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Semi-Synthetic Responsive Matrices for Artificial Photosynthesis

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3 Semi-Synthetic Responsive Matrices for Artificial Photosynthesis

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List of Abbreviations

Aa	amino acids
Bb	building blocks
cLIFT	laser induced forward transfer for combinatorial synthesis
DNA	desoxyribonucleic acid
EET	excitation energy transfer
FRET	Förster resonance energy transfer
LCA	life cycle assessment
LH2	light harvesting 2
MAS NMR	magic angle spinning NMR
NA	numerical aperture
NCAP	non-adiabatic conversion by adiabatic passage
NMR	nuclear magnetic resonance

POR	porphyrins
PS	polystyrene
PV	photovoltaic
PYR	styrylpyridinium salts
RC/LH1	reaction center/light harvesting 1 core complex
REDOR NMR	rotational-echo, double-resonance NMR
TRL	technology readiness level

Nature engineers responsive protein matrices to control pigments' properties for light energy conversion in photosynthesis, in contrast to the standard chemists' approach where the chemical properties of the dye molecules are modified and the matrix is ignored. Engineering the matrix offers very subtle ways to enhance the quantum efficiency of the breaking and making of chemical bonds in photochemistry and catalysis by non-adiabatic conversion of reactants into products. We present a roadmap for the development of "next-generation," high quantum efficiency artificial photosynthetic devices that convert reactants into products with long living twisting modes. These devices are based on learning from nature how photosynthetic proteins are activated for non-adiabatic conversion with high yield by structural control over collective modes in the thermal molecular dynamics. When driven far from equilibrium by optical excitation, energy transfer, or charge transfer, conformational twisting develops quantum states that are not eigenstates by the crossing of reactant and product energy levels. The off-diagonal elements in the Hamiltonian drive photochemical reactions in a lossless non-adiabatic conversion by adiabatic passage (NCAP) process where information from handedness in the structure is transiently converted into quantum information and back into structural information. Truncation of the Hamiltonian in the interaction frame of the nuclear motion associated with a long living vibration coupled to conformational twisting in a chiral responsive matrix enables coherent conversion.

The construction of proof-of-principle responsive matrix functional materials that implement this NCAP concept in biohybrid and bioinspired architectures for incorporation into artificial photosynthesis devices is currently emerging. We propose tailoring sturdy bacterial light-harvesting and reaction center complexes to enable the exploration of structure-dynamics

relationships for the maximisation of functional quantum coherence induced by NCAP. With such a blueprint at hand, high-density protein-like arrays can be generated with high throughput peptide synthesis, assembled for bottom up construction of semisynthetic organic-inorganic hybrid architectures and screened for high yield, quantum-coherent enabled energy transfer and charge separation. To resolve the anisotropic motion from non-aligned enhanced twisting modes in the ground-state dynamic structure, and the spatial and temporal extent of coherences in the excited state, we advocate MAS NMR on isotope labelled preparations and ultra-fast optical spectroscopy. Input from experiments can guide the accurate multi-scale simulation of high yield light harvesting and charge separation to determine the optimal characteristics for complex bottom up construction of artificial photosynthesis device vehicles, such as size of the responsive matrix; the number, type and combination of chromophores; architecture; nature of the inter-chromophore electronic coupling; and means to promote robustness including withstanding oxidation.

The principle ethics of artificial photosynthesis is that it has to disappear into its practice of decentralized application. Environmental, humanities and design researchers can evaluate the environmental, energetic and economic consequences of artificial photosynthesis, envision the potential for systemic transformation in our relationship with energy and natural resources, and highlight the benefits and challenges we are likely to encounter on a path to large-scale deployment of responsive matrix technology in the densely populated environment.

I. Introduction

Around the world, large-scale deployment of wind and solar energy to generate renewable electricity is expected. However, to achieve a zero-carbon energy system, the world will need more than intermittent electricity. It will continue to rely massively on fuel for certain applications, such as heavy transport, aviation and iron ore reduction, and a long-term dependence on hydrocarbons is likely. Thus, the case for research and development into the field of artificial photosynthesis — systems to directly convert solar energy into fuel without oil or biomass intermediate — is strong. Furthermore, artificial photosynthesis, in contrast to other

solar-to-fuel technologies, has the potential to be deployed in a small-scale, decentralized fashion. We have a vision of artificial photosynthesis becoming a common technology, and a significant contributor to the future energy resource mix. Although artificial photosynthesis is still a scientific challenge, all aspects of its deployment in urban environments, such as energy and resource/material availability, ecofriendliness and efficiency, and pathways from niche application to large-scale implementation and approval will need to be investigated. In this chapter, we present a roadmap for the development of “next-generation” artificial photosynthesis devices.

