A ring cycle of currents. Persistent currents flow through an ordinary metal ring penetrated by a magnetic field. Bleszynski-Jayich et al. fabricated either a single ring or an array of rings near the tip of a nanomechanical cantilever that serves as an oscillator (the rings vary in diameter from 0.6 to 1.6 μm, while the cantilevers are 450 μm long and 40 to 80 μm wide). The magnetic field perpendicular to the plane of the rings, $B_{||}$, produces magnetic flux through the rings, which causes the persistent currents to appear. The interaction of the persistent current with the magnetic field parallel to the plane, $B_{||}$, causes a torque on the cantilever, which changes its oscillation frequency slightly. The vibration amplitude is highly exaggerated in the figure.

gold rings (11). They observed a persistent current with flux periodicity of h/e, but with a magnitude at least 30 times greater than predicted by theory. Later experiments by Webb's group on an array of 30 rings gave results closer to the theoretical prediction (12), but still left several questions unanswered. Experiments on semiconducting rings (13) have given results in closer agreement with theory.

The field received a huge boost in the past year from two experiments. Bluhm et al. used a scanning microscope to measure the persistent currents in 33 gold rings, one ring at a time (4). Magnetic fields were detected with superconducting quantum interference devices, or SQUIDs. The ability of the microscope to spatially scan over the sample led to several improvements over previous measurements, including a better understanding of the background signals and better statistics from measuring many individual rings. Nevertheless, the small magnitude of the signals required 12 hours of signal averaging to obtain each data point. The observed h/e-periodic persistent currents varied randomly in sign from ring to ring, as expected, and had an overall magnitude in good agreement with theory.

Bleszynski-Jayich et al. used a much different technology to improve the measurement sensitivity and enable measurements in high magnetic fields. They adapted methods from nanoelectromechanical systems. Specifically, they fabricated the rings on the ends of ultrasmall mechanical cantilevers, as shown schematically in the figure. The cantilevers oscillate at a frequency determined by their stiffness and mass, and this oscillation frequency can be measured with extremely high precision.

When the cantilevers are placed in a large magnetic field, the interaction of the persistent current with the field leads to a very small torque on the cantilever, which in turn changes its oscillation frequency ever so slightly. Using this technique, Bleszynski-Jayich et al. achieved a sensitivity about 100 times greater than the SQUID-based measurements. The large magnetic field suppressed any background signal caused by contamination from impurity spins, and the large range of field enabled the experimentalists to obtain a statistical sampling of the persistent current in a single ring. They measured the h/e persistent currents in a single ring and in arrays containing 242, 990, and 1680 rings.

The total signal is proportional to the square root of the number of rings, confirming the randomness of the sign discussed above. Both the overall magnitude of the persistent current and its temperature dependence agree extremely well with theory (14). The $h/2e$ persistent currents, however, are not visible in this experiment because of the presence of the large magnetic field.

It is safe to say that the h/e persistent currents in isolated metal rings are now well understood. So where do we go from here? Bleszynski-Jayich et al. propose coupling small rings to more complicated circuits, to see how the latter influence the former. The $h/2e$ puzzle remains, at least until the recent hypothesis (10) can be checked experimentally.

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7. The square-root behavior is well known in many areas of science, most notably in the context of particle diffusion. Imagine a drunken sailor taking a series of steps in random directions. After taking N steps, his distance from his starting point is typically equal to the square-root of N times his step size.
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CHEMISTRY

Energy Flow Under Control

Victor S. Batista

Laser pulses can be shaped to control energy transfer at the molecular scale in light-harvesting systems.

Controlling energy transfer at the molecular scale has been a long-standing goal since the development of high-power lasers in the 1960s. Appreciable advances toward this goal have been made with demonstrations of laser-controlled energy flow in natural and artificial light-harvesting antennas (1, 2). Based on closed-loop control experiments (3, 4), these techniques can efficiently shape femtosecond laser pulses to control and optimize a variety of molecular processes. However,

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the details of the resulting control mechanisms are difficult to extract from a cursory examination of the shaped pulses. On page 263 of this issue, Kuroda et al. (5) report an important contribution toward understanding shaped laser pulses that control energy transfer at the molecular scale. The reported insights on the control mechanism are valuable to understand laser control, in general, in a variety of molecular systems with common relaxation processes.

The goal of Kuroda et al. was to elucidate how to optimize the flow of energy in donor-acceptor dendrimer aggregates in liquids, as monitored by the radiative fluorescence of

the acceptor energy trap (see the figure, top panel). These extended π-conjugated structures, attached to a central ring that is tethered to the acceptor perylene moiety, function as biomimetic light-harvesting systems by absorbing ultraviolet-visible light and transferring the captured energy to the perylene trap. Such a mechanism mimics the primary steps of natural photosynthesis, where solar energy is harvested by multichromophoric aggregates and then funneled to an energy trap where reactions are initiated.

The laser control reported by Kuroda *et al.* reveals fundamental aspects of energy flow mechanisms that might be common to a variety of branched dendrimers. In most para-conjugated dendrimers (i.e., linear chains), the optically excited charged carriers are thought to move coherently and become fully delocalized across the molecular aggregate. In contrast, meta-substitutions (i.e., branched chains) are thought to decouple the constituent linear segments (*6*). Therefore, coherent and incoherent energy transfer pathways usually compete (*6, 7*).

