

Fine-tuning photosynthesis

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Graphic: Christine Daniloff

A new analysis by MIT researchers could make it possible to design more efficient artificial systems that mimic the way plants harvest the energy of sunlight through photosynthesis.

The study is the latest in an ongoing series examining the process of <u>photosynthesis</u> and the different variables that determine its efficiency, conducted by Associate Professor of Chemistry Jianshu Cao and his postdocs and colleagues. The new work, which looks at artificial photosynthetic systems based on self-assembling molecules designed by researchers at of the University of California, Berkeley, follows a paper <u>they published</u> in October in the *New Journal of Physics* that examined the factors that determine the efficiency of natural photosynthesis.



The hope, being pursued by various research teams around the world, is to be able to eventually produce synthetic chemical systems that mimic nature's process of photosynthesis and thereby produce a more efficient way of harnessing the sun's <u>energy</u> than today's photovoltaic panels, and that can be used to produce some kind of fuel that can be stored and used when needed, eliminating the intermittency problems of solar power. Understanding how to maximize the efficiency of the process is one step toward being able to create such a system.

The new research, by Cao and postdoctoral fellow Ji-Hyun Kim, found that there are many possible shapes that can be formed by bundles of chromophores — the reaction centers within <u>molecules</u> that actually absorb particles of light from the sun, or that transfer that energy or convert it into chemical forms that can be stored for later use. Among other configurations, the chromophores readily either adopt a helical shape (like a bedspring) or form a stack of disks. In their analysis, the stacked-disk configuration proved especially easy to fine-tune for optimal efficiency.

There are three basic types of chromophores: acceptors, which absorb the light's energy; donors, which emit light; and bridges, which transfer the energy from one reaction center to another. In systems composed mainly of donors and acceptors, the addition of extra bridges can greatly increase the efficiency of the process, the researchers found. In addition, specific ratios of acceptor to donor sites lead to the most efficient transfer of energy. Their findings <u>were published</u> in *The Journal of Physical Chemistry*, and the work was supported by the MIT Energy Initiative, the Singapore-MIT Alliance for Research and Technology, the National Science Foundation and the MIT Center for Excitonics.

In the related work published last month, Cao, Class of 1942 Professor of Chemistry Robert Silbey, and their postdoctoral fellow, Jianlan Wu, had found that the efficiency of natural photosynthesis can be improved



by adding just the right amount of noise — that is, random fluctuations. Since noise usually reduces efficiency, this finding was somewhat counter-intuitive. Adding more noise could also decrease the efficiency, they found. "There's an optimum amount" of noise, Silbey explains, that produces the most efficient transfer of energy.

To explain why a certain amount of noise could be helpful, he offers the analogy of friction from the road while driving a car. Of course, friction slows the car somewhat, thus decreasing efficiency, and with too much friction the car could grind to a halt. But if there were no friction at all — such as on a perfectly smooth icy surface — the wheels would just spin and the car would not move at all. There is an optimum amount of friction somewhere in the middle, and that's also the case with noise in a photosynthetic system. In the case of photosynthesis, energy is being transferred from one part of the molecule to the next, and random environmental fluctuations — or noise — can add a push to the moving electrons carrying the energy and help propel them along, up to a point; but too much of this extra push can have the opposite effect, scattering the excitons so they are less likely to make it to the reaction center where that energy is harnessed.

The specific photosynthetic systems the team studied included those from green sulfur bacteria, which have a very common type of multichromophoric aggregates that perform the energy conversion, Silbey says.

While many teams of researchers have studied the way photosynthesis takes place in different plants, algae and bacteria, this work looked at the underlying quantum-mechanical processes and calculated how a variety of different variables affected the efficiency of the system, Cao says. "We think we have a very general picture of it now, that can be used for optimal design" of new, synthetic light-harvesting systems. This could allow fine-tuning of the timescales, temperatures and molecular



configurations to get the maximum energy output from a given amount of <u>sunlight</u>. The search for general optimization in light-harvesting systems is currently being pursued by several other groups, including those of MIT professor of mechanical engineering Seth Lloyd, Alan Aspuru-Guzik of Harvard University, and Martin Plenio of Ulm, Germany.

This theoretical analysis was triggered by experiments in the last few years, including those by Greg Engel, an assistant professor of chemistry at the University of Chicago, which demonstrated the quantummechanical basis for biological photosynthesis. "That's what got the theorists all worked up," Cao says, and led them to search for basic understandings that could lead to the most efficient possible systems. The next step will be for others to apply this understanding to the design of new synthetic systems.

Engel, who was not involved in this MIT research, says it is "a beautiful piece of work." He adds that "for a long time we have known that photosynthesis has been optimized by evolution, but understanding the way it was optimized provides a way to move forward" in trying to design similarly optimized synthetic systems. "Now that we can take advantage of this and copy some of the underlying design principles" nature has used, he says, "it opens up many new opportunities for us to take advantage of the three-and-a-half billion years of R&D that nature has done."

But this is just the beginning of a long process in terms of applying this understanding, Engel says: "There is still a great deal of work to be done. This is not the answer, this is the beginning of the roadmap, the first signpost along the way."



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