

Oh Lord.

This is a very hard problem – do you have any interesting inputs to add here?

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**From:** Lowell Wood [REDACTED]  
**Sent:** Saturday, September 03, 2011 11:38 PM  
**To:** Rod Hyde; Jordin Kare  
**Cc:** 'Nathan Myhrvold'; Chuck Whitmer - External; 'Jeff Bowers'; Boris Nikolic (BGC3); [REDACTED]  
David B. Tuckerman; 'Casey Tegreene'  
**Subject:** A Quantum-Thermodynamic Ratchet For Photonic Frequency Up-Pumping?

I continue to puzzle over Bill's "cheaper-&-cleaner-&-more abundant electricity for everyone" challenge-to-Inventors – currently 'aided' (entirely legally – physician's orders! ☺) by the modern version of the traditional opium-eater's favorite ingestible. ☺ [Dr. Nikolic admonishes me to comply completely with "the doctor's orders" along these lines – which call for remarkably heavy-&-frequent dosings -- so please do blame him entirely for this missive! ☺]

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In order to generate the maximum voltage-current product from a given area of (single-composition) semiconductor illuminated with a given flux, it's clearly desirable to have monochromatic radiation that's 'matched' to the bandgap, n-&-p Fermi levels, etc. of the chosen semiconductor. However, what God gives us – in generous total quantities, if not pleasantly high fluxes ☺ -- is a ~0.5 eV Planckian spectrum with a batch of holes chewed in it, i.e., the solar spectrum at AM1, for which the maximum-attainable energy conversion efficiency is widely believed to be  $\leq 0.5$ .

Even these performance levels are attained only with a half-dozen p-n junction artfully (i.e., very expensively) 'stacked' on each other, each taking its bandgap-designated 'bite' from the incoming radiation (and thus being semi-insanely expensive, even for USG purposes) – cf. appended Figure. It clearly would be greatly preferable to have a large fraction of the energy of the solar spectrum 'presented' to a suitable photovoltaic converter-assembly after being 'transfigured' to single-energy (e.g., ~2.5 eV) photons.

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So what are the basic prospects for usefully – i.e., practically -- monochromatizing the AM1 solar spectrum in the photovoltaic context?

These prospects would seem to be of non-trivial magnitudes – at least to me-in-present condition! – as suggested by the appended items (which ‘connection’ is admittedly somewhat distant)?

Molecular quantum oscillators can have very high Qs in/about the visible optical spectrum, e.g.,  $10^6$ , when they’re in vacuum-type circumstances, i.e., are ‘natural linewidth’-constrained. However, these Qs can be depressed by as much as  $\sim 4$  orders-of-magnitude, e.g., via collisional interactions in normal (zero-P, non-resonant) media.

So, what can we do with sets-of-(preferably, high-Q molecular) oscillators ‘physically-&-spectrally associated’ with each other in a suitably engineered environment (seemingly likely enabled by contemporary lithographic capabilities, which already offers minimum features sizes most of an order-of-magnitude smaller than visible spectral wavelengths of interest)?

We would presumably arrange these molecular assemblies in stacks of planar sheets of ‘unit cells’ containing something of the order of a dozen high-oscillator strength transitions (perhaps carried on something like a half-dozen well-chosen molecules – or quantum dots?) which would together ‘cover’ the AM1 spectrum between, say, 0.5 and 1.5 microns free-space wavelength.

These would serve to ‘harvest’ most all of the inputted solar radiation over this  $\sim 1.6$  octave-width spectral band and then make it available for re-radiation by a ‘master molecular’ oscillator located proximate to the ‘unit cell’ to whose upper-level they would each be (chosen to) be chosen to couple by short-range non-radiative energy transfer while concurrently making an ‘energy contribution’ of the order of a few kT to the local medium – so as to helpfully make up energy differences between the two donating quantum oscillators and the donated-to one and (not quite incidentally) to confer a degree of thermodynamic irreversibility onto the energy transfer process.

