Powering a Supramolecular Machine with a Photoactive Molecular Triad**

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Functional molecular materials[1–3] are becoming recognized[4–6] as active components at the nanoscale level where the derived properties can be realized without the effects of scaling.[7] In this context, hybrid top-down/bottom-up methodologies are defining how molecular materials can be incorporated into nanoscale electrical[8] and mechanical[9] systems. An alternative perspective considers artificial molecular machines,[2] such as [2]pseudorotaxanes[6d] and bistable [2]rotaxanes,[10] as fully integrated systems that utilize electrical circuitry as a platform on which to organize,[8a] power,[8b] and control[6e] molecular actuation. As a means of incorporating a source of electrical energy directly into either nanoscale[8] or molecular[11] systems, we have studied a photoactive donor–chromophore–acceptor molecular triad[12,13] that mimics, to a certain degree, the photodiode response of a semiconductor p–n junction. Such an idea has been investigated[14] in a biological context with molecular triads comprised of carotene as the electron donor and either naphthoquinone or C_{60} as the electron acceptor. These triads facilitated the active transport of H^+ and Ca^{2+} ions across liposomal membranes by mimicking the photosynthetic energy transduction mechanism. Here in this communication, we show, in a wholly artificial system, that a photocurrent is gated by light, the wavelength of which is specifically tuned to the maximum absorption of the light-absorbing porphyrin chromophore of a molecular triad (Figure 1 a). This nanoscale power supply is used subsequently to drive an artificial supramolecular machine in the form of a pseudorotaxane.

Donor–chromophore–fullerene molecular triads, where the donor and chromophore have been widely varied, are one of the most successful approaches to mimicking[1,14] photosynthetic reaction centers on account of the unique electron-accepting properties of fullerenes (e.g., C_{60}). Two classes of fullerene-based molecular triads, bearing a porphyrin (P) as the chromophoric unit, constitute the basis of our design. When ferrocene (Fc) is employed[12a–c] as the donor, a self-assembled monolayer (SAM) of the appropriate triad converts light energy into an electrical current in an aqueous photoelectrochemical cell. With tetrathiafulvalene (TTF) as the donor, organic solution-phase studies on the derived triad show[13a] that efficient charge-separation is produced after light excitation. Photoinduced electron transfer (PET) from the porphyrin to the fullerene unit is followed by a charge shift (CS) to the TTF unit that ultimately leads to a relatively stable charge-separated intermediate ($TTF^{+\bullet}$-P-$C_{60}^{-\bullet}$).[15] Electronic reset through back electron transfer (BET) within the charge-separated species restores the neutral ground state.

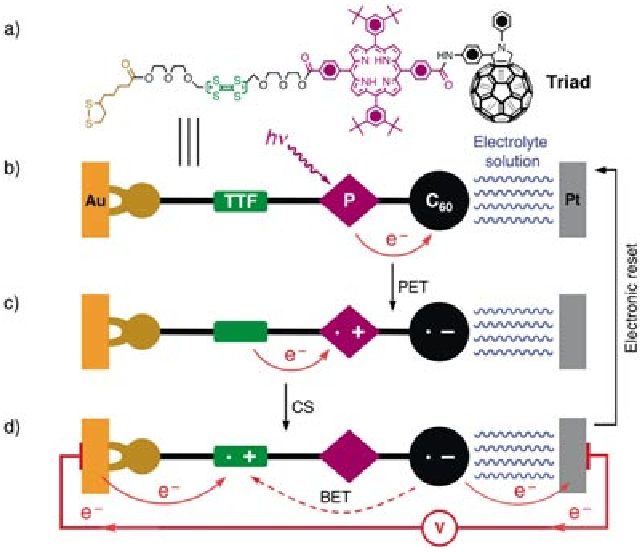

Figure 1. a) The structural formula of the tetrathiafulvalene–porphyrin–fullerene molecular **Triad**, which bears a disulfide tether to enable the formation of a SAM. The triad was used in a photoelectrochemical cell to demonstrate the generation of electrical energy from light; b–d) proposed vectorial electron transfer mechanism for the photoresponse of a photoelectrochemical cell comprised of a SAM of the triad on a Au electrode in contact with an electrolyte solution that contains a Pt counter electrode (Ag/AgCl reference electrode not shown) connected externally to a potentiostat (PET: photoinduced electron transfer; CS: charge shift; BET: back electron transfer).

