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Notes:

Photoinduced electron flow in a self-assembling supramolecular extension cable

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We report the design, bottom-up construction, characterization, and operation of a supramolecular system capable of mimicking the function played by a macroscopic electrical extension cable. The system is made up of a light-powered electron source, an electron drain, and a cable as the molecular components programmed to self-assemble by means of two distinct plug/socket junctions. Such connections are reversible and can be operated independently by orthogonal chemical inputs. In the source–connector–drain supermolecule, photoinduced electron transfer from source to drain occurs, and it can be switched off by dual-mode chemically controlled disassembling of the molecular components.

electron transfer | luminescence | molecular device | photochemistry | supramolecular chemistry

Information processing at the molecular level could open the way to the design and construction of “molecular computers” (1) much smaller and more powerful than the current silicon-based computers. It can be noted that the term *molecular computer* is still an emotive one, despite the fact that more than 20 years ago the Pimentel report (2) was quite encouraging in this regard:

There are those who dismiss as far-fetched the idea of man-made molecular scale computers... But since we know that molecular computers are routine accessories of all animals from ants to zebras, it would be prudent to change the question from *whether* there will be man-made counterparts to questions concerning *when* they will come into existence and *who* will be leading in their development. The *when* question will be answered on the basis of fundamental research in chemistry; the *who* question will depend on which countries commit the required resource and creativity to the search.

As research toward signal processing at the molecular level advances, it becomes more and more evident that two quite different strategies can be exploited. One strategy relies on the use of molecules to create nanoscale electric circuits that would replace those used in the current microelectronic solid-state technology (3–6). An alternative strategy, which receives inspiration from information transfer processes in living organisms, is based on chemical input and output signals that can be generated by chemical, photochemical, and electrochemical reactions and combined with light inputs (absorption) and outputs (fluorescence, transmission) (7–14). The two strategies are different, not only in a philosophical sense, but also from a chemical viewpoint: molecules that are used as the components of a nanoscale electrical circuit in the solid state must be irreversibly linked together, whereas signal exchange among molecules in solution takes place by self-assembling/controlled-disassembling processes (15–20).

We report herein the design, bottom-up construction, characterization, and operation of a nanometric self-assembling

system capable of performing signal processing in solution. In such a “wet” system that mimics, at the molecular level, the function served in the macroscopic world by an electric source, an extension cable, and a drain, the electron flow is driven by light and it is switched on/off by two distinct, reversible assembling/disassembling processes that are governed by chemical inputs and operate in series. The present system represents a substantial improvement on a previously described one (21), which was based on two (of three) different molecular components and could not mimic a real extension cable.

A system capable of exploiting the role of a working extension cable (Fig. 1A) must consist of three components, programmed to operate as an electron source, a connecting wire, and an electron drain. The three components must be designed so that one end of the wire can be plugged in/out of the source, and the drain can be plugged in/out of the other end of the wire. Furthermore, each plug in/out function has to be reversible, independent, controllable by an external input, and monitorable. Finally, when the three parts are connected, an electron flow from the source to the drain must occur. The system made of components 1^{2+} , 2-H^+ , and 3^{2+} , shown in Fig. 1B, meets these requirements at the (supra)molecular level.

The electron source component 1^{2+} comprises (i) a $[\text{Ru}(\text{bpy})_3]^{2+}$ -type unit (bpy = 2,2'-bipyridine), which is an electron donor in its excited state (22), and (ii) a dibenzo[24]crown-8 (DB24C8) macrocycle capable of playing the role of a hydrogen-bonding socket (9, 21, 23). The extension cable 2-H^+ is made up of three moieties, namely (i) a dialkylammonium ion center, which can insert itself as a plug into a DB24C8 socket, (ii) a conducting biphenyl spacer, and (iii) a benzonaphtho[36]crown-10 (BN36C10) unit, which fulfills the role of a π -electron-rich socket (9, 21). Finally, the 1,1'-dioctyl-4,4'-bipyridinium dication 3^{2+} , which was selected among several bipyridinium derivatives because of its solubil-

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Abbreviations: bpy, 2,2'-bipyridine; BN36C10, benzonaphtho[36]crown-10; DB24C8, dibenzo[24]crown-8; SCE, saturated calomel electrode; TBA, tributylamine.