II. Nature’s Paradigm

The early stages of photosynthesis can operate at high quantum efficiency across many different antenna and reaction center configurations. These natural systems are an inspiration for the next-generation of artificial photosynthesis devices and act as a blueprint for their construction. A key aspect of nature’s approach is that biology engineers the matrix to control the properties of the pigments. This is in contrast to the standard chemists’ approach of changing the properties of the pigment and ignoring the matrix. Engineering the dynamic structure of the matrix offers a whole new toolbox for subtle ways to enhance the outcome of both photochemistry and catalysis. This concept has become known as the responsive matrix.

A paradigm shift in artificial photosynthesis research can be achieved by engineering quantum coherent conversion at avoided crossings in chiral responsive matrices, similar to proteins found in nature. In photosynthetic complexes, the ubiquitous quantum instabilities that result from transient off-diagonal or non-adiabatic matrix elements in electron-nuclear Hamiltonians lead to resonant conversion of reactants into product states through vibronic coherence. Well out of equilibrium, chemical conversions can proceed in a deterministic fashion, transiently violating the limitations of the Carnot process. Quantum beats^{1,2} with lifetimes of up to several ns have been observed in natural photosynthetic samples for both excitonic energy transfer³ and charge separation^{4,5} following optical excitation by means of 2D electronic spectroscopy. Here, we propose a much more general structure-function concept: non-adiabatic conversion

by adiabatic passage (NCAP). Guided by our recent extensive analyses of semi-classical interconversion of electronic states with vibrational coherence in natural and artificial systems, we propose that photoexcitation of a responsive matrix leads to a conformational twisting response along a low frequency supramolecular mode with enhanced spectral density.^{6,7} This leads to vibronic coupling of exciton levels and semi-classical coherent conversion of exciton states by resonance with a more rapid, second low frequency mode.⁸ Although NCAP is a dissipative process out of equilibrium, it parallels the cross correlation detection of “NMR spin noise” without photoexcitation and “noisy light spectroscopy” with incoherent excitation that were recently taken to the level of 2D coherent spectroscopy.^{9–12} During the dissipative adiabatic passage in a responsive matrix, near-unity resonant conversion from reactant $|r\rangle$ to product $|p\rangle$ is enabled by a transient semi-classical channel through the energy barrier (Figure 1). $|r\rangle$ and $|p\rangle$ are two pure states that describe, for example, antennae, charge separation or catalysts motifs during photoinduced excitation energy transfer, charge transfer or catalysis, respectively. Since resonators have a low impedance for the matching oscillation, the elec-

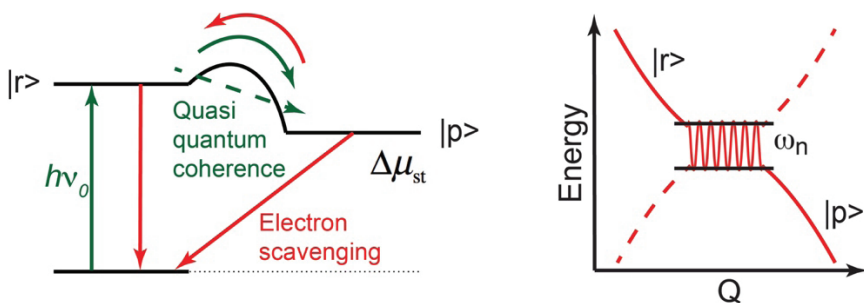


Figure 1. Conversion from a reactant state $|r\rangle$ to a product state $|p\rangle$. Forward processes are shown in green and reverse processes in red. Semi-classical transfer from $|r\rangle$ to $|p\rangle$ proceeds with a channel through the barrier (green dashed arrow, left) by a conformational twisting response of the matrix for dynamic level crossing of $|r\rangle$ and $|p\rangle$, and is driven by a ω_n twisting mode (right). This is in contrast to the Carnot process, which is shown as a hop over the barrier (green curved arrow, right). The Carnot process may be subject to back transfer (red curved arrow) and subsequent relaxation (red downwards arrow) or direct recombination as a result of electron scavenging on the nanoscale (red diagonal arrow).

tron-nuclear system can take up energy from the environment and give it back again, which leads to a robust mechanism for selection of a matching vibration.

Dynamic symmetry breaking is essential for such a vibrationally-coupled process, because without it, crossing of the electronic states is forbidden. We derived an analytic expression for the conversion by writing the equations of motion in the interaction frame of the nuclear circulation in terms of a Rabi oscillation with semi-classical angular momentum from molecular twisting in the chiral matrix, as opposed to spontaneous symmetry breaking, by selecting one of two counter rotating components representing a linear vibration.⁸ Our perturbative approach to renormalize quantum and classical degrees of freedom along different directions in Hilbert space, follows a similar physical approach for describing the interaction of nuclear spins with macroscopic classical rotation.¹³

The physics of NCAP is fundamentally different from the current practice in quantum biology. It induces complete conversion by time reversal during adiabatic passage instead of stochastic decoherence. Adiabatic passage enables long-range transfer by recurrent deterministic coherence/decoherence and touches upon a fundamental property of quantum networks: systems in a pure state subject to non-adiabatic couplings self-select the fastest channel to the output. The dissipative character of NCAP provides a handle for kinetic control over the conversion process by trading time for energy efficiency. With minimal dissipation, slow and lossless conversion is realized, such as in rubisco;¹⁴ while large dissipation leads to ultrafast conversion, as in the visual pigment rhodopsin.^{15–18}

