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Data and signal processing using photochromic molecules

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Photochromes are chromophores that are reversibly isomerized between two metastable forms using light, or light and heat. When photochromes are covalently linked to other chromophores, they can act as molecular photonic analogues of electronic transistors. As bistable switches, they can be incorporated into the design of molecules capable of binary arithmetic and both combinatorial and sequential digital logic operations. Small ensembles of such molecules can perform analogue signal modulation similar to that carried out by transistor amplifiers. Examples of molecules that perform multiple logic functions, act as control elements for fluorescent reporters, and mimic natural photoregulatory functions are presented.

Introduction

The transistor (and its predecessor the vacuum tube) have allowed the development of electronics and electronic data processing. A field effect transistor acts as an amplifier, in which current flowing from an input (source) to an output (drain) is controlled by the voltage at a second input (gate). In addition to this analogue function, transistors can also act as binary digital switches. Application of a gate voltage above a suitable threshold level switches on the transistor current between the source and drain. A gate voltage less than the threshold switches the current “off,” which means that the current is reduced to a lower-level “leakage” current.

Suitably designed molecules (or strictly speaking, ensembles of molecules) can behave as photochemical analogues of transistors. In digital applications they can function as binary switches and much more complex Boolean logic gates. In analogue applications, they can both act as photonic “amplifiers” and mimic the kinds of control functions found in biology. Below, we exemplify these types of molecular behaviour with molecules from our laboratory, and reference some of the excellent research of others working in this area.

Photochemically active molecules as digital switches and logic devices

Broadly defined, a binary switch is a system that can be placed reversibly in either of two states by the application of an input, coupled with a means of observing in which state the switch exists. Thus, there are a huge number of switching operations possible in molecules, such as protonation, binding of a ligand or substrate, oxidation or reduction, isomerization, base paring, light absorption to produce an excited state, etc. For example, the common indicator dye phenolphthalein is colourless in acidic solution, but turns pink upon addition of base, allowing it to act as a simple single-throw-single-pole binary switch whose state is detected by light absorption.

The ability to employ molecules as switches has inspired chemists to consider using molecules as replacements for transistors for carrying out digital operations. A significant literature on molecular logic has developed, and the subject has been reviewed.[1-20]

Molecules that act as switches using only light as inputs and outputs are particularly attractive for molecular logic applications. They have several actual and potential advantages:

- Light does not require addition of chemicals or build-up and removal of products from repeated cycling of the switch.
- Physical access to the switching element, other than light transmission, is not necessary. This allows the placement of many switching elements in planar or three-dimensional arrays.
- Molecular switches can be small, and in principle function at the diffraction limit, or even below if near-field optical techniques are employed.
- Molecular photoswitches can be fast. Light can be delivered as pulses, and reversible photochemical reactions such as photoisomerizations occur rapidly in order to compete with deactivation of excited states by other pathways. Typically, this means the ps or ns time scales. The actual time necessary to switch a small ensemble of molecules depends on the light flux, the molar extinction coefficient, and the quantum yield of the switching reaction. In addition, unimolecular reactions activated by light do not require diffusion, and reaction rates are therefore not diffusion limited.
- Light-activated molecules can be cycled many times, although in practice this is often limited by competing unimolecular reactions, or photodestruction by oxygen.

In 2006 we reviewed some of the applications of photochemistry and photochemical reactions to molecular logic.[1] Significant progress has been made since then. Illustrative examples from our laboratories appear below.

Simple molecular switches

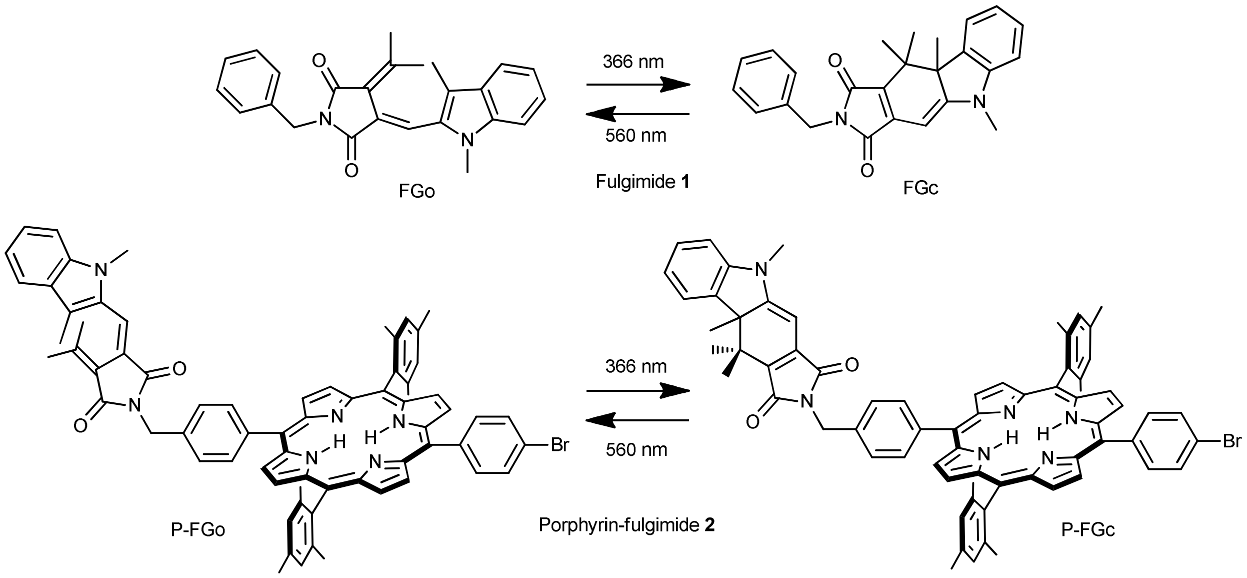

Fig. 1. Structures of fulgimide photochrome **1** and porphyrin-fulgimide dyad **2**. Each molecule is shown with the photochrome in the open (FGo) and closed (FGc) forms, and wavelengths for photoisomerization between the two forms of each molecule are indicated.

One of the most useful classes of light-operated molecular switches is the photochromes. Photochromic compounds exist in two metastable isomeric forms, and light can be used to interconvert them by photoisomerization. An example is fulgimide **1** (Fig. 1).[21,22] The compound exists in solution as an open form FGo (actually a mixture of *E*- and *Z*-isomers) with an absorption maximum at 380 nm (see inset, Fig. 2a). Irradiation at, for example, 366 nm leads to cyclization to the closed isomer FG_c. A photostationary distribution consisting of mainly FG_c results, and displays absorption maxima at 400 and 510 nm (Fig. 2a). Photochrome FG_c fluoresces (λ_{max} = 600 nm). Irradiation of FG_c in the visible (e.g. 560 nm) results in photoisomerization back to FG_o. Thus, **1** is a photochemically operated molecular switch whose inputs and outputs are light.