Initially, we report here on the ability of a molecular **Triad** (Figure 1 a), which uses TTF as the donor group (TTF-P-C_{60}), to perform (Figure 1 b–d) photo-to-electrical energy conversion. This design incorporates the efficient motifs of charge separation in TTF-based triads,[13] together with a disulfide-based tether for attachment to a gold electrode. The **Triad** was designed and synthesized in a modular fashion (see Supporting Information) from its components in order to allow its electronic properties (namely, the lifetime of the charge-separated intermediates, and redox energies) to be optimized according to Marcus theory by subsequent structure–property feedback loops. In this **Triad** con-

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stitution, a long and flexible diethylene glycol spacer has been incorporated between the TTF and porphyrin units in order to enable the subsequent template-directed[16] synthesis of a [2]rotaxane. This structural feature influences the distance between the TTF and C_{60} units and will have an effect[1] on the lifetime of the charge-separated state, and hence on the efficiency of the energy conversion.

UV/Vis spectroscopy shows (Figure 2) that the absorption spectrum of the **Triad** is a linear combination[12c,13] of the spectra associated with the constituent units. Consequently, the porphyrin chromophore in the molecular **Triad** can be photoexcited selectively by irradiating near its Soret band (420 nm) where the TTF and C_{60} units have negligible absorptions. The cyclic voltammogram (CV) of the **Triad** SAM on a gold wire electrode shows (Figure 2, inset) a prominent quasi-reversible[13b] peak at 680 mV assigned to the two-electron oxidation of the TTF unit. The C_{60} unit displays two closely-spaced reduction processes at −390 and −500 mV.[17] The surface coverage of the **Triad** on the gold surface is estimated from the oxidation peak of the TTF unit to be 1.4 $nm^2\,molecule^{-1}$, a finding that is consistent with a close-packed monolayer.[18] The same CV was obtained after a period of five days, thus establishing the stability of the SAM, which is an advantage for the long-term operation of these devices.[19]

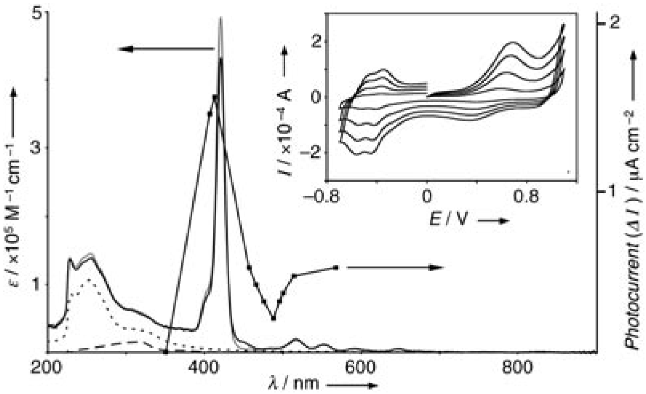

Figure 2. The photoaction spectrum (■) of a SAM of the **Triad**, along with the UV/Vis spectra of the **Triad** (——), as well as those of the **Triad**'s building blocks (see Supporting Information); the P–C_{60} dyad (——), a C_{60} derivative (-----) and a TTF-diol (– – –). The photoaction spectrum of the SAM of the **Triad** was collected using excitation from a Kr-ion laser and an Ar-ion laser at 34 ± 3 $mW\,cm^{-2}$. The inset displays the CV of the **Triad** SAM on a gold wire recorded at 100, 300, 500, and 700 $mV\,s^{-1}$ (Pt counter electrode, Ag pseudo-reference electrode, 0.1 M $LiClO_4$, MeCN), which illustrates the linear dependence of the current peak intensity with scan rate.