A principle challenge is thus to learn from nature and develop responsive matrices with quantum coherent kinetic control for high yield. We consider the absorption of ~90% of the incoming photons over as large as practicable part of the solar spectrum, an internal quantum efficiency of ~80%, and stability on the timescale of months a realistic target for practical implementation of photochemical conversion. The photon to product yield of the solar-to-fuel conversion technology will then be $90\% \times 80\% = 72\%$ of the thermodynamic limit. The higher the quantum efficiency, the less materials and surface area is needed. Current laboratory scale devices that produce hydrogen do not achieve anywhere near 72% external quantum efficiency and 80% photochemical yield.

Going from chemical yield to energy efficiency, the detailed balance energy conversion efficiency limit for near-quantitative conversion of photons to hydrogen is 42%, for a tandem absorber with cut off wavelengths of 700 and 1100 nm that drives water splitting and fuel production with two photons per electron transported into fuel. A realistic energy efficiency is thus $90\% \times 80\% \times 42\% = 30\%$, which takes into account losses such as reflection at the surface, variation of the intensity over the optical spectrum during the day or between seasons, and a limited filling factor.¹⁹ Most state of the art devices operate at around 5–10% solar-to-hydrogen efficiency.^{20,21} There are a few very expensive devices that achieve around 15%.²²

III. State of the Art

Current research strategies for converting sunlight to fuel with artificial photosynthesis are mostly heuristic and lead to similar scientific problems across a wide range of materials. Entropy and unavoidable irreversibility place a detailed balance thermodynamic limit on the efficiency of adiabatic photochemical energy conversion

$$\Delta\mu_{st} = h\nu_0 - k_B T \ln \frac{t}{\tau} \quad (1)$$

where $\Delta\mu_{st}$ is the chemical potential of energy storage and there is no $P\Delta V$ work involved from a volume change.²³ The first term in equation 1 is the energy difference for light absorption between the highest occupied molecular orbital and the lowest unoccupied molecular orbital. The second term is the mixing entropy for detailed balance between the concentrations of the photoproduct in the light and in the dark, where t is the lifetime of the storage reservoir, and τ is the excited state lifetime of the absorber. The longer the energy needs to be stored, the more mixing entropy needs to be generated in the chemical network to prevent light reactions running backwards and wasteful recombination. This is shown schematically in Figure 1.

When photochemical conversion proceeds near equilibrium (i.e. adiabatic) with a series of incoherent (i.e. Carnot type) conversion steps with intermediate dilution and concentration, as in PV coupled to electrolysis,

the entropy and unavoidable irreversibility losses factorize rapidly. In contrast, the experimentalist designing an artificial photosynthetic system is faced with the choice of either ensuring that there is a big enough drop in energy built into the system to shift the photochemical equilibrium towards chemical storage and prevent light-driven reactions from running backwards during long storage times t leading to an energetically inefficient device; or, reducing the energy difference across the system, but then having a very poor quantum efficiency owing to recombination losses from higher probability back transfer followed by rapid fluorescence recombination with a rate $1/\tau$. In addition, for multi electron catalysis, charges need to be separated sufficiently on the nanoscale to prevent direct recombination by tunneling, but not too far apart to avoid unnecessary concentration losses. This requires matching of the tunneling distances with the storage times t for intermediate stages. Currently, there are no good solutions to overcome these two fundamental hurdles.

IV. Design Principles for Artificial Photosynthesis Based on Nature's Paradigm

The materials that we can use to mimic the responsive matrices that nature uses to enable high yield light reactions are limited to substances that can sustain correlated electrons and are capable of breaking and making chemical bonds with long-lived vibrational modes. Also, materials need to foster dynamic symmetry breaking in the NCAP mechanism. In natural photosynthesis, this is almost certainly provided by the intrinsic and induced chirality of the protein complexes and the embedded cofactors. Artificial materials that fulfil these criteria are, for instance, supramolecular systems, which, when biomimetically designed, are ready for quantum coherence. Paracrystalline or semicrystalline polymers with control over the dynamic structure,²⁴ too, may prove to be a fruitful avenue of investigation. There may be some parallels with the material requirements for quantum computing and spintronics, so some of the semiconducting materials used there may also be appropriate. While the use of conductors with free, uncorrelated electrons is problematic, materials with macroscopic quantum effects such as high- T_c superconductors may offer promises.

In nature, materials for light harvesting, charge separation, and catalysis are integrated in high-density arrays in the photosynthetic membrane. Such an arrangement enables high optical densities for efficient light absorption and efficient energy and electron transfer between neighboring components. Analogs of these high-density arrays have been successfully employed in artificial photosynthesis in the form of nanowire arrays for efficient light absorption.^{25–27} Furthermore, high-density arrays are amenable to high-throughput manufacturing processes such as tiling and printing. High-density arrays are therefore another aspect of natural photosynthesis that should be mimicked in artificial systems.