The donated-to molecule then fluoresces the up-pumped (in the frequency sense) quantum energy with high quantum efficiency – helpfully conferred by lack-of-competing de-excitations in its surroundings, e.g., the energy-going-uphill inability to effectively back-transfer its excitation to adjacent donating molecules.

These up-pumped, quasi-monochromatic photons are then 'inputted' (via device-internal reflectors, etc. aimed at optical transfer efficiency optimization) to a photovoltaic conversion section of the device.

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Yes, of course I also have-in-mind the analogous photochemical trick, in which we convert such 'spectrally-enhanced sunlight' into high-energy chemical bond-rearrangements, e.g., energy efficiency-enhanced photosynthesis! ☺

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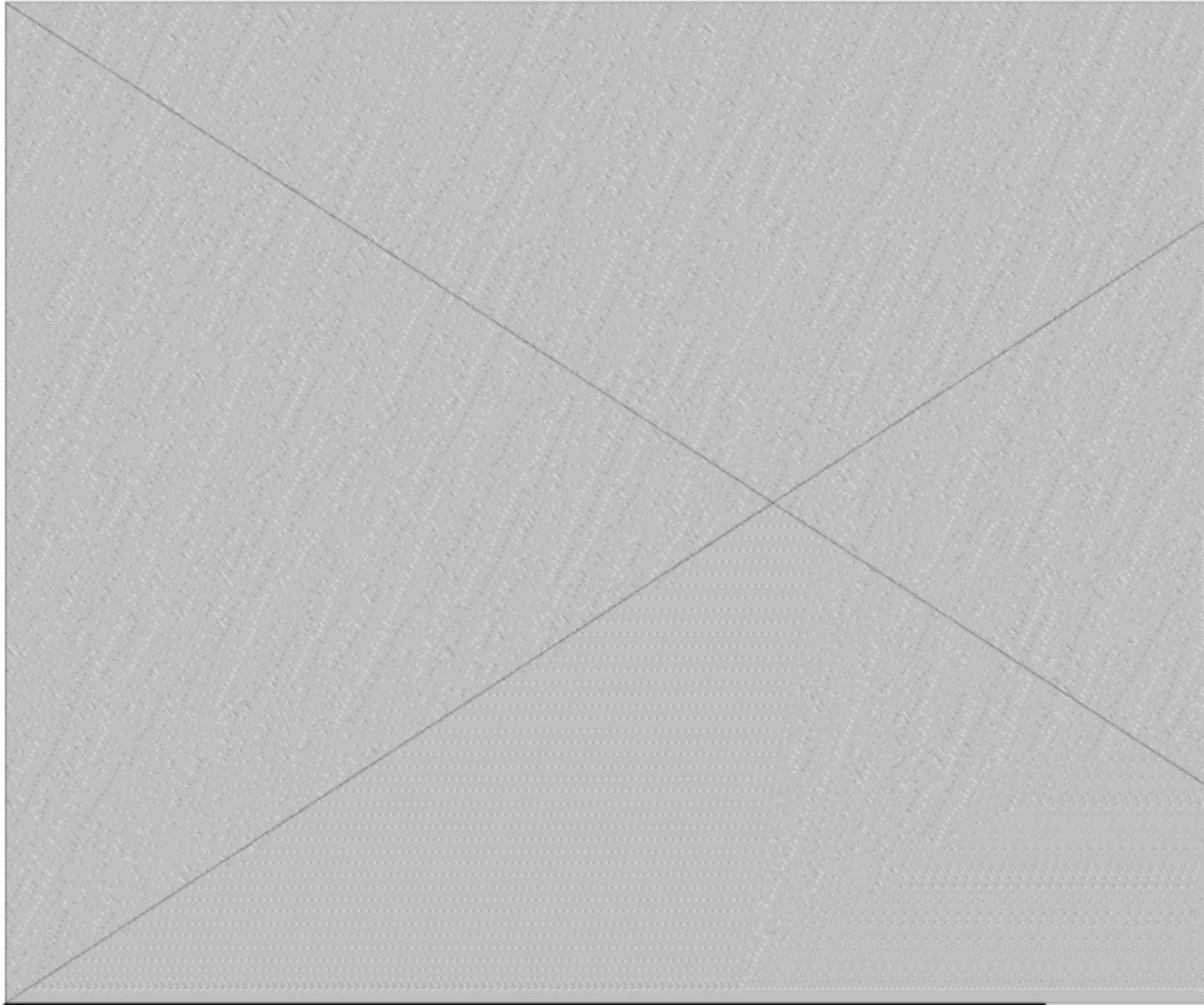
Of present interest are two distinct items:

