

Silicon has a number of other advantages, such as a comparatively high stiffness and a turning point in its thermal expansion near 124 K. Building on a knowledge of conventional systems, Kessler and co-workers<sup>1</sup> have exploited these properties to design a cavity and an ensemble of thermal shields that provide high isolation from external heat and mechanical perturbation. The team also developed a novel liquid-nitrogen-based cryogenic environment that can maintain the cavity assembly at the desired temperature of 124 K with no more than 1 mK of fluctuation without introducing vibrations. Furthermore, their cryostat can be placed on a small optical breadboard to implement coupling of the laser light into the cavity and detection of the cavity resonance using simple, conventional approaches. Another advantage is it can operate continuously at an affordable cost.

When using a monocrystalline silicon cavity, there are a few constraints, in addition to the need for a cryogenic environment. One is a comparatively involved (and probably costly) fabrication process. For instance, Kessler *et al.*<sup>1</sup> report using X-ray diffraction to determine the crystalline axes before machining and aligning the crystalline axis of the mirror substrates with that of the spacer. A second constraint is the accessible wavelength range, which does not extend to the near-infrared and visible regions needed to address optical clock transitions. Practically, this means that to use such cavities with optical clocks, it is necessary to transfer the extreme stability by means of a tightly stabilized optical frequency comb and another prestabilized laser at the desired wavelength, a non-negligible degree of extra

complexity for a system that must ultimately be reliable in continuous operation. The transparency window of silicon, however, allows the cavity to operate in the 1.5  $\mu\text{m}$  wavelength range, where excellent narrow-line lasers are available and which is directly matched to the wavelength of optical frequency combs based on erbium-doped fibre lasers.

Kessler and co-authors<sup>1</sup> have compared their new silicon cavity laser to two other state-of-the-art lasers and used the three pairs of comparisons to infer the stability of their device, which is a well-known way of characterizing an oscillator with unequalled performance when only one device is available. They find a stability of  $10^{-16}$  for averaging times of 0.1–10 s, which is better than any known oscillator of any type. The beat note between their two best lasers has a remarkable linewidth of  $49 \pm 4$  mHz, and it can be inferred that the silicon cavity laser alone has a linewidth of less than 40 mHz.

The first natural continuation of this work will be to construct a second silicon device that will aid and improve characterization, and will allow the limits of these systems to be investigated and the predicted thermal noise limit of  $7 \times 10^{-17}$  to be reached. The second step will be to apply this laser to optical clocks via an optical frequency comb and to demonstrate the improvement in stability that a silicon cavity provides.

Ultrastable lasers will continue to be developed. Kessler and co-workers<sup>1</sup> have demonstrated that the use of a silicon Fabry–Pérot cavity is among the most promising approaches. It will be interesting to follow the competition between this method and the spectral hole-burning approach<sup>8</sup>. Better ultrastable lasers will

improve the stability of optical clocks, enhancing their capability to unveil new science (atomic properties, atomic interactions, light shifts and tests of atomic structure calculations) and increasing their contributions to precision measurements, tests of fundamental physical laws, the search for physics beyond the standard model, advanced timescales and frequency dissemination for scientific applications, and the redefinition of the second. Clocks with the highest stability and accuracy could also find new applications in fields such as relativistic geodesy, and could consequently contribute to advances in Earth science. Ultrastable oscillators have by themselves a wide range of applications that could benefit from developments similar to the one reported by Kessler and co-workers<sup>1</sup>. This includes gravitational wave detection (some detectors will use cryogenic silicon optics at 1.5  $\mu\text{m}$  to overcome the thermal noise limit) and ultralow-noise microwave generation applied to atomic fountains, radar and very-long-baseline interferometry at submillimetre wavelengths.  $\square$

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## ORGANIC PHOTONICS

# Blending organic building blocks

Multifunctional organic materials can be used to make optically tunable organic transistors that can operate on microsecond timescales, thus opening new perspectives in the design of organic integrated circuits.

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Organic semiconductors have been widely investigated for their potential use in electronic applications owing to their low-cost, solution-based manufacturing, flexibility and their chemically tunable electronic properties<sup>1–4</sup>. At present, a major challenge in the field of organic electronics is finding multifunctional organic materials combining two or more types of physical

property in a single device such as an organic thin-film transistor (OTFT). Addressing this challenge is crucial for technological applications because printable OTFTs are the basic building blocks in more complex organic-based circuits and large-area electronics.