Photoelectrochemical experiments were carried out in a standard three-electrode electrochemical cell (0.1 M Na_2SO_4 (aq), aerated).[12c] A gold foil, coated with a SAM of the **Triad**, was used as the working electrode, a platinum gauze as the counter electrode, and Ag/AgCl (saturated KCl) as the reference electrode. In these experiments, a photocurrent was generated (Figure 3 a) when 413 nm laser light (Kr ion laser, 34 ± 3 $mW\,cm^{-2}$) was switched ON or OFF, while the cell was biased at −500 mV. Bare gold and a SAM of decanethiol on gold did not display the light-gated response (Figure 3 a). The photoaction spectrum (Figure 2) reveals that when the SAM of the **Triad** was irradiated within the porphyrin unit's Soret band using 413 nm light, a maximum in the photocurrent intensity was observed. In addition, there was some photosensitization coincident with the porphyrin unit's Q bands at excitation wavelengths of 514 and 568 nm. The photo-to-electrical energy conversion is linear (Figure 3 b) for all laser powers used in this study. Furthermore, it was observed that a range of cell biases (−200 to −600 mV in aqueous solution, or −300 to 600 mV in acetonitrile; see below) is needed to produce a photocurrent.[20] This result is consistent with the passage of a photocurrent that flows through the SAM from the gold to the platinum electrode.

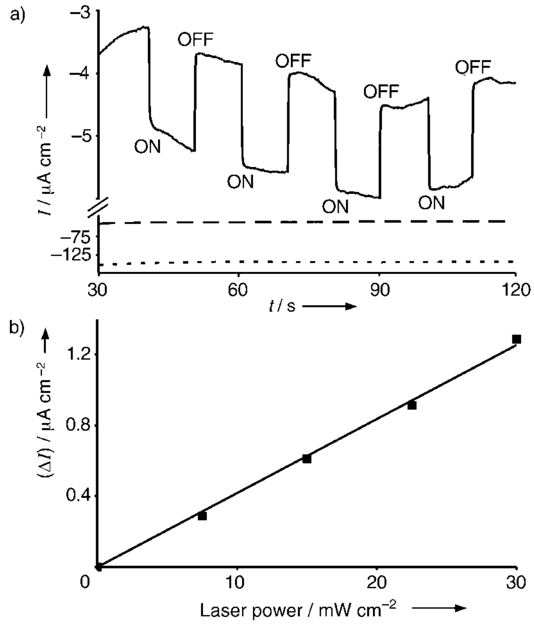

Figure 3. a) The photocurrent switching cycle of a **Triad** SAM (——), recorded in a photoelectrochemical cell by gating 413 nm excitation ON and OFF every 10 s after the current response has reached an equilibrium value with polarization at −500 mV (0.1 M Na_2SO_4, aerated). The bottom two traces were recorded under identical conditions on a SAM of decanethiol (– – –) and on bare Au (-----); b) A plot illustrating the linearity of the difference between the ON and OFF signals in the photocurrent response (ΔI) with laser intensity, recorded under the same conditions as those described in a).

Finally, this nanoscale source of electrical energy was utilized (Figure 4) to drive[6a,d,21] the dethreading of a pseudorotaxane comprised of the cyclobis(paraquat-*p*-phenylene)($CBPQT^{4+}$) cyclophane complexed with 1,5-bis-[(2-hydroxyethoxy)ethoxy]naphthalene (BHEEN). For the dethreading experiment, similar conditions were used as for the photoelectrochemistry, except that MeCN was employed as the solvent in order to solubilize the weakly fluorescent pseudorotaxane and its intensely fluorescent dethreaded component, namely BHEEN. At −100 mV, the BHEEN-based fluorescence (Figure 4 b) increases gradually when the **Triad** generates an average photocurrent of 1.09 $\mu A\,cm^{-2}$ (Figure 4 c) in response to excitation at 413 nm. It was observed that the population of the dethreaded BHEEN de-