[1] Constructive (i.e., repair-oriented!) criticism-as-may-be-indicated of the proposed physical mechanisms and stringing-togethers thereof;

[2] Comments of a 'practical' or implementation-focused character, e.g., how can this proto-device be made to work significantly better – i.e., in-any-&-all-ways-more-practical -- than as-sketched above?

Thanks!

Lowell



**Artificial light-harvesting method achieves  
100% energy transfer efficiency**

By arranging porphyrin dye molecules on a clay surface using the “Size-Matching Effect,” researchers have demonstrated an energy transfer efficiency of approximately 100%, which is an important requirement for designing efficient artificial light-harvesting systems. Image credit: Ishida, et al. ©2011 American Chemical Society

**(PhysOrg.com) -- In an attempt to mimic the photosynthetic systems found in plants and some bacteria, scientists have taken a step toward developing an artificial light-harvesting system (LHS) that meets one of the crucial requirements for such systems: an approximately 100% energy transfer efficiency. Although high energy transfer efficiency is just one component of the development of a useful artificial LHS, the achievement could lead to clean solar-fuel technology that turns sunlight into chemical fuel.**

The researchers, led by Shinsuke Takagi from the Tokyo Metropolitan University and PRESTO of the Japan Science and Technology Agency, have published their study on their work toward an artificial LHS in a recent issue of the *Journal of the American Chemical Society*.

“In order to realize an artificial light-harvesting system, almost 100% efficiency is necessary,” Takagi told *PhysOrg.com*. “Since light-harvesting systems consist of many steps of energy transfer, the total energy transfer efficiency becomes low if the energy transfer efficiency of each step is 90%. For example, if there are five energy transfer steps, the total energy transfer is  $0.9 \times 0.9 \times 0.9 \times 0.9 \times 0.9 = 0.59$ . In this way, an efficient energy transfer reaction plays an important role in realizing efficient sunlight collection for an artificial light-harvesting system.”

As the researchers explain in their study, a natural LHS (like those in purple bacteria or plant leaves) is composed of regularly arranged molecules that efficiently collect sunlight and carry the excitation energy to the system’s reaction center. An artificial LHS (or “artificial leaf”) attempts to do the same thing by using functional dye molecules.

Building on the results of previous research, the scientists chose to use two types of porphyrin dye molecules for this purpose, which they arranged on a clay surface. The molecules’ tendency to aggregate or segregate on the clay surface made it challenging for the researchers to arrange the molecules in a regular pattern like their natural counterparts.

“A molecular arrangement with an appropriate intermolecular distance is important to achieve nearly 100% energy transfer efficiency,” Takagi said. “If the intermolecular distance is too near, other reactions such as electron transfer and/or photochemical reactions would occur. If the intermolecular distance is too far, deactivation of excited dye surpasses the energy transfer reaction.”

In order to achieve the appropriate intermolecular distance, the scientists developed a novel preparation technique based on matching the distances between the charged sites in the porphyrin molecules and the distances between negatively charged (anionic) sites on the clay surface. This effect, which the researchers call the “Size-Matching Rule,” helped to suppress the major factors that contributed to the porphyrin molecules’ tendency to aggregate or segregate, and fixed the molecules in an appropriate uniform intermolecular distance. As Takagi explained, this strategy is significantly different than other attempts at achieving molecular patterns.

“The methodology is unique,” he said. “In the case of usual self-assembly systems, the arrangement is realized by guest-guest interactions. In our system, host-guest interactions play a crucial role for realizing the special arrangement of dyes. Thus, by changing the host material, it is possible to control the molecular arrangement of dyes on the clay surface.”