In order to perform more sophisticated logic operations, the output of one molecular switch must be transmitted to another. That is, the two switches must be "wired together" to form a more complex system. This can be achieved by chemically linking the switches together in a single molecular device. In such a molecule, two chromophores can "communicate" by energy transfer or electron transfer between them. For example, the isomerization state of a photochrome can affect the properties of an adjacent chromophore, thus transferring information between the two.

Such communication is illustrated by porphyrin-fulgimide (P-FG) dyad **2** (Fig. 1).[21] The absorption spectrum of P-FGo, where the fulgimide is in the open form, shows that the absorption properties of both chromophores are virtually unchanged from those of model compounds (Fig. 2a). The porphyrin Q-bands (648, 591, 547 and 513 nm) and Soret (418 nm) band are present, as well as absorption in the ultraviolet by the fulgimide. Irradiation at 366 nm results in photoisomerization of the fulgimide, giving a photostationary distribution containing mainly P-FGc, as evidenced by increased absorption between 430 and 600 nm and decreased absorption between 320 and 400 nm (Fig. 2). The P-FGc is thermally stable, but may be readily isomerized back to P-FGo by irradiation in the visible (e.g. 560 nm). Both isomers display normal free base porphyrin emission (λ_{max} = 650 and 720 nm, Fig. 2b), but no fluorescence from the fulgimide of P-FGc is observed. Fluorescence excitation experiments demonstrate that this is because singlet-singlet energy transfer from FGc to P occurs with ~100% efficiency. This conclusion is supported by time-resolved emission experiments.[21] While the fluorescence of FGc is quenched in this dyad, the porphyrin fluorescence is enhanced due to the energy transfer when the molecule is excited at wavelengths where FGc absorbs. For example, with excitation at 470 nm where FGFc absorbs strongly, porphyrin emission from P-FGc is 2.5 times more intense than that from P-FGo. Through energy transfer, the porphyrin moiety of **2** receives information about the isomerization state of the fulgimide, and its fluorescence output is adjusted in response to this information.

Photochemical molecular logic gates

This ability of photochromic molecules to both act as molecular switches and communicate with other chromophores makes possible the construction of all-photonic Boolean logic gates. These gates have inputs that embody two or more simple on-off switches and internal "circuitry" that generates a certain output based on the state of the input switches.

A particularly striking example of such a molecule is **3** (Fig. 3), which consists of three covalently-linked photochromes.[22,23] Molecule **3** bears two fulgimides and a dithienylethene (DTE). Each of these photochromes may exist in two photoisomeric forms, as shown in Fig. 3. The molecule may therefore exist in six constitutionally isomeric forms (there are stereoisomers as well, but these are not relevant for this discussion). For our purposes, only the four isomers in which the two identical fulgimides are in the same form (open or closed) are relevant:

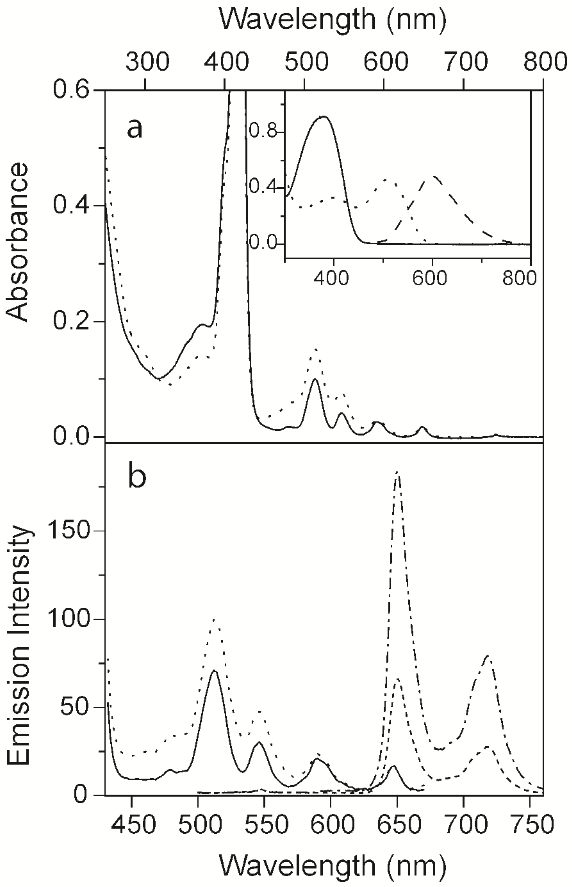

Fig. 2. (a) Absorption spectra of dyad **2**, with the fulgimide in the open form, P-FGo (□□□) and with the fulgimide in the cyclic, closed form P-FGc (• • • • •). The inset shows the absorption spectra of model fulgimide **1** in the open (□□□□) and cyclic (• • • • •) forms, and the emission spectrum of FGo (□ □ □ □). (b) Emission spectra of P-FGo (- - - -) and the same sample after UV irradiation to form P-FGc (□ • □ • □ • □) with excitation at 470 nm, and corrected fluorescence excitation spectra of P-FGo (□□□□) and the same sample after UV irradiation to form P-FGo (• • • • •), with detection at 720 nm.

FGo-DTEo, FGc-DTEo, FGo-DTEc, and FGc-DTEc. As shown in Fig. 4, each isomer of **3** has a unique spectral signature in absorption and emission. Thus, if **3** is present as a solution in a suitable solvent, such as 2-methyltetrahydrofuran, wavelengths may be identified which will convert any mixture of isomers to a solution that is very highly enriched in any of the four forms.

Such wavelengths and the corresponding interconversions are identified in Fig. 5.

It is important to note that isomer FGc-DTEc does not show FGc emission, whereas FGc-DTEo does. This is because the molecule was designed so that singlet excitation energy is rapidly (τ < 5 ps) transferred from FGc to DTEc, thus quenching the fluorescence. As will be explained below, this behaviour is achievable only in a covalently linked system, and is vital for several logic functions.

Simple logic gates

The photochemistry of **3** forms the basis for molecular logic. Irradiation into the various absorption bands constitutes device inputs. Each input causes photoisomerization, which comprises the switching operation central to binary logic. After each input is turned off, the molecule remains in the selected state, recording the result of an input or series of inputs and allowing subsequent readout. The choice of readout (absorbance or emission at a particular wavelength) selects the logic operation performed.