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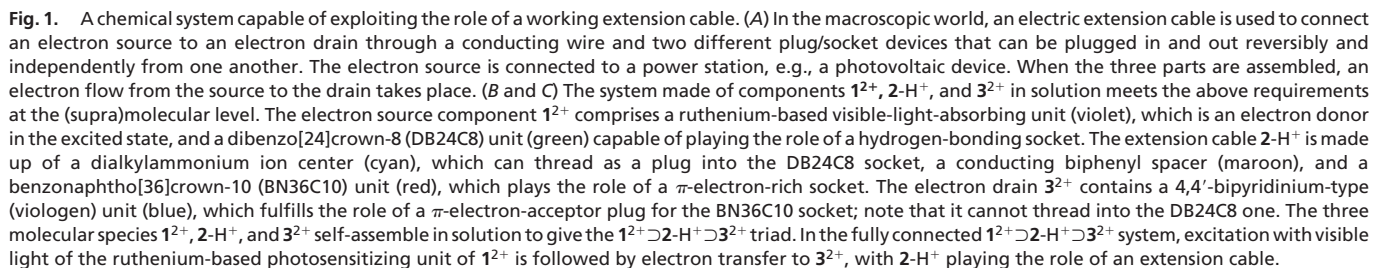
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ity in CH_2Cl_2 , can play the role of an electron drain plug (9, 24). The two plug/socket connections $1^{2+} \supset 2\text{-H}^+$ and $2\text{-H}^+ \supset 3^{2+}$ can be controlled by acid/base and red/ox stimuli, respectively, and monitored by changes in the absorption and emission spectra. In the fully connected $1^{2+} \supset 2\text{-H}^+ \supset 3^{2+}$ system, light excitation (25–27) of the ruthenium-based unit of 1^{2+} is followed by electron transfer to 3^{2+} , with 2-H^+ playing the role of an extension cable (Fig. 1C).

Compared with a previously described system (21), the one outlined in this article shows two conceptual and quite significant differences: (i) 2-H^+ consists of a plug and a socket components, and thus it really mimics an extension cable, whereas the previously used cable consisted of two plugs; (ii) the photoinduced electron transfer does take place from the first component, the ruthenium-based unit of 1^{2+} , to the remote 3^{2+} viologen unit, whereas, in the previous system, the electron-receiving viologen unit was a component of the cable.

Properties of the Molecular Components. Fig. 2 shows some of the compounds that have been used as references. Compound **1**²⁺ exhibits, in the visible region, the absorption ($\lambda_{\text{max}} = 450 \text{ nm}$, $\epsilon = 1.4 \times 10^4 \text{ liter}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) and emission (Figs. 3B and 4; $\lambda_{\text{max}} = 608 \text{ nm}$, $\tau = 333 \text{ ns}$) bands of its [Ru(bpy)₃]²⁺ moiety, does not show redox processes in the range 0/−1 V versus the saturated calomel electrode (SCE), and is unaffected by addition of tributylamine (TBA) or zinc powder (see below). At $\lambda > 300 \text{ nm}$, 2-H⁺ shows the same absorption spectrum as that of **2** (obtained by deprotonation of 2-H⁺ with one equivalent of TBA) and of the BN36C10 reference compound **4**. Each one of these three compounds exhibits the fluorescence band (Fig. 3A; $\lambda_{\text{max}} = 345 \text{ nm}$) of its 1,5-dimethoxynaphthalene unit. The emission intensity is the same in **2** and **4**, and much weaker (23%) in 2-H⁺ (see Fig. 6 and Table 1, which are published as supporting information on the PNAS web site). This behavior can be accounted for

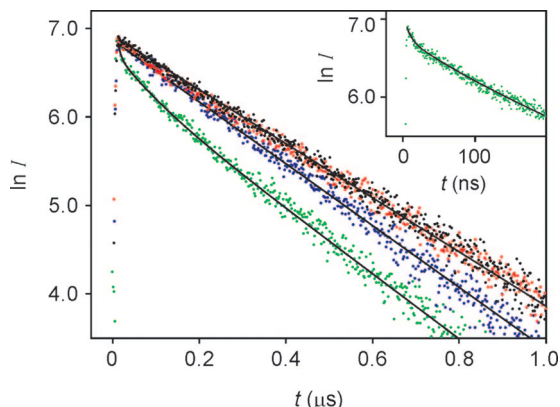


Fig. 4. Decay of the ruthenium-based luminescence ($\lambda_{\text{exc}} = 407$ nm) for 1^{2+} alone (black dots) and in the presence of 2-H^+ (red), 3^{2+} (blue), and $2\text{-H}^+ + 3^{2+}$ (three-component system, green). I , intensity of luminescence. The first three data sets correspond to single-exponential decays, whereas the latter (see *Inset* for a detail) corresponds to a triple-exponential decay. The fitted curves are represented as full lines. The experimental conditions are the same as those described for Fig. 3.