V. Reverse Engineering Nature

Evolution has engineered the control of properties by photosynthetic matrices in biology by historical contingency over approximately three billion years. It is thus wise to use the biological matrix as a starting point and work from semi-synthetic materials, instead of *de novo* bottom up design of complex matrix systems with a controlled dynamic response for chemical conversion. With access to the universal principles that govern NCAP in natural systems, reverse engineering of natural photochemistry and catalysis in semi-synthetic materials using modified molecular building blocks and mimicking natural protein environments in supramolecular chemistry can rapidly become reality.

A variety of close-packed 2D arrays of photosynthetic complexes in native membranes can be used as a natural test bed for the generation, retention and quenching of coherences during intra- and inter-complex NCAP energy transfer and charge separation reactions. We will need natural photosynthetic samples that are robust, abundant, easily modified and in which quantum coherent behavior has been observed. The photosynthetic apparatus of photosynthetic purple bacteria is an example of such a system. A typical purple bacterial photosynthetic unit consists of reaction center/light harvesting 1 core complexes (RC/LH1) and light harvesting 2 complexes (LH2). The X-ray crystal structures of these complexes have been determined and are shown in Figure 2.^{28,29–30} They are all constructed from the same basic design principle. They are circular oligomers of pairs of small, hydrophobic apoproteins. Each pair of apoproteins binds non-covalently a small

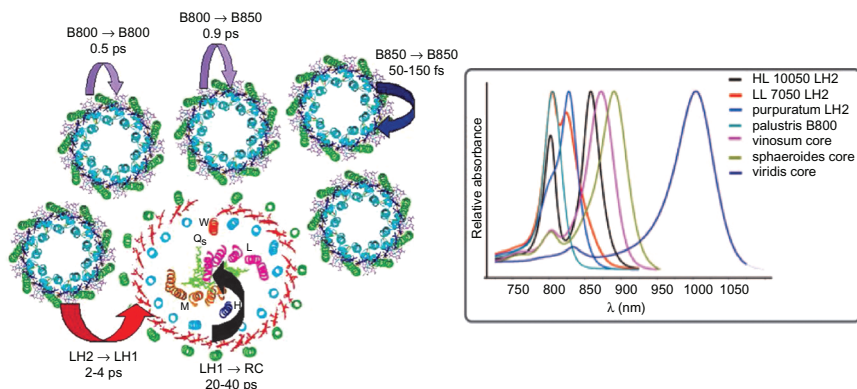


Figure 2. Membrane organization (left) and dispersion of the optical absorption for different LH species (right).

number of bacteriochlorophylls and carotenoids. The characteristic absorption spectra of these complexes are shown in Figure 2. The different pigment groups seen in the 3D structures in Figure 2 absorb light in separate regions of the spectrum. This makes functional studies straightforward in that each group can be specifically excited and their energy transfer and charge separation reactions clearly monitored. We know a great deal, therefore, about the basic structure and functional mechanisms of these purple bacterial complexes. The size and composition of the purple bacterial photosynthetic unit is controlled by the light intensity and wavelengths at which the bacterial cells are grown.^{31,32} This gives exquisite control over which complexes are made and their relative arrangement in the native membranes.

With a view to artificially producing high-density arrays of photosynthetic units, and also with the aim of studying interactions between photosynthetic units, tiled arrays of purple bacterial photosynthetic units can be produced. Since purple photosynthetic bacteria are genetically amenable, mutant complexes and complexes tagged with DNA-binding zinc finger domains can readily be made so that they can be attached to DNA tiles in a sequence-specific manner.³³ This procedure is shown schematically in Figure 3. Photosynthetic complexes can be placed on these tiles with exquisite precision, enabling the investigation of the effects of distance (and hence coupling) between neighboring complexes upon both energy transfer efficiency and retention of coherences.