An AND gate is an example of a simple logic gate. As shown in the truth table in Table 1, the gate has two binary inputs, either of which may be in the OFF (0) or ON (1) state. The gate outputs a signal reflecting the result of the AND logic operation: the output switches ON (1) only if both inputs have been switched ON. A solution of **3** can operate as a molecular photonic AND gate, as shown in Fig. 6a. The initial state is FGo-DTEo, inputs are light pulses at 397 nm and 302 nm, and the output is absorbance at 535 nm above a threshold value (dashed line in Fig. 6a). An output above the threshold is observed only after both inputs have been applied. Chemically, this occurs because only the two inputs together, applied at the same time or in any sequence, generate isomer FGc-DTEc (Fig. 5). This is the only isomer having the necessary absorbance at 535 nm (Fig. 4). Other combinations of inputs give outputs at levels below the threshold, corresponding to subthreshold leakage currents in a transistor.

Many examples of molecular AND gates, and indeed other Boolean logic gates, have been reported. Triad **3**, however, is unique in that it can be reconfigured to carry out a total of 13 different logic operations. All of these operations have the same initial state, FGo-DTEo. Reconfiguring simply requires changing the input and output wavelengths as required. In fact, the compound can even perform several operations simultaneously by monitoring several outputs at once.

Table 1 Truth table for binary arithmetic functions. Wavelengths (nm) for the various inputs and outputs (Absorption *A* or emission *Em*) are shown on the third line.

Inputs		Outputs			
a 397	*b* 302	AND A 535	XOR |ΔA| 393	INH1 A 393	INH2 Em 624
0	0	0	0	0	0
1	0	0	1	0	1
0	1	0	1	1	0
1	1	1	0	0	0

Table 1 shows three different logic gates that are important for performing binary arithmetic. Triad **3** can carry out all of these, as shown in Fig. 6, using the same initial FGo-DTEo state and the same inputs (397 nm and 302 nm). For example, an XOR (exclusive OR) gate delivers an ON output (1) only when either input is turned ON, but not when neither or both are ON. For triad **3**, the XOR output is the absolute value of the absorbance at 393 nm, |ΔA| (Fig. 6b). An INH (inhibit) gate gives an output of 1 only when one particular input (not the other or both) is applied. Triad **3** can function as two different INH gates as shown in Table 1 and Figs. 6c and 6d. Each gate responds to a different input (302 nm or 397 nm), and the outputs differ (absorbance at 393 nm and emission at 624 nm, respectively). The photochemistry responsible for these different gate functions is apparent from Fig. 5.

Adders and subtractors

Just as simple binary switches may be combined to act as more complex logic gates, these logic gates may be combined to

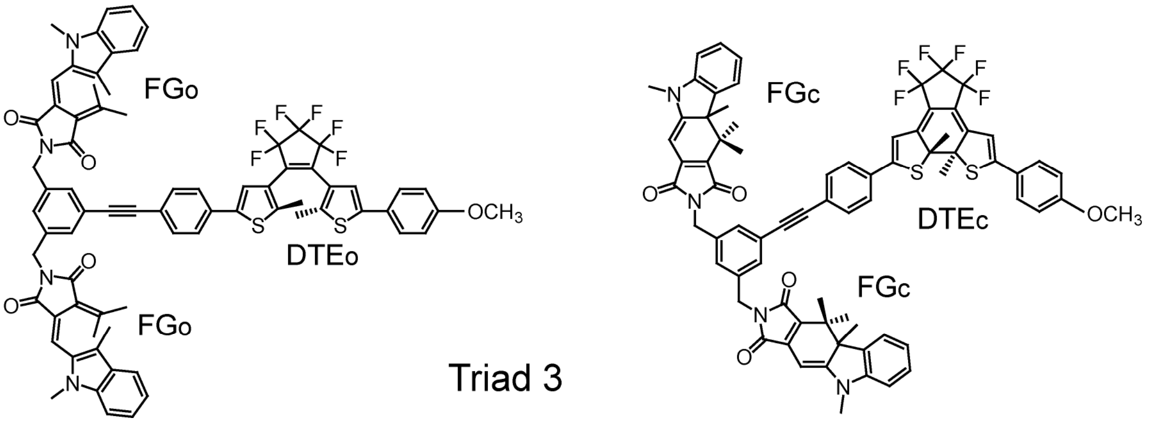

Fig. 3. Triad **3** contains two different kinds of photochromes, fulgimides (FG) and a dithienylethene (DTE). In the structure at the left, all photochromes are in the open forms. On the right, all chromophores are in the closed, cyclic forms. Other isomers are possible, as discussed in the text.

perform yet more complex operations. Because **3** can perform several logic functions, the device is capable of carrying out more complex binary arithmetic. For example, combination of AND and XOR gates which use the same two inputs produces a half-adder. The half-adder adds two binary digits represented by the two inputs, each of which may be OFF (binary 0) or ON (binary 1). The readout of XOR represents the sum digit, and that of AND the carry digit. If neither input is ON, both gates read out 0. This gives the binary sum 00, representing the decimal sum of 0 + 0 = 0. If either input is turned ON, AND reports a 0 whereas XOR reports a 1. Now, the binary sum reads 01 (0 + 1 = 1 in the decimal notation). If both inputs are ON, XOR reads out 0, and the AND gate delivers a 1 output. The binary output combination 10 represents the decimal 2 (1 + 1 = 2). Inspection of Figs. 6a and 6b demonstrate that **3** functions as required for a half-adder.

If instead, the XOR function of **3** is paired that of the INH1 function, a binary half-subtractor is generated. The inputs remain as previously described. The output of the XOR gate (Fig. 6b) represents the difference output, and the INH1 output gives the borrow output. If instead, XOR and INH2 are used, the order of the subtrahend and minuend is switched.[23]

Non-arithmetic logic

Molecular logic may be used for non-arithmetic purposes as well. For example, **3** may function as a digital 2:1 multiplexer (Fig. 7a). Multiplexers are analogous to mechanical rotary switches that connect any one of several inputs to a single output. They are used to combine several data input streams into a single line for transmission. The initial state for the operation of **3** as a multiplexer is FGo-DTEo. The two data inputs are 397 nm (In1) and red light (>615 nm, In2). There is a third input, the selector (Sel, 366 nm) which determines the input from which the data will be taken for transmission to the output (fluorescence at 624 nm). As shown in Fig. 7a, if Sel is not applied, the output is ON only when In1 is ON, and the state of In2 is ignored. Alternatively, if Sel is ON, the output reflects the state of IN2, and In1 is ignored.

