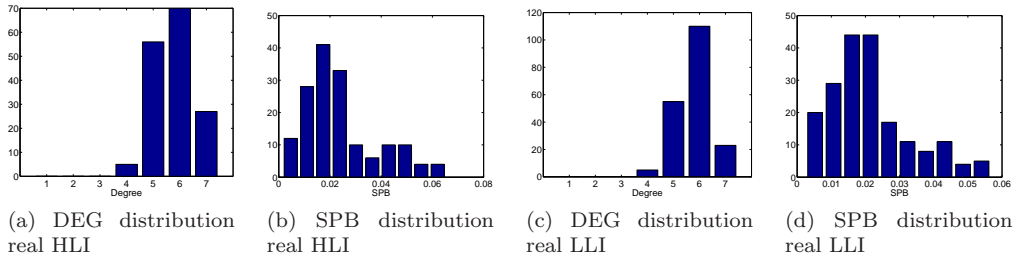


Figure A2: Distributions of DEG, SPB for real HLI and LLI networks

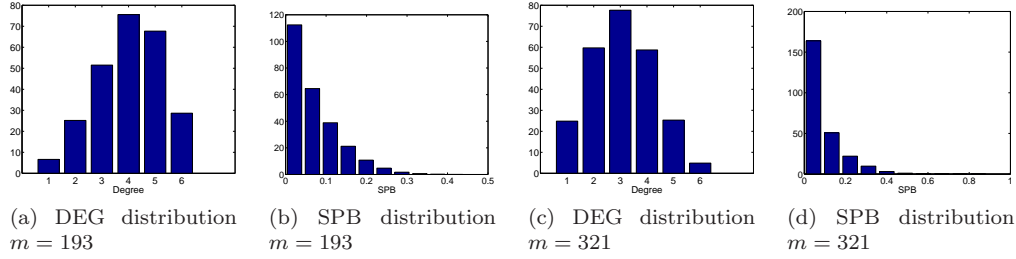


Figure A3: Distributions of DEG, SPB for random networks

As for the CTs: the DEG distribution is trivial, there are $d(d-1)^{n-1} = 108$ nodes with $\text{DEG} = 1$ (peripheral nodes) while all the others have $\text{DEG} = d = 4$; SPB is a strongly decreasing function of the generation of the nodes (their distance from the center). The number of nodes of generation k scales as $\sim d^k$, so most nodes (144) have a small SPB (< 0.1), while 12 nodes have $\text{SPB} \sim 0.2$, 4 nodes have $\text{SPB} \sim 0.4$, and one single node (the central one) has $\text{SPB} \sim 0.8$). The DEG and the SPB are poorly correlated (linear correlation coefficient $c = 0.57$).

As for the RHF: the DEG distribution is simple, a number $(f+1)^{n-1} = 36$ of the nodes (the central nodes of the component star graphs) have $\text{DEG} = f = 5$, a number $\frac{(f^{n+1}-1)}{(f-1)(f+1)^n} = 26$ have $\text{DEG} = 2$ and the remaining ones have $\text{DEG} = 1$; SPB is again a decreasing function of the distance from the central node, the majority of nodes (166) have $\text{SPB} < 0.1$ while a smaller fraction has values SPB in the range $0.2-0.4$, and one node (the central one) has a $\text{SPB} \sim 0.8$). Again, the DEG and the SPB are poorly correlated ($c = 0.47$).

As for the RNs: the DEG distribution is peaked around $\text{DEG} \sim 4$, $\text{DEG} \sim 3$, corresponding to $m = 197$, $m = 321$ and it is skew, showing a tail for small/high DEG $m = 197$, $m = 321$; the SPB distribution is decreasing, all nodes have small values of SPB (quite differently than in the case of CT and RHF), values of SPB ($\sim 0.2-0.3$) are attained only for a few nodes. The DEG and the SPB are poorly correlated ($c = 0.60$ for $m = 197$ and $c = 0.55$ for $m = 321$).

As for the real biological networks: the DEG distribution is sharply peaked around $\text{DEG} \sim 6$; the SPB distribution is irregular, all nodes have small values of SPB ($0.01-0.06$), with most node having $\text{SPB} \sim 0.02$. The DEG and the SPB display a weak correlation for LLI networks ($c = 0.70$) and a stronger one for HLI networks ($c = 0.82$).

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