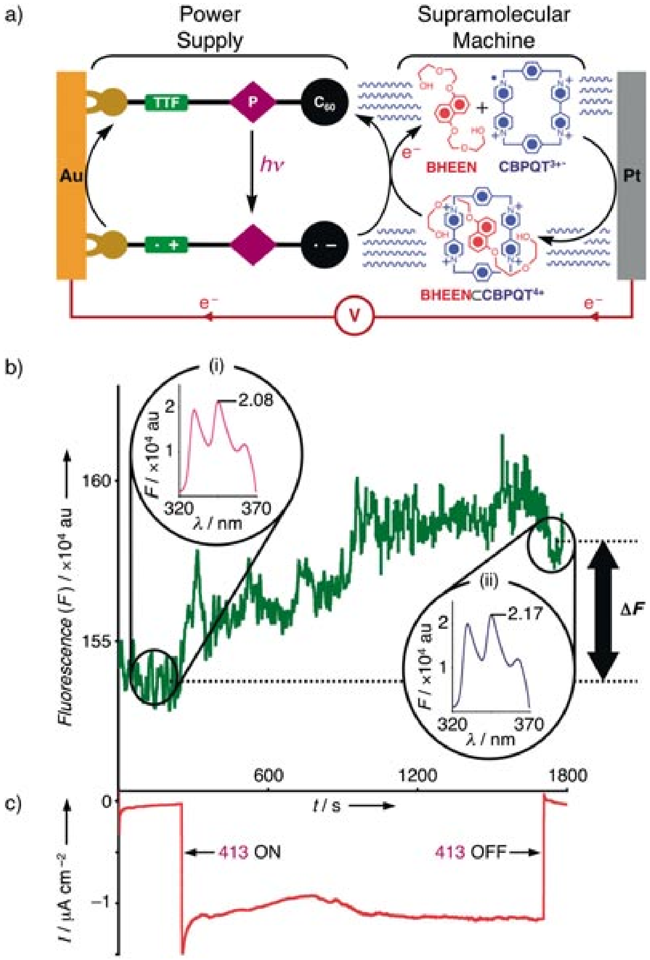

Figure 4. a) Schematic representation illustrating how a SAM of the light-driven power supply (**Triad**) provides the electrical energy to dethread a pseudorotaxane comprised of BHEEN (red) complexed with CBPQT^{4+} (blue). The curved arrows indicate the vectorial electron pathway from the Au electrode to the TTF unit and then to the C_{60} unit, following photoexcitation of the **Triad**. Subsequently, the electron is transferred to the CBPQT^{4+} ring of the pseudorotaxane, leading to dethreading of the now reduced CBPQT$^{3+\bullet}$ before its electron is passed onto the Pt counter electrode; b,c) The dethreading was monitored by the increase in the fluorescence of BHEEN (green line, $\lambda_{exc}=257$ nm), which is concomitant with the photocurrent generated by the **Triad** SAM (shown as the red line in c). The insets show the fluorescence spectra of BHEEN before (inset i, purple) and after (inset ii, blue) photoexcitation of the **Triad** SAM at 413 nm.

creases slowly (minutes) in the solution volume that was sampled by emission spectroscopy.[22] The fluorescence spectra of BHEEN were recorded before (inset i) and after (inset ii) the **Triad** SAM was irradiated with 413 nm light.