10^{-5} mol·liter $^{-1}$, and $[3^{2+}] = 1.3 \times 10^{-4}$ mol·liter $^{-1}$. On the basis of the association constants mentioned above, under these conditions, >95% of 1^{2+} should be connected to 2-H^+ and $\approx 50\%$ of the $1^{2+} \supset 2\text{-H}^+$ dyad should be connected with 3^{2+} to yield the $1^{2+} \supset 2\text{-H}^+ \supset 3^{2+}$ triad. The real concentration of the triad was estimated by measuring the *static* quenching of the luminescence of the ruthenium-based unit of 1^{2+} by the 3^{2+} component, plugged into the BN36C10 moiety of 2-H^+ . Because 3^{2+} is also expected to quench the long-lived luminescence of the ruthenium-based unit of 1^{2+} by a dynamic process, we have first investigated the quenching of the luminescence of $[\text{Ru}(\text{bpy})_3]^{2+}$ model compound and of the ruthenium-based unit of 1^{2+} by 1.3×10^{-4} mol·liter $^{-1}$ 3^{2+} (in the absence of 2-H^+), and found that, for both compounds, quenching of emission intensity (Fig. 3*B*) and lifetime (Fig. 4) take place. In particular, the lifetime of the ruthenium-based unit of 1^{2+} decreased from 333 to 266 ns. Then we measured the quenching of the luminescence intensity (taken as 100) and lifetime (336 ns) of the $1^{2+} \supset 2\text{-H}^+$ dyad upon addition of 1.3×10^{-4} mol·liter $^{-1}$ 3^{2+} . We found that the emission intensity was reduced to 58 (Fig. 3*B*) and that a triple-exponential decay took place, corresponding to lifetimes of 260, 75, and 7 ns (Fig. 4 and Table 2, which is published as supporting information on the PNAS web site). The longest lifetime can be attributed straightforwardly to the dynamic quenching process, which, from quantitative analysis, accounts for 27% of the observed quenching—in reasonable agreement with the 20% of quenching found in the absence of 2-H^+ . The two shorter lifetimes, accounting for the remaining 15% of quenching, can be assigned to static quenching processes taking place in two different (co)-conformations, possibly stretched and folded, of the $1^{2+} \supset 2\text{-H}^+ \supset 3^{2+}$ triad.

Photoinduced Electron Flow in the Supramolecular Triad. Direct observation of the visible-light-induced electron flow from the ruthenium-based unit of 1^{2+} to 3^{2+} in the fully connected triad came from transient absorption experiments. Selective excitation of the ruthenium-based unit of 1^{2+} with nanosecond laser pulses (532 nm) in deaerated solutions containing the three components led to the prompt (within the laser pulse) appearance of an absorption signal at 398 nm (Fig. 5), where the monoreduced 3^+ species exhibits (24) an intense absorption band. Such a signal, which was not present in the control

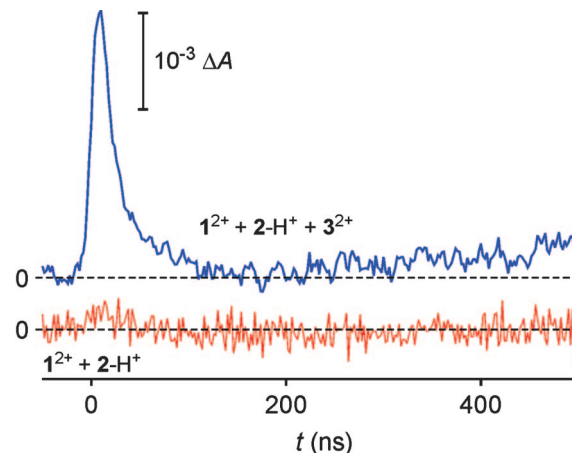


Fig. 5. Transient absorption kinetics monitored at 398 nm (isosbestic point between the ground and excited ruthenium-based unit) upon nanosecond laser excitation at 532 nm of solutions containing 1^{2+} , 2-H^+ , and 3^{2+} (blue), and only 1^{2+} and 2-H^+ as a control (red). The immediate increase and the successive fast decrease ($\tau = 28$ ns) of absorbance is assigned to the formation and disappearance of the 3^+ species in the $1^{2+} \supset 2\text{-H}^+ \supset 3^{2+}$ triads, and the signal after 200 ns is assigned to the 3^+ species originating from the dynamic quenching of the ruthenium-based unit of 1^{2+} by 3^{2+} . Conditions: deaerated CH_2Cl_2 solutions, room temperature; $[1^{2+}] = 3.7 \times 10^{-5}$ mol·liter $^{-1}$, $[2\text{-H}^+] = 4.6 \times 10^{-5}$ mol·liter $^{-1}$, and $[3^{2+}] = 3.0 \times 10^{-5}$ mol·liter $^{-1}$.