As the researchers demonstrated, the regular arrangement of the molecules leads to an excited energy transfer efficiency of up to 100%. The results indicate that porphyrin dye molecules and clay host materials look like promising candidates for an artificial LHS.

“At the present, our system includes only two dyes,” Takagi said. “As the next step, the combination of several dyes to adsorb all sunlight is necessary. One of the characteristic points of our system is that it is easy to use several dyes at once. Thus, our system is a promising candidate for a real light-harvesting system that can use all sunlight. We believe that even photochemical reaction parts can be combined on the same clay surface. If this system is realized and is combined with a photochemical reaction center, this system can be called an ‘inorganic leaf.’”

**More information:** Yohei Ishida, et al. “Efficient Excited Energy Transfer Reaction in Clay/Porphyrin Complex toward an Artificial Light-Harvesting System.” *Journal of the American Chemical Society*. DOI:10/1021/ja204425u

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## Article

# Efficient Excited Energy Transfer Reaction in Clay/Porphyrin Complex toward an Artificial Light-Harvesting System

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Yohei Ishida†‡, Tetsuya Shimada†, Dai Masui†, Hiroshi Tachibana†, Haruo Inoue†, and Shinsuke Takagi\*†§

Department of Applied Chemistry, Graduate Course of Urban Environmental Sciences, Tokyo Metropolitan University, Minami-ohsawa 1-1, Hachiohji, Tokyo 192-0397 Japan

Japan Society for the Promotion of Science (DC1), Ichibancho, Chiyoda-ku, Tokyo 102-8471, Japan

PRESTO (Precursory Research for Embryonic Science and Technology), Japan Science and

Technology Agency, 4-1-8 Honcho Kawaguchi, Saitama, Japan

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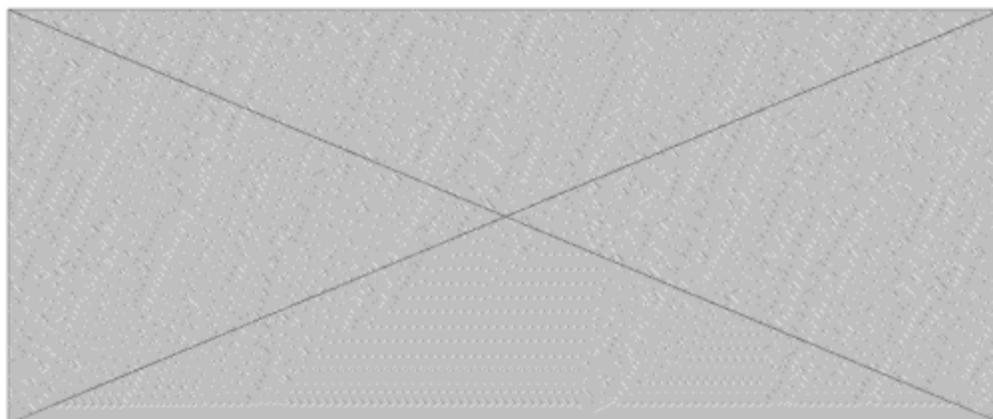
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[takagi-shinsuke@tmu.ac.jp](mailto:takagi-shinsuke@tmu.ac.jp)

 Section:

Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes

## Abstract



The quantitative excited energy transfer reaction between cationic porphyrins on an anionic clay surface was successfully achieved. The efficiency reached up to ca. 100% owing to the “Size-Matching Rule” as described in the text. It was revealed that the important factors for the efficient energy transfer reaction are (i) suppression of the self-quenching between adjacent dyes, and (ii) suppression of the segregated adsorption structure of two kinds of dyes on the clay surface. By examining many different kinds of porphyrins, we found that tetrakis(1-methylpyridinium-3-yl) porphyrin (*m*-TMPyP) and tetrakis(1-methylpyridinium-4-yl) porphyrin (*p*-TMPyP) are the suitable porphyrins to accomplish a quantitative energy transfer reaction. These findings indicate that the clay/porphyrin complexes are promising and prospective candidates to be used for construction of an efficient artificial light-harvesting system.