A simple calculation verifies that the total change in the fluorescence of the solution (+3.36 %) is consistent with the degree of dethreading based[23] on an initial pseudorotaxane concentration of 0.37 mM at equilibrium. Over the 1450 s of the experiment, an average photocurrent of 1.09 μA generates 9.86×10^{15} electrons that, in turn, dethread[24] 3.44 % of the pseudorotaxane by reducing its CBPQT^{4+} ring to the monoreduced CBPQT$^{3+\bullet}$ form. [25] The amount (3.44 %) of dethreaded BHEEN estimated for the photocurrent observed in this experiment is consistent with the percentage increase (3.36 %) in the fluoresence intensity of BHEEN, as measured at the end of the 413-nm excitation. The observed increase in the steady-state population of the dethreaded pseudorotaxane is a consequence of electron transfer from the photoreduced $C_{60}^{\bullet -}$ unit to the CBPQT^{4+} ring—a result that is ultimately related to the gated photocurrent (Figure 4 c), concomitant with switching the 413 nm light ON and OFF.

In summary, a TTF-P-C_{60} molecular **Triad** that forms a SAM on gold-electrode surfaces generates a switchable photocurrent that serves as a basis for incorporating local nanometer-sized power supplies into molecular machines and, in principle, other nanoscale systems. The photocurrent was recorded in both aqueous and organic solutions. The observed photocurrent at 0 V in acetonitrile bodes well for optimizing the system to obtain[26] a true photocell that can generate an open-circuit photovoltage.

Keywords:
energy conversion · fluorescence · molecular devices · pseudorotaxanes · self-assembled monolayers

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[17] Our observation of the reversible reductions of the C_{60} unit in the **Triad** SAM is in contrast with the irreversible reduction of the C_{60} unit observed in the CV of a Fc-P-C_{60} triad SAM reported by Imahori (see Ref. [12c]). However, Kodis (see Ref [13b]) has reported the observation of the first reduction of the C_{60} unit at −560 mV in a solution-phase CV of a TTF-P-C_{60} based triad.

[18] The molecular footprint of the **Triad** ($1.4\,\mathrm{nm^2\,molecule^{-1}}$) in a SAM is larger than that ($0.86\,\mathrm{nm^2\,molecule^{-1}}$) reported by Imahori (see Ref. [12c]) for a Fc-based triad SAM. The difference is attributed to the larger *N*-phenyl substituent, which replaces an *N*-methyl substituent on the C_{60} unit, as well as a longer and more flexible spacer between the porphyrin and TTF units.

[19] Imahori (see Ref. [12c]) reported a Fc-based triad SAM in aqueous solution where a photocurrent was observed between applied voltages of −200 and +400 mV.

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[22] The rate of rethreading and thus the decrease of the BHEEN component's fluorescence was recorded in a control experiment by direct reduction of the CBPQT^{4+} ring at −400 mV in the absence of 413 nm light (see Supporting Information).

[23] The initial concentrations of 0.5 mM of the BHEEN unit and the CBPQT^{4+} ring generate 0.37 mM of pseudorotaxane (BHEEN$\subset$CBPQT^{4+}) at equilibrium, a concentration which has been calculated based on the association constant (K_a) of $2.53\times10^{4}\,\mathrm{M^{-1}}$ (MeCN, 298 K). In a solution volume of 3 mL, the concentration of 0.37 mM provides 1.11×10^{-6} mol of the pseudorotaxane. For the original determination of the K_a value, see: R. Castro, K. R. Nixon, J. D. Evanseck, A. E. Kaifer, *J. Org. Chem.* **1996**, *61*, 7298–7303.

[24] In a control experiment at an applied potential of −500 mV at a bare gold electrode (see Supporting Information), an average current of 6.12×10^{-5} A for 750 s, which generated 2.86×10^{17} electrons, completely dethreads all of the initial pseudorotaxane molecules (1.11×10^{-6} mol) by directly reducing its CBPQT^{4+} ring. Accordingly, 9.86×10^{15} electrons, originating from the photocurrent at −100 mV, dethreads 3.44% of the initial pseudorotaxane molecules.

[25] On average, the CBPQT^{4+} ring is believed to be monoreduced at a potential of −300 mV. See also Figure 8a in R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi, M. Venturi, *Acc. Chem. Res.* **2001**, *34*, 445–455.

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