Multiplexed signals must be separated again in order to make sense of the separate data streams. This is the job of a demultiplexer. Triad **3** can function as a 1:2 digital demultiplexer. The initial state is again FGo-DTEo. There are only one data input, In (397 nm), and two data outputs, O1 (624 nm emission) and O2 (absorbance at 535 nm). An additional input (302 nm) serves as the address (Ad), which determines to which output the input is sent. As shown in Fig. 7b, the state of O1 reflects that of In when Ad is OFF, and O2 has a zero output. When Ad has been applied, the state of In appears in O2, and O1 has a zero output.

Several other logic operations are available with **3**. For example, the molecule can act as a single-bit 4-to-2 encoder and 2-to-4 decoder.[11] These devices translate numbers in base-10 into binary numbers, and vice versa. The initial state for both functions is FGo-DTEo. Briefly, the encoder inputs are light at four different wavelengths, 460, 397, 302 and 366 nm, and the outputs are absorbance at 475 and 625 nm. When acting as a decoder, the inputs are light at 397 and 302 nm, and the outputs are absorbance at 393 and 535 nm, transmittance at 535 nm, and fluorescence at 624 nm. A set of dual transfer gates is also possible. These simply transfer the state of an input to that of an output with no logical change. These two gates comprise a logically reversible system, where each combination of inputs gives a unique output.[23]

Sequential logic

The logic functions described thus far are mainly combinatorial functions, where the state of the output is determined solely by the input combination, with no dependence on the order in which the inputs are applied. In sequential logic, the output depends on the order in which inputs are given. A simple example is the keypad door lock, which opens only when the correct inputs are applied in the correct sequence.

Triad **3** functions as a keypad lock with the initial state FGo-DTEo. There are two inputs: red light at >615 nm and UV light at 366 nm. The output of the lock is fluorescence emission of FGc at 624 nm. Fig. 8 shows this output as a function of not only the state of the two inputs, but also the order in which they are applied. It is clear from the figure that the output requires not only that both inputs be turned ON, but that the UV input be applied *before* the red light is switched on. Thus, of the 8 possible ordered combinations of the two inputs, only 1 opens the lock.

Advantages and limitations

Triad **3** illustrates the current stage of development of photochemical molecular logic in a single molecule. Some

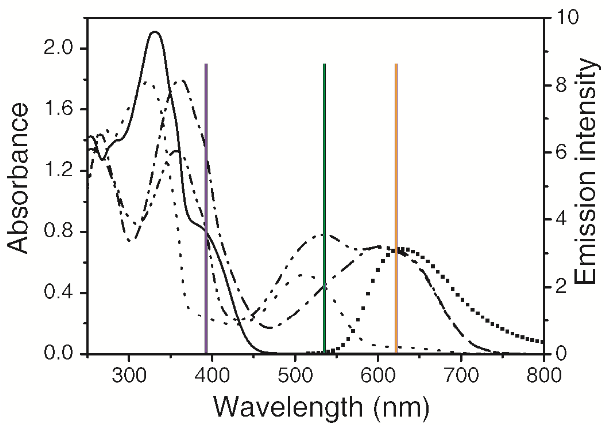

Fig. 4. Absorption and emission spectra of different forms of FG-DTE triad **3**. Solid line: thermally stable FGo-DTEo. Dotted line: FGc-DTEo. Dash-dot: FGo-DTEc. Dash-dot-dot: FGc-DTEc. Also shown is the emission from FGc in the FGc-DTEo form of the molecule (squares). The coloured vertical lines indicate wavelengths that are used as outputs for the various binary arithmetic functions of the triad.

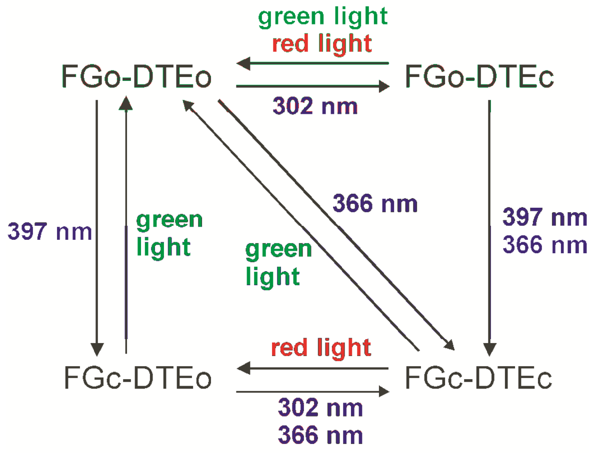

Fig. 5. Photochemical isomerizations among the 4 isomers of **3** that are relevant for the logic operations discussed. Green light signifies ($460 < \lambda < 590$ nm) and red light indicates $\lambda > 615$ nm.

important features are:

- Simple photochromic binary switches may be combined to form more complex logic gates (e.g., XOR). This is facilitated by communication among photochromes and other chromophores by energy transfer and electron transfer.
- Simple logic gates may be combined within a molecule to perform more complex mathematical operations (e.g., half-adder).
- Non-arithmetic logic operations are possible (e.g., multiplexer).
- Sequential logic is possible (e.g. keypad lock).
- In all these operations, the individual photochromes record the last input for later use or readout. The actual input may be applied as a pulse of light, and all inputs do not need to be applied at the same time.
- The triad is a multifunctional system that can be readily reconfigured to carry out a variety of logic functions. All 13 functions have the same initial state, and different applications require only choosing different photonic readouts and/or inputs.
- The triad may be cycled many times between the same or different applications by resetting to the initial state with green light.

These qualities demonstrate that the triad and similar systems are true nanoscale information processing units. Although a useful device will in general require a small ensemble of molecules rather than a single molecule, the volume necessary can still be at the diffraction limit or, in principle, below. It is unlikely that the first applications of such molecules will be in the construction of analogues of modern electronic computers. One reason for this is that photodamage ultimately occurs, limiting the number of cycles that the molecules can endure. Restricting oxygen access can greatly diminish photodamage, but photochemical side reactions will eventually take a toll, even if their quantum yields are extremely small. Secondly, computing applications will generally require concatenation of switches, gates, etc. so that the output of one device forms the input of the next. This problem is circumvented to some extent in molecules like the triad by combining several logic elements in the same molecule, so that the components may communicate. However, this approach is limited. Concatenation could be achieved with these photonic systems by using external electronic devices to receive the output from one operation (e.g. fluorescence or absorption), and generate a new input (light pulse) based on the output received. In this way, a functional computer *could* be made based on these molecules. However, a more direct method for communication between molecules would be preferable.