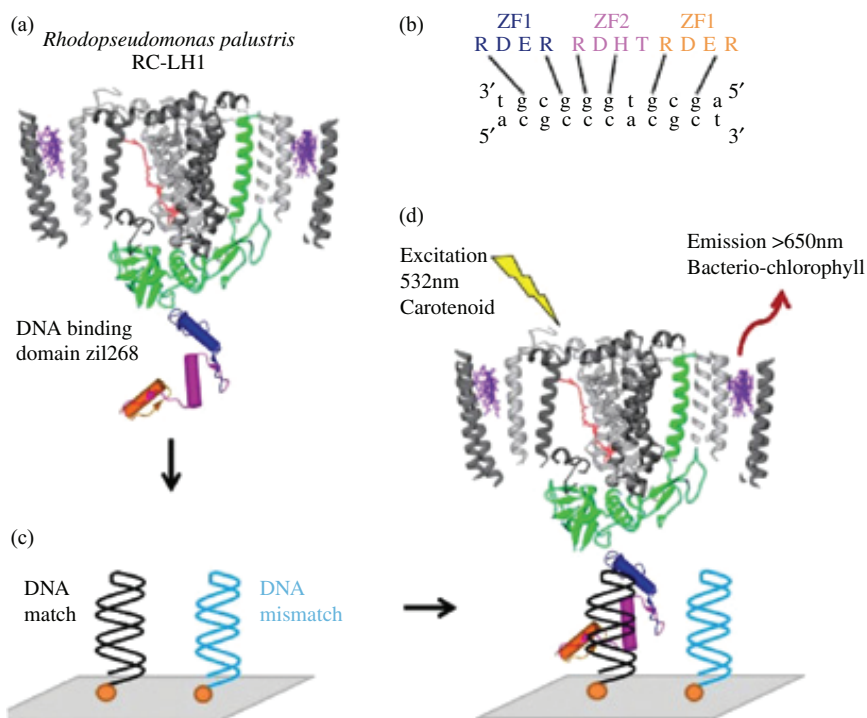


Figure 3. (a) Structure of the RC-LH1 from *Rhodospseudomonas palustris* (gray) with the H-subunit highlighted in green. (b) An 11 bp DNA zif268 recognition sequence. (c) Immobilization of cyclooctyne-tagged dsDNA to an azide-modified surface. (d) Excitation Energy Transfer (EET) was measured between the carotenoid pigment (in red) and bacteriochlorophyll (highlighted in purple) as a test for photosynthetic function. Reproduced from Henry *et al.*³³ with permission from The Royal Society of Chemistry.

Photosynthetic components are pre-programmed in the electronic ground state by their protein environment for optimal operation in the excited state. To guide the optimization of these processes in semi-synthetic systems, we will need to determine the global dynamics and local order parameters of pigments and amino acid side chains. MAS NMR is here the method of choice, since it enables sub-Å characterization of the dynamic structure.³⁴ In particular solid-state NMR relaxation and REDOR dipolar anisotropy measurements are excellent ways to obtain information about conformational twisting ground state dynamics. Purple

bacteria can be grown on a variety of supplemented media to achieve isotope labeling to tailor samples for NMR analysis.

For the excited state, ultrafast optical spectroscopy is an excellent tool to elucidate the role of vibrations and the extent of coherences on the 10–100 nm level following coherent excitation or by noisy light spectroscopy.^{35,36} Persistent coherences can also be addressed with single molecule detection in a confocal microscope with high NA (1.4-oil) excitation/detection and the sample in controlled atmospheric or liquid conditions. In this way, the fs-ps energy transfer path of the coherences and inter complex energy transfer can be traced. Localized coherent excitation enables the resolution of spatio-temporal energy transport on the quantum transfer network.^{37,38} Such an experiment is shown conceptually in Figure 4.

To enhance our understanding of the structure-function relationships for NCAP, experiments should be complemented by theoretical methods. Guided by experimental data, modeling and simulations at various levels can be performed to inform the design process. Theoretical investigations should include quantum classical simulations of light harvesting and charge separation with NCAP.^{6,7,39,40} Also, multi-scale modeling may yield insight into aspects of NCAP such as the size of the responsive

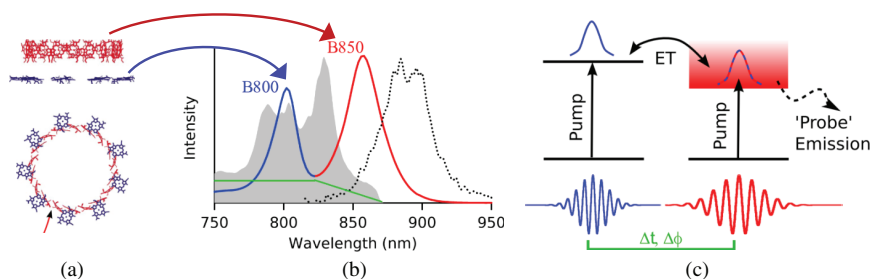


Figure 4. Concept of ultrafast phase-coherent excitation of individual light-harvesting complexes at room temperature. (a) Simplified structure of LH showing B800 (blue) and B850 (red) bands. (b) Absorption spectrum of B800 and B850, and the emission spectrum shown as dotted line. Broad band exciting laser spectrum (gray) and the applied spectral phase for pulse shaping (green line). (c) Concept of the experiment: interference of energy transfer (ET) and direct excitation is recorded in the fluorescent “probe” emission. Modified from Hildner *et al.*³⁷ with permission from AAAS.

matrix; the number, type and combination of chromophores; architecture (linear, cyclic, dendrimeric, lateral *vs.* layered); nature of the interchromophore electronic coupling (weak, strong); and means to promote robustness including withstanding oxidation.

Such an approach will enable the exploration of fundamental questions about energy transduction with NCAP and to use this improved understanding to boost quantum coherence with recurring adiabatic-passage events driven by interacting modes of molecular twisting. Questions such as the extent to which these coherences vary depending upon the size of the complexes and whether the coherences can be modulated by site-directed mutagenesis of apoproteins can be addressed. In this way, we can establish the physical principles that enable the maximisation of the functional role of NCAP in energy transduction in photosynthesis to efficiently concentrate energy for the long-term goal of fuel production. Study of the natural system will produce a blueprint for how to fabricate an artificial photosynthetic system with quantum coherences.