solution, decays according to a first-order process with a lifetime of 28 ns.

The concentration of the $1^{2+} \supset 2\text{-H}^+ \supset 3^{2+}$ species in the solution containing all three components was also estimated by measuring the quenching of the BN36C10 fluorescence by the 3^{2+} component plugged into the BN36C10 moiety of 2-H^+ (Fig. 3*A*). In this case, dynamic quenching processes do not interfere because of the short lifetime (7 ns) of the BN36C10 excited state. The results obtained from intensity quenching are comparable to those obtained for the quenching of the ruthenium-based unit of 1^{2+} . They are, however, somewhat less precise because of interference caused by band overlapping. The quenched lifetimes were too short to be measured, in keeping with similar systems (21).

Controlled Disassembly of the Extension Cable System. Addition of one equivalent of TBA to the solution containing the three components caused an 11% increase in the luminescence intensity of the ruthenium-based unit of 1^{2+} , in agreement, within experimental errors, with the 15% quenching attributed to the presence of $1^{2+} \supset 2\text{-H}^+ \supset 3^{2+}$ triad (see above). Moreover, a monoexponential luminescence decay was restored. These results show that the $1^{2+} \supset 2\text{-H}^+$ junction of the triad can be acid/base controlled. Addition of a 20-fold excess of zinc powder to deaerated solutions containing the three components caused, besides the appearance of the strong absorption bands for 3^+ (see Fig. 12, which is published as supporting information on the PNAS web site), a revival of the BN36C10 fluorescence of the 2-H^+ unit, showing that the $2\text{-H}^+ \supset 3^{2+}$ connection can be red/ox controlled.

Conclusion

We have designed, synthesized, and characterized a multicomponent molecular level system that operates in CH_2Cl_2 solution and mimics the function played in the macroscopic world by a light-powered electric source, an extension cable, and a drain (Fig. 1). In the self-assembled, fully connected $1^{2+} \supset 2\text{-H}^+ \supset 3^{2+}$ supramolecular system, electrons generated by visible photoexcitation of the ruthenium-based unit of 1^{2+} are transmitted to

3^{2+} on the nanosecond time scale. The system can be switched on/off by two distinct, reversible assembling/disassembling processes that are governed by chemical inputs operating in series and therefore can play the role of an NAND logic gate.

The present system represents a substantial improvement on a previously described one (21) that was based on different molecular components. In particular, 2-H^+ consists of a plug and a socket components and thus it really mimics an extension cable. Furthermore, at variance with the previously reported system (21), the photoinduced electron transfer does take place from the first component, the ruthenium-based unit of 1^{2+} , to the remote 3^{2+} viologen unit. It may be noticed that, in the present supramolecular system, electrons do not flow through the intermediate component in the same way as they do in the metallic wire of a macroscopic extension cord. Nevertheless, the electron transfer in the system discussed in this article takes place most likely by a superexchange mechanism that implies an electronic role of the bridge.

Interestingly, the extension cable component 2-H^+ exists in a self-threaded conformation, which cannot host the electron drain until it is opened up by complexation with the socket unit of the source component. This feature, which can be viewed as a limitation because it reduces the efficiency, in fact plays the function of a safety-catch device. Moreover, the photoinduced electron-transfer process can be powered by sunlight because the $[\text{Ru}(\text{bpy})_3]^{2+}$ -type component shows a broad and intense absorption band in the visible spectral region.

Materials and Methods

The synthesis and characterization of 1^{2+} and 6-H^{3+} have been reported elsewhere (21). $1,1'\text{-Diocetyl-4,4'-bipyridinium } 3^{2+}$, crown ether **4**, and $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ were available from previous investigations. Crown ether **5** (Aldrich, Milwaukee, WI), TBA (Fluka, Buchs, Switzerland), trifluoromethanesulfonic acid (Fluka), and the solvent CH_2Cl_2 used for the photophysical (Uvasol from Merck, Darmstadt, Germany) and electrochemical (Hi-Dry from ROMIL, Cambridge, U.K.) experiments were used as received. The synthesis of compound 2-H^+ is outlined in Scheme 1, which is published as supporting information on the PNAS web site. More details can be found in the *Supporting Text*.

