Light-powered molecular logic goes nonlinear

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A unique way to increase the dimensions of molecular logic schemes is reported in PNAS (1). What is molecular logic? Does it promise the ultimate flexible electronics—a liquid computer? Not exactly, although switchable molecules could be used in logic components, perhaps augmenting traditional electronics (2). The field of molecular logic, however, is much broader than that (3, 4). A good way to appreciate the promise and motivation for molecular logic is to realize how biology uses highly developed chemical switches connected to sophisticated sensors and feedback loops (5).

Bio-Inspired Logic

It is a powerful idea that robust information processing can be carried out in complex systems rather than perfectly arranged semiconductor switches. In biological systems, multiple input signals can be processed, and seemingly intelligent choices are expressed as the output. For example, this is seen in the way plants respond to excess sunlight—a process called nonphotochemical quenching that deactivates excited electronic states in light-harvesting complexes when reaction centers are running at capacity (6). Various input signals are used, including pH of the thylakoid lumen. A remarkable range of responses are coordinated: from rerouting electrons to chemically modifying carotenoids to gene regulation (7). These responses are invoked over an expanse of timescales to help protect nature's solar cells.

Biology is a rich ground of inspiration for sensors based on molecular logic. Examples have been reported where, instead of simply detecting the concentration of an analyte, the way the concentration is modulated in time is sensed. Such an instance is the report that the frequency of Ca^{2+} concentration oscillation helps control gene expression in some instances (8). Intriguing ways to detect radiation have also been documented. For instance, it is thought that birds can image their orientation (or inclination) relative to the earth's magnetic field, thus helping them to navigate during migration (9). Snakes have evolved an incredible system for thermal imaging, not

based on the kind of optical layout an engineer would naturally imagine (10).

Molecules that can be switched by light have played an important role in the development and demonstration of molecular logic (11). Typically photochromic molecules are switched between bistable configurations (different chemical structures) using light of different wavelengths (4). Fresch and coworkers (1) propose a unique angle on light-triggered logic—that is, to use multiple input and output channels enabled

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by nonlinear optical processes. They envision that photo-induced dynamics in a supramolecular compound initiated and read out by a sequence of femtosecond laser pulses can provide a platform for installing and processing logic operations. This pioneering idea has exciting possibilities, as well as some interesting challenges.

Fresch et al. (1) describe the potential of 2D electronic spectroscopy (2DES) for mapping out the results of logic operations. The 2DES experiment uses femtosecond laser pulses to excite electronic absorption bands of molecules, which could be in solution. It uses a sequence of laser pulses to monitor how populations generated through these electronic transitions change over time. This allows for information to be obtained on how energy has been redistributed among the excited states; for example, by energy transfer causing excitation energy to transfer from one chromophore to another. 2DES is similar to pump-probe spectroscopy, where a probe pulse arriving after a pump pulse is used to obtain the

difference absorption spectrum. One main way that 2DES differs from pump-probe spectroscopy is that the pump pulse (as well as the probed signal field) is spectrally resolved in a 2D electronic spectrum. Often in 2D spectroscopy one thinks of the pump pulse as effectively “labeling” the system according to the electronic absorption bands and reporting this labeled state along the excitation axis. Then after some time, the waiting (or population) time, in which the system evolves, the probe pulse interacts to effectively “read out” the current state of the previously labeled system. That current state is recorded along the detection axis. In this manner a frequency–frequency correlation map is generated where each excitation frequency is correlated to each detection frequency (12, 13). This map is proposed to be the read-out for the logic operation.

The Challenge of Nonlinear Logic

There are challenges to address before this method can reach its potential. One challenge, which is common to all applications of 2DES to molecular spectroscopy, is that the signals are invariably complicated. The diagonal peaks are often broad and overlap, thereby obscuring cross-peaks. Global analysis methods that deconvolve entire sets of 2DES data can be valuable for disentangling such 2DES spectra (14). The time needed to scan the laser pulses and acquire sufficient signal-to-noise can sometimes present an issue. This might be alleviated to some extent by using cutting edge techniques such as compressed sensing (15, 16). One of the requirements for capitalizing fully on the 2DES method for implementing molecular logic is that signal generation pathways need to be deconvolved. These pathways are really ways of categorizing and calculating how nonlinear signals are generated (17), and they cannot necessarily be physical discerned. It could turn out to be necessary to perform some kind of state or process tomography to extract relevant information about the system's

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density matrix from experimental data. Recent work has started to explore such possibilities (18–20).

Molecule design of the multichromophore system used for demonstrating 2DES decision trees will be crucial. Quite advanced multichromophore systems for light-switched molecular logic have already been demonstrated (4). In the case of the logic scheme proposed by Fresch et al. (1), electronic coupling and energy transfer need to be optimized because it is the interaction between the chromophores that enables the logic processing. In the case of energy transfer, an excited state population flows from molecular to molecule while strong electronic coupling links electronic transitions on different molecules coherently (21). In addition, radiationless relaxation should be controlled so it is not too fast to depopulate the higher-energy exciton levels before information can be processed and retrieved. Another direction of inquiry could be to design systems incorporating photochromic switches, perhaps even triggered by electronic energy transfer. Then it could be possible to capitalize on the high spatial resolution of nonlinear optical processes to spatially address the system in three dimensions (22, 23).

Highly advanced logic operations might be possible by even further increasing the complexity at a node with more than two interacting chromophores. However, how could we design these systems? It can be useful to envision relevant multichromophore assemblies as a kind of circuit. Given all we have learned about electronic energy

transfer (e.g., from studies of photosynthetic complexes that specialize in light harvesting), we should be able to design molecular circuits that control the flow of electronic excitation between molecules. Inspiration can be taken from photosynthesis (24). However, we cannot actually do this at the present time (except for rather trivial cases like incoherent downhill energy flow). The challenges stem principally from length scale: the functional molecular arrangements envisioned are

molecular scale and therefore scale 10 times smaller than the smallest transistor. In fact, it is the length scale together with the nature of the quantum-mechanical interactions between molecules in the circuit that provide the challenges (25). The 2DES molecular logic scheme will likely develop hand-in-hand with rational design of multichromophore systems optimized for the right balance of energy transfer and exciton coupling.

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