# Switching tracks: Reversing electrons' course through nature's solar cells

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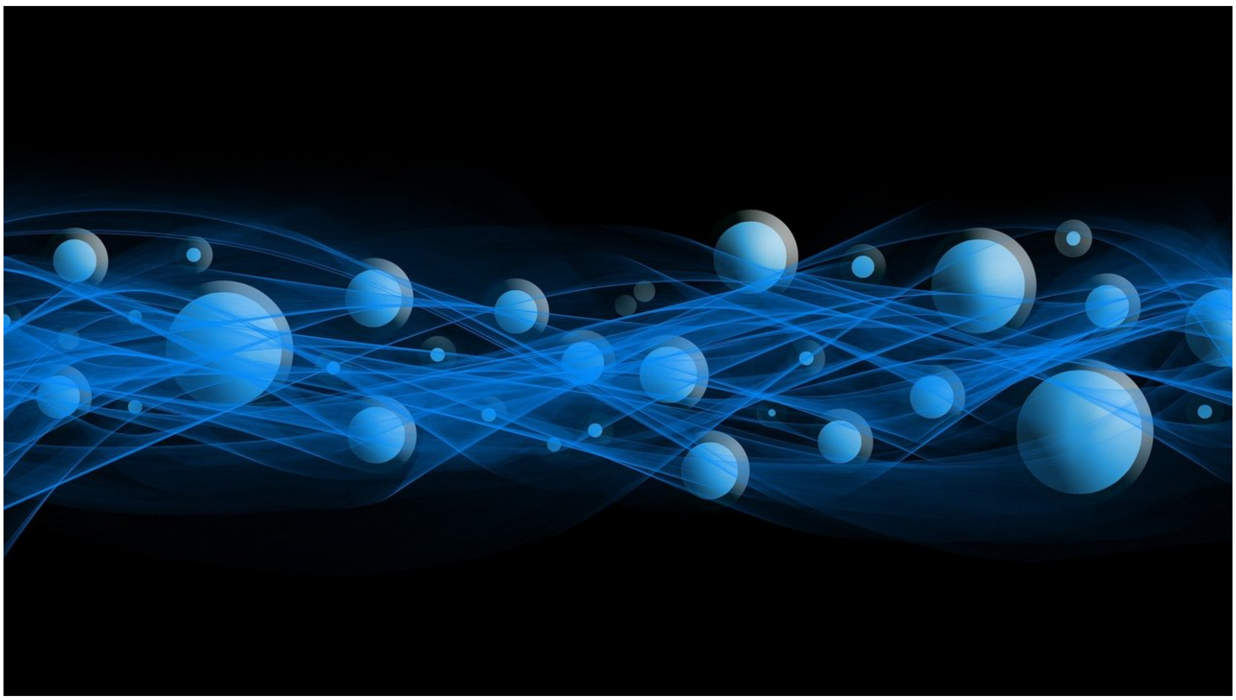

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Think of a train coming down the tracks to a switch point where it could go either to the right or the left—and it always goes to the right.

Photosynthetic organisms have a similar switch point. After sunlight is absorbed, energy transfers rapidly to a protein called the reaction center. From this point, the electrons could move either to an A-branch (or "right-track") set of molecules, or to a B-branch ("left-track") set of identical molecules.

New research from Washington University in St. Louis and Argonne National Laboratory coaxes electrons down the track that they typically don't travel—advancing understanding of the earliest light-driven events of photosynthesis. The findings were published Dec. 31 in the *Proceedings of the National Academy of Sciences* (*PNAS*).

"In the bacterial reaction center, an electron goes to the A-branch of molecules 100% of the time. We have made it go to the B-branch molecules 90% of the time," said Christine Kirmaier, research professor of chemistry in Arts & Sciences.

"After all, if you think you understand how the train and the tracks work, why shouldn't you be able to make the train go to the left rather than the right? That's essentially what we've done," Kirmaier said.

"Why two tracks have evolved is still an open question, but the ability to control which track is utilized is exciting," said Philip D. Laible, a biophysicist in the biosciences division at Argonne National Laboratory and another lead author on the paper.

"We would like to make the switching between them a more well understood phenomenon so that we could readily conduct electrons (pardon the pun) to any destination in a biological process," he said. "Right now, we are controlling features that allows for electrons to transverse a biological membrane—the first step in making energy from sunlight in this organism."

## Re-engineering a pathway

Plants, algae and photosynthetic bacteria convert the energy of sunlight into charge-separated units that they use to power life processes on Earth. And they do it in a very specific way: The reaction centers in these organisms feature two mirror image-like arrangements of protein and pigment cofactors, the A and B sides. Only one of these chains is active—the A side—while the B side is silent.

Kirmaier, with collaborator Dewey Holten, professor of chemistry at Washington University, and the team at Argonne National Laboratory have designed many iterations of photosynthetic mutants with the goal of achieving charge separation using the B branch instead. The new research re-engineers a pathway in a purple photosynthetic bacteria, one of nature's solar cells.

"Using molecular biology, we've been changing the amino acids around the pigments to try and find the magic combination to make the B branch work," she said.

The game was to make structural changes that de-tune, or make less optimal, electron transfers along the A side or normal path—and then, at the same time, speed up the reactions along the B side.

The researchers were able to step up this trial-and-error process by testing all possible amino acids at a specific target site on the A or B side, finding one or more that improve the B-side yield. They then carried that "hit" forward in the mutant background to probe the next target site, and so on.

"It was unexpected," Kirmaier said. "We picked a site, and in one of our best mutant backgrounds, placed all 20 amino acids there—and one of them gave us a 90% yield."

"This is a breakthrough achievement and something that [everyone in] the field has been actively trying to figure out for decades—ever since we first set eyes on the two tracks in a high-profile structural study in Nature nearly 35 years ago," said Deborah K. Hanson of the biosciences division, Argonne National Laboratory, another lead author of the *PNAS* paper.

## Rethinking the history of photosynthesis

The new work illuminates basic structure-function principles that govern efficient, light-induced electron transfer.

This knowledge can aid design of biohybrid and bioinspired systems for energy conversion and storage, the researchers said. The findings also will provoke additional experiments and analysis.

"The results raise lots of questions about what is required to get unidirectional charge separation," Holten said.

In nature, purple bacteria do initial charge separation with a two-step process that takes place in several trillionths of a second. But the team's new B-branch solution gets almost the same yield, even though it uses a tandem one-step process that takes 5-10 times longer.

"In the original history of photosynthesis, maybe such a combination of a fast two-step and slower one-step processes gave a 80 or 90% yield—and then, over time, it optimized," Holten said.

**More information:** Philip D. Laible et al, Switching sides—Reengineered primary charge separation in the bacterial photosynthetic reaction center, *Proceedings of the National Academy of Sciences* (2019). DOI: 10.1073/pnas.1916119117

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