There are, however, applications for which molecular photonic systems are much better suited than are electronic devices. Because they are nanoscale and require no wires or similar connections, they may be applied in an almost unlimited variety of milieus. For example, molecular photonic switches have been used to specifically label nanoparticles so that they can be differentiated in solution.[24] Molecular logic systems are in principle compatible with biological systems. Photonic switches could be used to initiate drug delivery only at certain sites (for example a volume element where light beams of two different colours intersect). They could also be used to track the history of nanoparticles (biological or non-biological) circulating in complex flow systems. Because they are non-metallic and are not influenced by low-frequency electromagnetic radiation, they can be applied where conventional electronics are not suitable. Doubtless many more possible applications will arise as the field becomes more mature.

Photochemically active molecules as analogue devices

As mentioned in the Introduction, transistors can act both as digital switches and as analogue amplifiers or signal transducers. In the latter mode, the device again has inputs and outputs, but the output magnitude is a continuously variable function of the magnitude of one of the inputs. The triode amplifier tube or its transistor analogue are examples. Although the properties of a

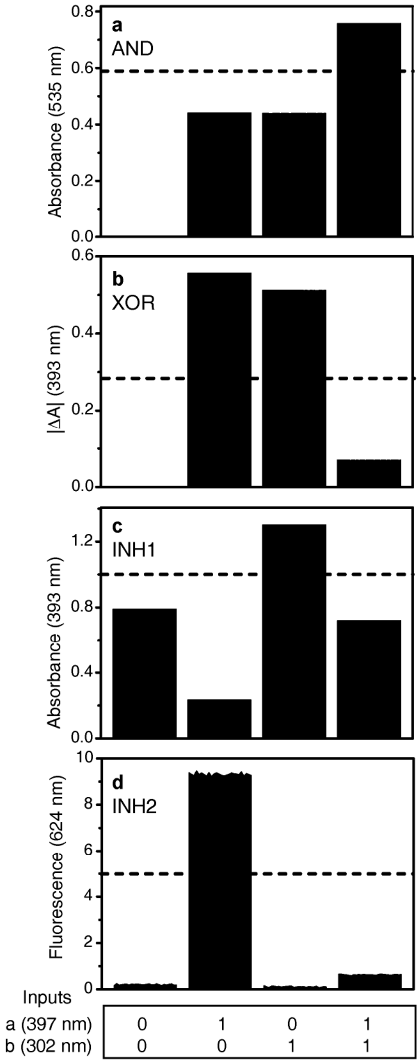

Fig. 6. Performance of arithmetic functions by triad **3**. The states of the two inputs for each column are shown at the bottom The outputs of the various gate functions are shown in a (AND), b (XOR), c (INH1) and d (INH2). The dashed lines represent threshold values, and the top of each bar shows the actual experimental data and associated noise. The half-adder is the combination of AND and XOR, whereas the half-subtractor is XOR combined with INH1 or IHN2.

single molecule are quantized by nature, it is possible to employ ensembles of photochemically active molecules in this analogue fashion. Two examples will be presented.

A photochemical “triode” molecular signal transducer

Molecular hexad **4** (Fig. 9) features five bisphenylethynylanthracene (BPEA) fluorophores and a dithienylethene photochrome organized by a central hexaphenylbenzene core.[25] The core is relatively rigid, as rotation of the aryl groups linked to the central phenyl ring is slow, and serves to restrict interchromophore distances and orientations, which in turn affect energy transfer rates.[26] The BPEA units are strong fluorophores that absorb in the 430 nm region and emit in the 520 nm region with a quantum yield of ~0.94. The BPEA singlet excited state lifetime is 2.8 ns. The DTE in the open form (DTEo, see **4o**, Fig. 9) does not absorb in the visible region, and has no effect on the photophysics of the BPEA moieties. In addition to fluorescing, the BPEA units exchange singlet excitation energy with time constants of 0.4 fs and ~60 ps, as determined by fluorescence anisotropy measurements. As mentioned above, UV light photoisomerizes the DTE to the closed form DTEc (as in **4c**), which has a broad absorption in the 600 nm region (see Fig. 4). The DTEc is thermally stable, but isomerized back to DTEo with red light, as discussed above. In **4c**, the DTEc absorbs strongly in the wavelength region where BPEA emits. Thus, it is ideally suited to accept singlet excitation

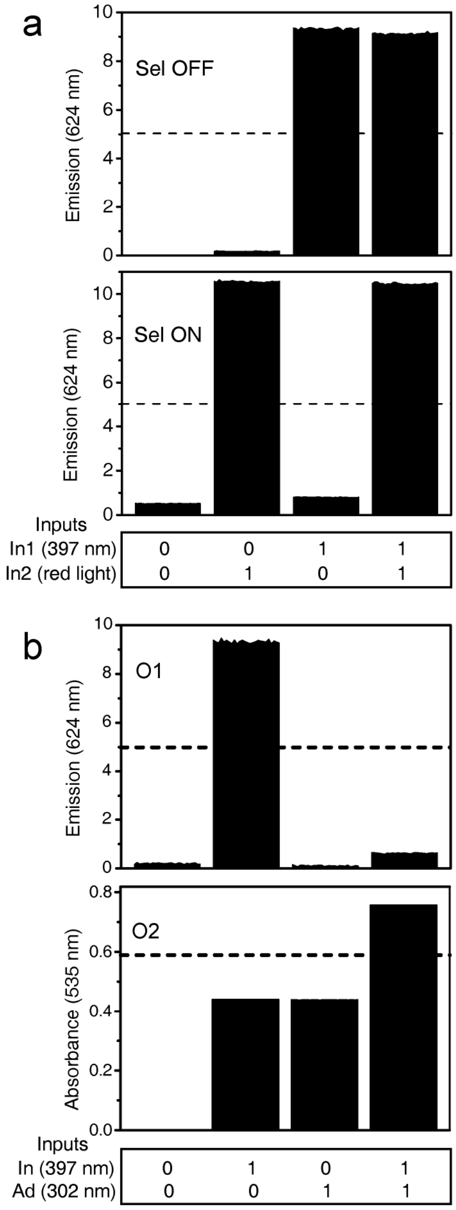

Fig. 7. (a) Triad **3** operation as a 2:1 digital multiplexer. The upper and lower sections show the output of the multiplexer with the Sel input OFF or ON under the application of the two inputs as shown at the bottom of the Figure. (b) Triad **3** as a 1:2 digital demultiplexer. The upper and lower sections show outputs O1 and O2 under the application of the data input at 397 nm when the Ad input is ON (1) or OFF (0).