To optimize energy transfer, Kuroda *et al.* designed laser pulses by using closed-loop optimal control experiments. Pulses shaped by maximization of the trap fluorescence were compared to those obtained by maximization of the dendrimer absorption. An important finding was that the optimum pulse was essentially a double pulse. The initial spike component was followed by a weaker subpulse, delayed by ~70 fs. From the analysis of such pulses, a "pump-pump" control mechanism was proposed (see the figure, bottom panel) in which the first pulse component pumps the absorption according to a nonresonant two-photon excitation, while the delayed subpulse promotes the system from the first excited state to a second excited state resonantly accessed through a one-photon transition. Such a mechanism controls (enhances) the trap fluorescence yield as the excitation to the second excited state detours the system away from detrimental nonradiative pathways. This control scheme can be placed alongside other double-pulse control scenarios, including the "pump-dump" method (*8*), in which the second transition dumps the system to a lower energy state instead of pumping it up to a higher energy level.

To support the proposed mechanism, Kuroda *et al.* performed several auxiliary experiments, including a pump-probe measurement where the dendrimer was resonantly excited with an ultrafast ~400-nm pump pulse (equivalent to the two-photon excitation at 800 nm) and probed with
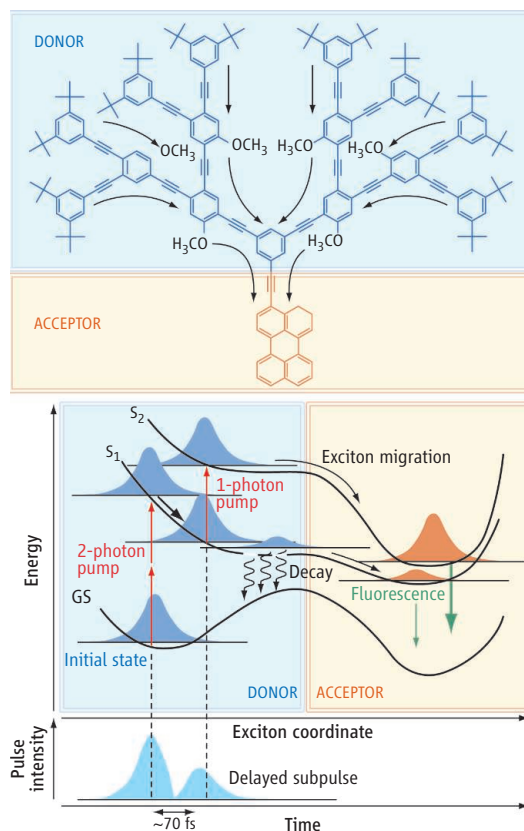
Energy migration under control. Kuroda *et al.* (**top**) achieved laser control of energy migration in a donor-acceptor dendrimer antenna. The "pump-pump" control mechanism (**bottom**) involves a two-photon excitation to a first excited state (S_1), immediately followed by a one-photon transition to a second excited state (S_2), detouring the system away from nonradiative decay pathways.

another pulse at 800 nm. Such a bichromatic double-pulse experiment demonstrated that a delayed femtosecond pulse, applied soon after the first excitation, could indeed pump the system to a second excited state, as in the proposed "pump-pump" scenario.

The "pump-pump" laser control can also be compared to double-pulse coherent control schemes, including femtosecond pulse versions of the bichromatic coherent control method (*9, 10*) and the bichirped coherent control scenario (*11*) (where the chirp gives the time-dependence of the pulse instantaneous frequency). In these methods, the second pulse is usually applied simultaneously with the first pulse (rather than delayed) to create a second excitation in the first excited state that could interfere with the one generated by the first pulse. Control is achieved by changing the relative phases between the two pulses (without pumping or dumping into higher or lower energy states). While the dynamics remains coherent, the manipulation of the pulse phase affects the interference phenomena and therefore the motion of the resulting excitation. Whether the flow

of energy transfer in dendrimers can be manipulated by these coherent control methods remains an open question that should be further investigated. In liquids, coherent control is typically compromised by decoherence unless the dynamical processes of interest are ultrafast. Otherwise, chromophore-solvent interactions randomize the quantum phases very quickly, rendering coherent control techniques ineffective. At later times, coherent control is ruled out by decoherence, and the dynamics can only be controlled by manipulating the laser intensity profile.

The success reported by Kuroda *et al.* (*5*) in achieving "pump-pump" laser control of excitations in dendrimer antennas and the similarities between the characterized control mechanism and other double-pulse laser control scenarios should motivate further experimental and theoretical work. Much remains unknown about the coherent and incoherent aspects of energy migration in light-harvesting systems, including the potential role that quantum interferences might play during the early time relaxation (*12*). Many of these fundamental aspects could be learned from understanding laser control of energy flow at the molecular scale, where branching ratios between coherent and incoherent relaxation pathways could be controlled either by affecting quantum interferences or by driving auxiliary transitions through the manipulation of laser intensities.

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