Once the “rules” by which NCAP operates in the natural system are established, this mechanism can be reverse-engineered in a more readily manufactured semi-synthetic material. High-throughput manufacturing techniques such as printing and tiling are good avenues to explore. In particular, there are two recently developed novel methods to synthesize and validate millions of different protein-like structures in unprecedented high-density array format. The one-cavity-one-peptide method enables the synthesis of millions of protein-like structures with built-in chromophores and electron relaying “stepping stones” at low cost.⁴¹ A second technique uses Laser Induced Forward Transfer of materials for the combinatorial synthesis of high-density peptide arrays (cLIFT).⁴² These techniques enable some 5000 to 10000 peptides per cm² in very high quality to be synthesized. Designer pigments synthesized from amino acid building blocks, such as porphyrin, styrylpyridinium, corrole, boron dipyrromethene or pyridinophane, can be introduced into the peptides arrays at different, well-controlled sites (*i*, *k*) within the growing peptide chain. Figure 5 shows the general formula of the desired constructs incorporating porphyrins (POR) or styrylpyridinium salts (PYR) prepared by the group of Balaban, who was a pioneer in this field. Different building blocks can be assembled for bottom up construction of semi-synthetic architectures.

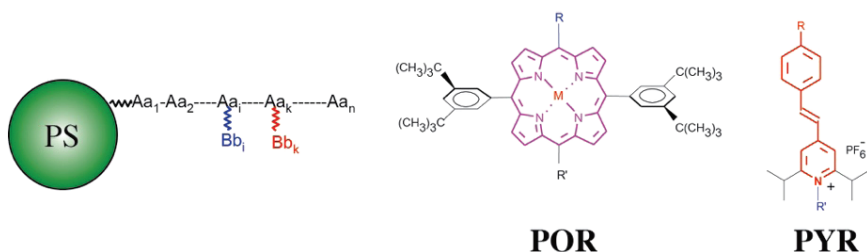


Figure 5. A peptide formed by n coupling steps of amino acids **Aa**. One or several building blocks **Bb** can be inserted at will, at any desired position within the peptide anchored on the solid support **PS**. The chromophoric system responsible for the photophysical properties is shown with coloured bonds while solubility inducing groups are black. M can be either $2H$ or various metals such as Zn , Cu , Ni , Mg , Cd , etc. The substituent R can be varied at will to both fine tune the absorption wavelength and redox potential while the blue substituents R' serve as anchors for the automated solid phase synthesis of combinatorial peptides.

Furthermore, quite a few proteins and peptides are known to nucleate or bind to a diverse range of inorganic materials, e.g. ZnO . With these building blocks at hand, miniaturised self-assembled architectures can be constructed, e.g. by tiling different peptides that would nucleate different materials to DNA-based origami structures. Especially, two such building blocks fused together on a nanoscale distance should generate janus type particles made of two different semi-conductor materials that could serve as an artificial reaction center, which, again could be placed into close contact with semi-artificial or artificial LHC proteins (Figure 6).

As with the investigations of the natural system, quantum classical simulations, multi-scale modeling, and spectroscopic analyses with NMR and single molecule spectroscopy will guide the design of the system. Novel, semi-synthetic constructs will be screened to find molecule-surroundings that influence the spectroscopic behavior of built-in chromophores and, eventually, have semi-classical coherent conversion of reactants into products upon excitation with light, assisted by conformational twisting.

These techniques can be used to systematically scrutinize large numbers of peptides for quantum coherence and their capacity to nucleate and grow inorganic materials in array format (semiconductors, magnetite,

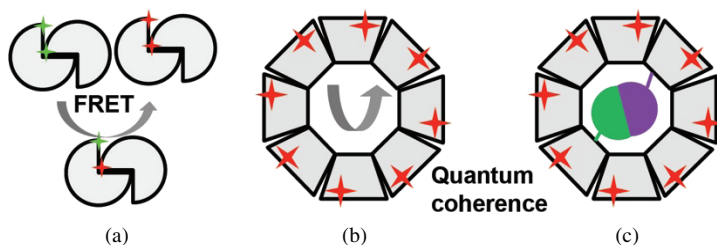


Figure 6. Screen for self-assembling protein-like structures. Peptides (> 40mers) are synthesized at high density in small cavities either with the one-cavity-one-peptide method (for initial screens), or with cLIFT (for systematic variations in the peptide's sequence), side chain protection groups are removed by harsh chemistry, the cavities are filled with a solvent (e.g. *n*-heptane), and sealed from each other, before the peptides are released by UV light into "their" cavity, where they self-assemble to dimers (a) or oligomers (b). Especially when "talking to each other" due to quantum coherence (one type of chromophore, see b), or by FRET (a mixture of two types of chromophores built into the peptides, see a), these oligomers drastically change their optical properties, which can be pre-screened with a high-resolution scanner equipped with three lasers and a large set of optical filters. Eventually, oligomerising peptides (doing quantum coherence) will be linked (by direct fusion, or by tiling them to DNA-origami structures) to additional peptides that nucleate inorganic material that could serve as an artificial reaction center (c).

insulators). With this step, proof of principle of the knowledge obtained from the natural system is provided. These protein-like materials explored with high-throughput peptide synthesis will be fundamentally different from the materials that are currently used in artificial photosynthesis research.