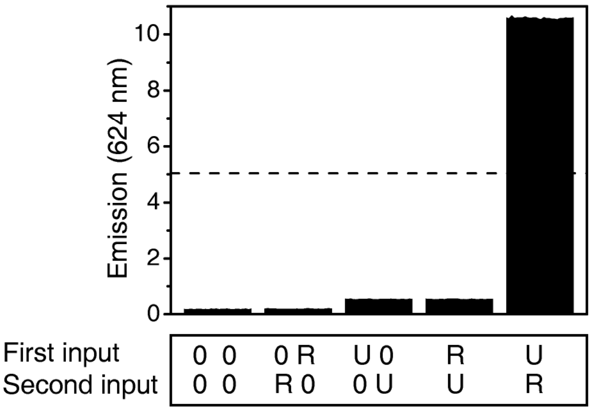

Fig. 8. Triad **3** as a keypad lock. Shown is the output of the lock (fluorescence at 624 nm) that results from sequential application of the inputs in the ON (R = red light >615 nm, U = UV light at 366 nm) or OFF (0) states. Note that an output above the threshold (dashed line) is only obtained if the U input is applied first, and the R input second.

energy from the BPEA singlet states. This energy transfer occurs with time constants of <13 ps, and with a quantum yield of essentially unity. Thus, although **4o** is strongly fluorescent when the BPEA moieties are excited, **4c** is essentially non-fluorescent due to energy transfer quenching.

These photochemical properties allow **4** to act as a molecular photonic analogue of a transistor amplifier or triode tube. The input (corresponding to the source contact of the transistor) is steady-state blue light at 350 nm which serves to excite BPEA green fluorescence. This fluorescence is monitored at 520 nm and comprises the output of the device (drain). The 350 nm light also photoisomerizes an ensemble of molecules of **4** to a mixture highly enriched in **4c**, which is essentially non-fluorescent as discussed above. Thus, any mixture of **4o** and **4c** is rapidly converted to nonemissive **4c** when exposed to the UV light. A second input, corresponding to the gate of a transistor, is red light of >610 nm. As noted above, light of these wavelengths is not absorbed by and cannot excite emission from BPEA, but does photoisomerize **4c** back to the fluorescent **4o** form. If the intensity of this red light is modulated while the intensity of the 350 nm light is kept constant, the photostationary distribution of **4o** and **4c** in solution is likewise modulated, and the fluorescence intensity from the BPEA chromophores is modulated accordingly. If the red light is modulated according to some waveform, the BPEA emission is likewise modulated.

A few examples of the operation of the molecular photonic transistor amplifier are shown in Fig. 10. In all these experiments, a solution of **4** in 2-methyltetrahydrofuran was irradiated with 350 nm light of constant intensity and red light with modulated intensity, and the BPEA fluorescent output was monitored at 520 nm. In Fig. 10a, the red light was modulated with a sine wave having a period of 3600 s. The BPEA emission traces out a sine wave with the same period. In Fig. 10b, the modulation period is decreased to 960 s. The BPEA fluorescence output is again a sine wave of this period, but there is a significant phase shift of 60°. This occurs because at the light intensities employed, each change in red light intensity initiates a change in the photostationary distribution of **4o** and **4c**, and photoisomerization does not quite "catch up" to the new photostationary distribution before the red light intensity changes once again. This effect becomes more pronounced as the modulation frequency is increased.

In addition to frequency modulation, amplitude modulation is possible. Fig. 10c shows BPEA emission when the sample is irradiated with red light whose intensity was modulated with the product of two sine waves of periods 200 s and 2000 s.

The modulation effects observed with **4** are unique. Although it might seem that a similar result could be accomplished by simply modulating the UV light beam that excites fluorescence, the hexad operates in a fundamentally different way. Fluorescence in **4** excited through light absorption by a shorter-wavelength electronic transition is modulated by light absorbed by a second, longer-wavelength transition in a second chromophore. Such a result is thermodynamically precluded in a single-chromophore system, or a multichromophoric system in which energy is simply transferred from an absorbing moiety to a fluorophore. It can occur in **4** because the long-wavelength transition modulates the population ratio of the two isomeric forms of the DTE, only one of which quenches BPEA fluorescence. This unique mode of operation also allows generation of an output waveform that is phase shifted relative to the modulating waveform, or is even of a different shape.[25] Simple modulation of light exciting a fluorophore cannot accomplish these things. These phenomena might be useful for limiting interference from background fluorescence in a variety of detection and labeling applications in biomedical imaging and elsewhere.[25] Phase-sensitive detection of fluorescence from a shorter-wavelength emitter at the modulation frequency of the longer-wavelength light absorbed by the modulating chromophore discriminates against stray light, including that from shorter-wavelength fluorescence of interfering substances.

A self-regulating molecular non-linear transducer that mimics photosynthetic photoprotection

The ideas presented above may also be applied to the field of artificial photosynthesis, which seeks to use the basic science underlying photosynthesis in the design of solar energy conversion systems.[27-32] In photosynthesis, sunlight is used to generate electrochemical potential energy in reaction centers. This electrochemical energy is used to drive production of biological energy, and fuels for energy storage. However, most of the light used in photosynthesis is gathered not by reaction centers, but rather by antenna systems. Because sunlight is diffuse, photosynthetic organisms use these antennas to optimize delivery of excitation energy to the reaction centers. However, if the sunlight intensity increases beyond a certain level, excitation is delivered to the reaction centers more rapidly than the resulting electrochemical energy can be used by downstream reactions to produce useful biological energy and fuels. The result of overdriving photosynthesis in this way is the build-up of reactive radicals, singlet oxygen, and other destructive species that can damage or kill the organism.

Photosynthetic organisms have evolved regulatory mechanisms to protect against such damage. One of these is called non-photochemical quenching, or NPQ. The consequence of NPQ is the quenching of excitation energy to harmless heat in the antennas before it arrives at reaction centers, where the