The absorption and luminescence experiments have been performed at room temperature ($\approx 300\text{ K}$) on dilute solutions (2.0×10^{-5} to $2.0 \times 10^{-4}\text{ mol}\cdot\text{liter}^{-1}$) in air-equilibrated CH_2Cl_2 (Merck Uvasol), unless otherwise stated. UV-visible absorption spectra were recorded with a $\lambda 40$ spectrophotometer (Perkin-Elmer, Wellesley, MA). Luminescence spectra were obtained with a LS-50 spectrofluorimeter (Perkin-Elmer) equipped with a R928 phototube (Hamamatsu, Hamamatsu City, Japan). Luminescence lifetimes were measured by the time-correlated single-photon counting (TCSPC) technique with Edinburgh Instruments (Livingston, U.K.) TCSPC equipment. The exciting light was produced by a gas arc lamp (model nF900, filled with D_2) or a laser diode ($\lambda_{\text{exc}} = 407\text{ nm}$) that delivered pulses of $\approx 1\text{ ns}$ (full width at mid-height). The light emitted was filtered by using a cutoff filter, and the detector was a cooled Hamamatsu R928 photomultiplier. More details on the fitting of the exper-

imental luminescence decay curves and on the absorption and luminescence titration experiments can be found in the *Supporting Text*. The experimental error on molar absorption coefficients, emission intensities, and luminescence lifetimes is estimated to be $\pm 5\%$. The error on the association constants, derived from titration experiment, is estimated to be $\pm 20\%$.

Transient absorption experiments were performed at room temperature by exciting the sample with 10-ns (full width at mid-height) pulses of a Surelite I-10 Nd:YAG laser (Continuum, Santa Clara, CA). A 150-W xenon lamp (model 720; power supply, model 620; Applied Photophysics, Surrey, U.K.) perpendicular to the laser beam was used as a probing light; for the kinetic investigations in the 0- to 10- μs time window, a pulsing unit (Applied Photophysics model 03-102, 2-ms pulses) was also used. Excitation was performed at $\lambda = 532\text{ nm}$ (obtained by frequency doubling). A shutter was placed between the lamp and the sample, and it was opened only during the measurements to prevent phototube fatigue and photodecomposition. Suitable pre- and post-cutoff and bandpass filters were also used to avoid photodecomposition and interferences from scattered light. The light was collected in a PTI (South Brunswick, NJ) monochromator (model 01-001; grating, 1,200 lines per mm; slit width, 0.25 mm; resolution, 1 nm), detected by a Hamamatsu R928 tube, and recorded on a Tektronix (Vimodrone, Italy) TDS380 (400 MHz) digital oscilloscope connected to a PC. Synchronous timing of the system was achieved by means of a built-in-house digital logic circuit. The absorption transient decays were plotted as $\Delta A = \log(I_0/I_t)$ versus time, where I_0 and I_t are the probing light intensity before the laser pulse and after delay t , respectively. Each decay was obtained by averaging at least 20 pulses. Transient absorption spectra were obtained from the decays measured at various wavelengths (10-nm increment), by sampling the absorbance changes at constant delay time. The experimental error on the wavelength and lifetime values is estimated to be $\pm 2\text{ nm}$ and $\pm 5\%$, respectively.

Voltammetric measurements (cyclic voltammograms, CVs, and differential pulse voltammograms, DPVs) were recorded in argon-purged CH_2Cl_2 (ROMIL Hi-Dry) solution at room temperature with an Autolab 30 multipurpose instrument (Eco Chemie, Origgio, Italy) interfaced to a PC. The concentration of the compounds examined was $5.0 \times 10^{-4}\text{ mol}\cdot\text{liter}^{-1}$; $0.050\text{ mol}\cdot\text{liter}^{-1}$ tetraethylammonium hexafluorophosphate was added as the supporting electrolyte. The working electrode was a glassy carbon microelectrode (0.08 cm^2). A complete description of the electrochemical cell and the electrochemical procedures is reported in the *Supporting Text*. The accuracy on the potential values is estimated to be $\pm 10\text{ mV}$.

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