VI. The Societal Implications of Large-scale Decentralized Deployment of Artificial Photosynthesis

The development of responsive matrices for artificial photosynthesis aims to address a conundrum in solar energy supply. On the one hand there is biomass from natural photosynthesis, which provides 10% of the primary energy mix, is both affordable and sustainable, but is not scalable; it is by far not enough.^{43,44} On the other hand, there is photovoltaics followed by electrolysis, which has been around for many decades, is in principle

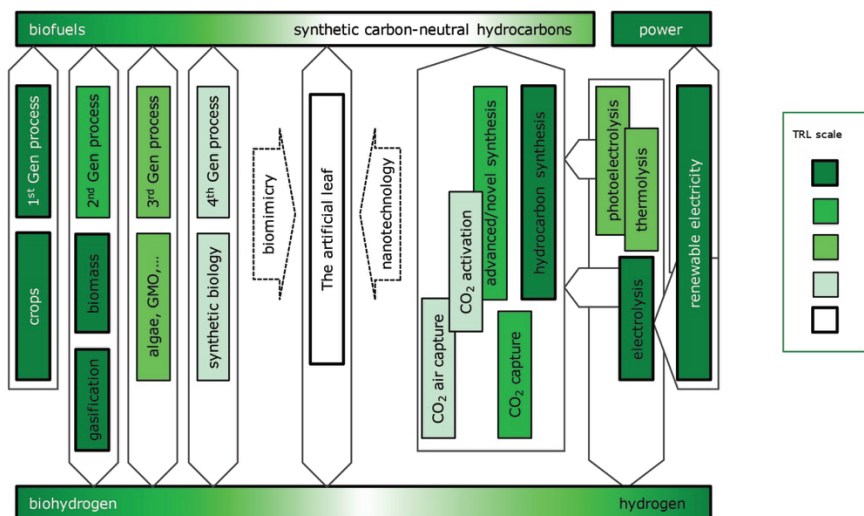


Figure 7. This schematic depicts the broad field of solar fuels, ranging from algal and other advanced biofuels, *via* synthetic biology to “the artificial leaf,” onto ‘conventional’ conversion of renewable electricity, using electrolysis and synthesis with activated CO₂. This is a vibrant area of research. One can justifiably have high hopes for advances, because of the advances in life sciences (on the left) and nanotechnology (on the right). Artificial photosynthesis has the potential to combine the for all practical purposes “infinite” potential of solar energy, with the versatility of hydrocarbon fuels. At the highest level, the challenge is to find a technically novel optimum that combines the benefits of biofuels (i.e. a renewable hydrocarbon fuel) with the “unlimited” availability of renewable electricity. The colors are indicative of the so-called Technology Readiness Level (TRL) of the technology, running from dark green (mature technologies) to white, indicating technologies that are still conceptual or lab-scale.

scalable, but so far has not taken off for economic reasons. The challenge of converting hydrogen to a hydrocarbon fuel critically relies on the separate capture of CO₂ from air, so far a distant promise. This opens the opportunity space for more radically new technologies as proposed in this paper. The relationship between these advanced technologies and more conventional technologies is depicted in Figure 7. As is explained in the previous sections, the key lesson from nature is to avoid chains of Carnot cycles by integrating PV and electrochemistry, and use non-adiabatic (i.e. quasi quantum coherent) conversions that transiently violate detailed

balance in semisynthetic NCAP responsive matrices. Artificial photosynthesis thus holds the potential to be both scalable and commercially viable as it takes the best aspects from biology and nanotechnology.

The Collingridge dilemma⁴⁵ states that in the early phases of development, a technology can still be changed, but the effects of the technology are hard to predict; when a technology is mature, its effects are clear, but it is difficult to change. By close collaboration with environmental, humanities and design researchers we hope that we can overcome the Collingridge dilemma by identifying, from the very beginning, semi-synthetic artificial photosynthesis technology development pathways that are not only technologically advanced, but also socially, environmentally and ethically compatible with large-scale urban deployment.