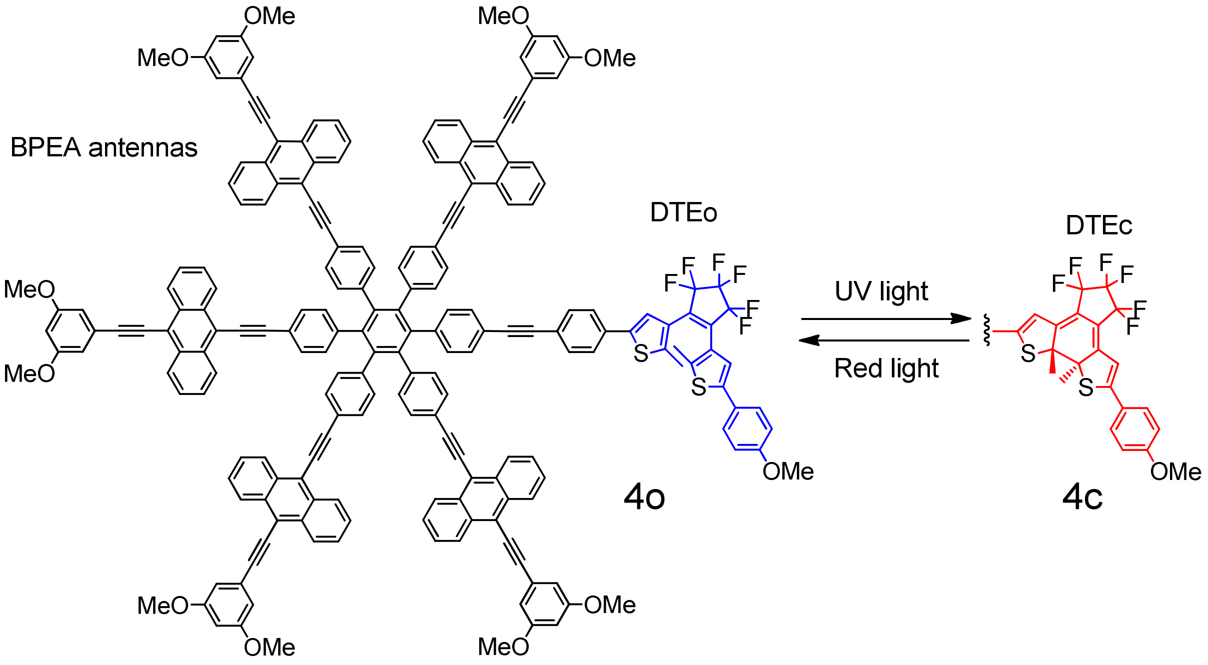

Fig. 9. Molecular "triode" **4**. In **4o**, the dithienylethene photochrome is in the open form, which absorbs only UV light. In **4c**, the dithienylethene is in the closed, cyclic form that absorbs in the red region.

deleterious species are produced. Thus, the quantum yield of photosynthesis is down-regulated at high light levels.

There are various forms of NPQ, none of which are completely understood. In cyanobacteria, the phycobilisome antenna systems contain a photoregulatory agent called orange carotenoid protein (OCP).[33] In its thermally stable form OCPo, the protein has no effect on energy transfer among antenna chlorophylls. However, blue-green light converts the protein to a red form, OCPr. The red form quenches chlorophyll excited singlet states, thus preventing some excitation energy from reaching the reaction centers. At a given temperature, the rate of thermal conversion of OCPr to OCPo is constant, but the rate of photoconversion of OCPo to OCPr is a function of light intensity. Thus, the photostationary distribution of the two forms, and the extent of down-regulation of photosynthesis, is a function of light intensity.

Molecular pentad **5** (Fig. 11a) is a functional mimic of photoprotection in cyanobacteria. The molecule consists of a porphyrin (P) bearing a fullerene electron acceptor (C_{60}), two BPEA antennas, and a quinoline-derived dihydroindolizine photochrome DHI. The spirocyclic form of the photochrome (see **5c**) is the thermodynamically more stable isomer. Thermal isomerization at ambient temperatures favours this form of the molecule, in which DHI has no effect upon the photochemistry of the remainder of the pentad.

The open, betaine isomer of the photochrome (BT, see structure **5o**) is produced by photoisomerization initiated by light absorption in the UV and blue light portions of the spectrum. The DHI has a maximum at 395 nm and absorbs out to around 460 nm. The absorption spectrum of BT, with a maximum at 685 nm, and the spatial arrangement of the photochrome relative to the remainder of the molecule are tuned so that BT can rapidly quench the excited states of both the porphyrin and the BPEA antennas by singlet-singlet energy transfer. At relatively low intensities of white light irradiation of **5c** in 2-methyltetrahydrofuran solution, the BPEA moieties absorb in the 430-475 nm region and efficiently ($\Phi = 1.0$) transfer excitation energy to the porphyrin ($\tau = 4.0$ ps) to yield the porphyrin first excited singlet state. The porphyrin excited state decays by photoinduced electron transfer to the fullerene ($\tau = 2.4$ ns) to yield the $P^{\bullet+}$-$C_{60}^{\bullet-}$ charge-separated state with a quantum yield of 0.82. The charge separated state has a lifetime of 14.0 ns. Thus, the molecule acts as a typical artificial photosynthetic antenna-reaction centre unit, and the DHI moiety has no influence. As the light intensity is increased, an increasing fraction of the sample is in the betaine form (**5o**). In **5o** the lifetime of the porphyrin first excited singlet state is reduced to 33 ps due to singlet-singlet energy transfer to BT. This quenching reduces the quantum yield of the $P^{\bullet+}$-$C_{60}^{\bullet-}$ state to only 1%.

This photochemistry allows **5** to act as an adaptive, self-regulating molecular nonlinear transducer that functionally mimics the role of the orange carotenoid protein. This is illustrated in Fig. 11b. Along the abscissa are plotted the results of experiments carried out on a solution of **5** in deoxygenated 2-methyltetrahydrofuran. Each point was obtained after 20 s of white light illumination of the solution of **5c** at relative intensities indicated by the open circles. The fluorescence emission from the porphyrin, excited at 480 nm, was immediately measured at each point, and the quantum yield of charge separation was determined (solid circles). Due to the increasing fraction of **5** that is present in the quenched form **5o** as the light level is increased, the overall quantum yield of charge separation in the solution decreases smoothly as the white light intensity increases, dropping from 82% at low light levels to 37% at the highest levels of white light employed in this particular experiment. When the white light intensity is reduced, the quantum yield rises, eventually returning to its initial value at low light.

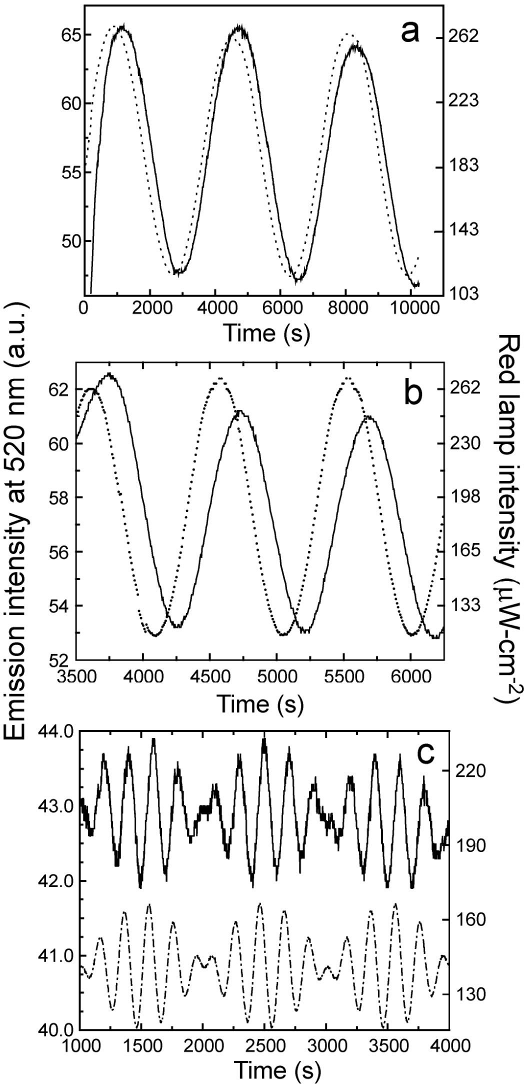

Fig. 10. Performance of hexad **4** as a molecular photonic "triode" tube. In each section, the solid curve shows the intensity at 520 nm of emission from the BPEA fluorophores. The broken curves show the intensity of the modulating red light beam. (a) Frequency modulation with a sine wave having a period of 3600 s. (b) Frequency modulation with a sine wave having a period of 960 s. (c) Amplitude modulation with the product of 2 sine waves having periods of 200 s and 2000 s.

Adaptation and self-regulation is central to the function of living organisms. Although chemists are becoming reasonably adept at designing and synthesizing molecules that carry out a specific function, relatively little attention has been paid to the design of molecules such as **5** that not only perform a function, but also regulate that function in response to an external stimulus. However, adaptive, regulatory behaviour will be required in order for ensembles of nanoscale objects to perform complex functions.

Conclusions

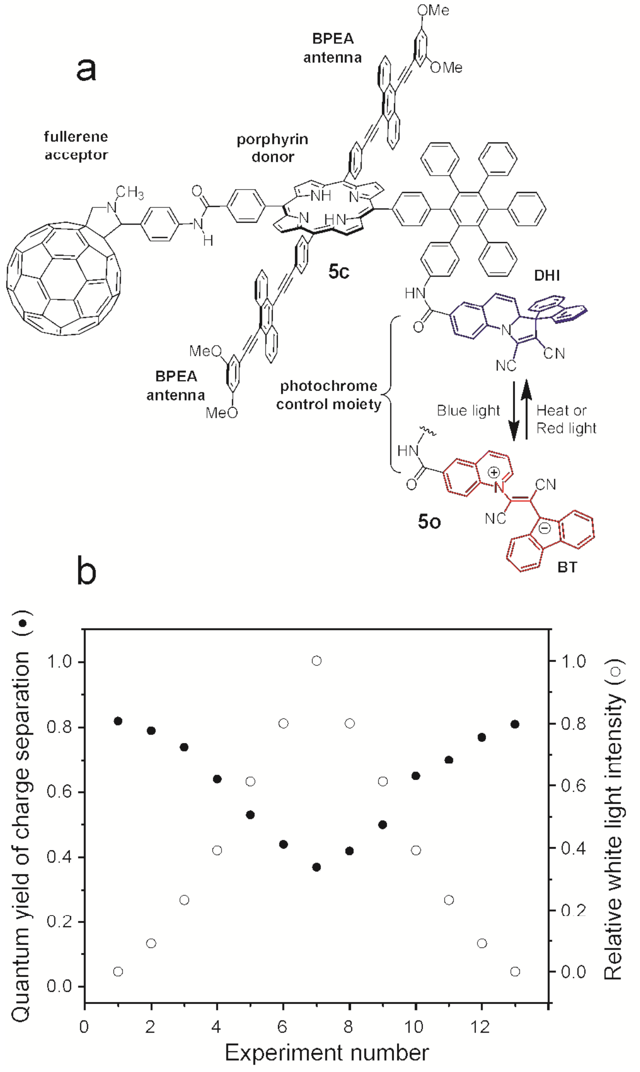

Fig. 11. (a) Pentad **5**, which functionally mimics photosynthetic regulation in cyanobacteria. In **5c**, the DHI photochrome has no effect on the photoinduced electron transfer behaviour of the remainder of the molecule. In **5o**, the open, betaine form of the photochrome quenches the porphyrin excited singlet state, and reduces the yield of charge separation to 1%. (b) Performance of **5**. Thirteen experiments are shown along the abscissa. The solid circles report the quantum yield of photoinduced electron transfer for the solution of **5** after irradiation with white light at different intensities (hollow circles). As irradiation with white light increases, the quantum yield decreases.

The molecules discussed above feature photochromes that can exchange information intramolecularly with other chromophores via energy or electron transfer. These properties allow them to carry out photonic versions of the two basic functions of a transistor – binary switching and analogue control of signal amplitude. Unlike many electronic devices, a given molecular system can respond to multiple inputs (light pulses of various wavelengths and intensities) and generate multiple outputs (absorption and emission at various wavelengths). These features allow a single device to be readily reconfigured to perform different operations by changing the inputs, outputs, and initial state. In fact, such molecules may carry out two or more binary logic steps concurrently by observation of different outputs. Linking multiple photochromes in the same molecule allows the output of one binary switch to affect the response of a second switch to inputs. This is a step towards solving a major problem that inhibits construction of complex computing devices using such molecules – concatenation of devices. On the other hand, two aspects of such molecules – the concatenation problem and photostability – continue to limit prospects for using molecules of this type to replace conventional electronic computers. Applications in quite different areas such as nanoscale labelling, identification and tracking, and controlled release of drugs or other materials, especially in biological and liquid media, are currently much more promising. In addition, these systems are good examples of the design of molecular systems that not only carry out a desirable function at the nanoscale, but also control and regulate this function in response to external stimuli. Self-regulation of the response of complex nanoscale systems to external signals will be vital to realizing the promise of nanotechnology.

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Notes and references

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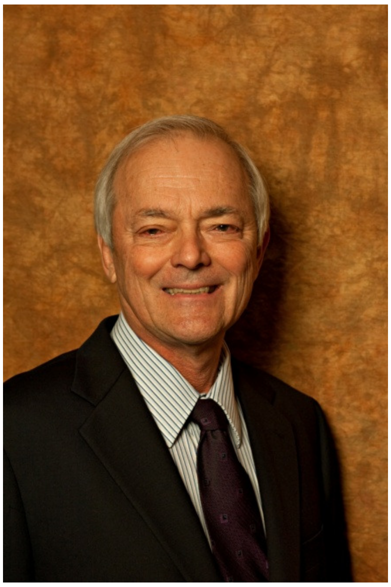

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