Life cycle assessment (LCA) is the prevailing quantitative framework for environmental assessment of energy and production systems. The combination of process-based life cycle inventories and input-output based models of the wider economy has been proposed to obtain both accurate and detailed descriptions of technologies while ensuring consistent and complete descriptions of the involved production network. This agnostic science approach ensures a basis for consistent environmental assessment across different technologies. For developing life cycle inventories of systems, several pieces of information are central: in particular, energy balances, and material and costs lists. Understanding the significance of different processes and emissions to different impact categories is at the heart of LCA. An understanding of how the impacts, and their uncertainties, accumulate throughout individual value chains, sub systems and network structures is best provided by application of methods such as structural path analysis. The lower the technological readiness of a technology, the greater is the uncertainty of its (future) performance and therefore of an LCA. Yet, the urgency of finding the most efficient solutions for high-yield, solar-energy conversion and storage in the context of the Paris agreement to establish a zero-emission energy system by 2045 and not later than 2065, with negative emissions thereafter, warrants that stakeholders are capable of deciding upon technology development paths with incomplete information. This is referred to as *ex-ante* technology life cycle assessment: the generation of a comprehensive assessment of opportunities and risks of technologies and their application, thereby providing

knowledge suitable for actively shaping technological development. *Ex ante* LCA can be used to evaluate the environmental, energetic and economic consequences of artificial photosynthesis technology. It is crucial to the further development of this technology to establish the future success factors. When aspects of technological performance, economic viability and environmental impact are included in an integrated, early assessment of the technology, its future competitiveness against alternative low-carbon technologies can be evaluated.

Artificial photosynthesis is a technological response to our demand for renewable fuel. As such, it relates to our notions of nature, sustainability and the environment. Confronted with our environmental challenges, humanities research has embraced the subject of the environment, exposing the assumptions inscribed in our environmental thinking and challenging traditional notions of nature and the dichotomy of nature/technology. The now established field of environmental humanities, including practices such as eco-criticism and environmental ethics, is an essential resource for coping with our present environmental crisis, while transdisciplinary approaches are urged with regards to sustainable development and energy research.^{46,47} Thanks to the humanities, we are getting more and more comfortable with the idea that humans are not fundamentally separate from nature, that nature is a socio-cultural construct, that the environment is in constant interaction with human technological activity and that even our cities and our urban environment are not necessarily in opposition to a “natural” ecosystem. At the same time, the framework of responsible innovation is gaining momentum in research and development.⁴⁸ It dictates continuous stakeholder involvement in responsive and reflective innovation.⁴⁹ Amongst various tools and methodologies involved, value sensitive design methodologies are attentive to the fact that our values are embodied in our technologies,⁵⁰ further justifying the significance of a philosophically informed conceptual investigation prior to the design process; yet, such methodologies may be inhibited by the dominant, and potentially outmoded, paradigms in our environmental thinking.

The ethics and aesthetics⁵¹ of energy is that it has to disappear into its practice. Contrary to photovoltaics, artificial photosynthesis produces hydrogen or hydrocarbons in gaseous or liquid form that have to be stored locally or transported into a grid. Humanities researchers and industrial

designers can work out a framework for understanding how the public may perceive (semi-synthetic) artificial photosynthesis, and interact with various stakeholders such as scientists, industry and the public to determine the design parameters required to make such a technology, on an unprecedented scale, desirable to the end user. We envision a deployment of artificial photosynthesis that is socially pioneering, socially responsible and one that fundamentally transforms our relationship with, and attitudes to, energy and natural resources. Such research may well include theoretical elaborations researched by means of design activities, such as envisioning and prototyping; and transform these concepts into tangible 3D artefacts, such as mock-ups. This approach safeguards that produced prototypes go beyond materialising current requirements, to become research artefacts that enable a critical reflection on the potential of artificial photosynthesis among all parties involved. Such research is relevant for developers of a technology such as artificial photosynthesis, as it promotes a consideration of technologies for renewable energy that is not agnostic to their broader societal implications but attentive to the fact that technologies are integrated into and interacting with socio-cultural systems.^{52,53} For the discipline of the humanities, this research is relevant, as it advocates a dynamic role for the humanities as a force that can contribute to the shaping of a technology at an early stage. It seeks empowerment for the humanities to become a responsible shareholder in the societal debate about renewable energy resources and to critically support the implementation of technological innovation in a dynamic exchange between the humanities and science.

Together, these activities will enable us to envision the future large-scale implementation of artificial photosynthesis technologies; both its potential for systemic transformation as well as the challenges along the way. This will provide new perspectives on the societal impact of artificial photosynthesis, ease its introduction to the public and provide a means for disseminating information about future artificial photosynthesis technologies to the public and other stakeholders.

VII. Conclusions and Next Challenges

We offer a novel paradigm for artificial photosynthesis, based upon a new class of responsive matrix materials reverse engineered from nature,

with many opportunities for scientific and applied research, and for innovation. When we have learned how to modulate the vibrational structure, established the symmetry breaking requirements for long-range quantum coherent energy transfer and applied it in a semi-synthetic material, this knowledge can be transferred and used non-heuristically to establish an entire new class of functional materials with superior properties at all scales, suitable for a broad range of energy conversion applications. This may prove to be an effective driver of all kind of catalytic conversion chemistries. Furthermore, the novel research methods advocated here, whereby science is combined with humanities and design, could well find broad application in the development of other future emerging technologies.

VIII. References

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