A simple approach to implementing multifunctionality relies on using different organic components to add multiple

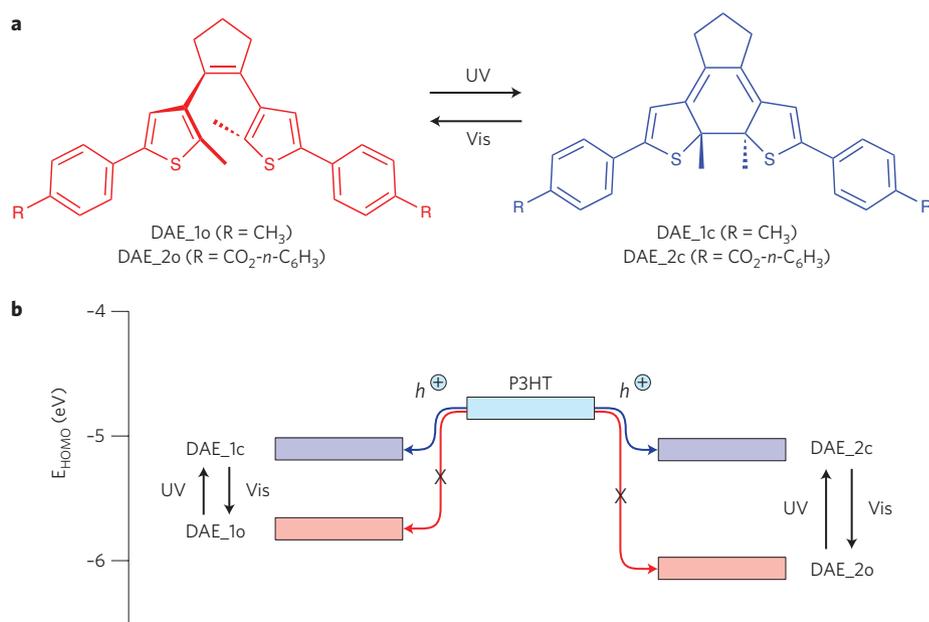
properties and functions to the resulting material. In the fabrication of OTFTs, blends of two or more electroactive components can be used to optimize the structural and electronic properties of the final system.

A recent breakthrough reported by Emanuele Orgiu *et al.*<sup>5</sup> demonstrates that blending a photochromic diarylethene derivative (DAE) with poly(3-hexylthiophene) (P3HT) results in

a film with photo-tunable energy levels to control hole transport. The blend film was integrated into an OTFT to demonstrate the modulation of the transistor current exposed to ultraviolet and visible light in sequential steps. The largest transistor current modulation was about 80%. The device response time was on the technologically relevant timescale of microseconds. The choice of the diarylethene photochromic molecules was based on their high fatigue resistance to switching states and to their thermal stability<sup>6,7</sup>. These characteristics make DAE molecules ideally suited to realizing transistor current modulation when blended with organic semiconductors.

In OTFTs that are based on pure P3HT, charge transport is achieved by injecting holes from one metal electrode into the highest occupied molecular orbital (HOMO) of the P3HT, which is located about 4.8 eV with respect to the vacuum energy level. Orgiu *et al.*<sup>5</sup> designed and synthesized two DAE photochromic molecules (DAE\_1 and DAE\_2) with different ionization energies. Each of these molecules has a ring-open isomer (DAE\_1o and DAE\_2o) and a ring-closed isomer (DAE\_1c and DAE\_2c) (Fig. 1a). In absolute terms, the ionization energies of DAE\_1o and DAE\_2o are 5.7 and 6.05 eV, respectively. After exposure to ultraviolet light, the respective ionization energies are 5.1 and 5.2 eV, for DAE\_1c and DAE\_2c. Therefore, the ionization energy of DAE decreases by about 0.8 eV on irradiation with ultraviolet light, such that the ionization energy in the ring-closed form better matches the ionization energy of P3HT (Fig. 1b). In turn, this makes hole transfer from P3HT to DAE more favourable (and so makes hole trapping more favourable). This process underpins the achievement of photo-controlled hole transport in OTFTs based on DAE–P3HT blend films.

Orgiu *et al.*<sup>5</sup> fabricated their OTFTs in a bottom-contact, bottom-gate configuration as a proof of concept. A chloroform-based solution, containing P3HT and DAE, was spin-coated over a SiO<sub>2</sub>/doped-Si substrate with prepatterned gold source and drain electrodes. Blends with concentrations ranging from 1 to 40 wt% of DAE\_1 with respect to P3HT were created. Atomic force microscopy revealed homogeneous blends for all blend ratios. Two-dimensional X-ray diffraction, a technique generally used to evaluate the degree of crystallinity and the structural type of a material, showed very similar patterns for pure P3HT films and DAE–P3HT blend films. This indicates that DAE molecules do not significantly disrupt the molecular packing of P3HT in either state of the isomer (ring-open or



**Figure 1** | Molecular photochromic building blocks, energetics and the working principle of an optically switchable organic transistor. **a**, Molecular structures of the photochromic molecules DAE\_1 and DAE\_2 in their ring-open (DAE\_1o and DAE\_2o) and ring-closed (DAE\_1c and DAE\_2c) forms. UV, ultraviolet; vis, visible. **b**, HOMO energy levels of P3HT, DAE\_1o, DAE\_2o, DAE\_1c and DAE\_2c and the working principle of the photo-controlled organic transistor. *h*<sup>+</sup>, hole. Arrows indicate the conversion of the ring-open isomers into their respective ring-closed isomers by the ultraviolet light and the reversion of the process by the visible light. UV = ultraviolet; Vis = visible. Adapted from ref. 5.

ring-closed). In fact, the static switching behaviour of the transistor was found to be stable, reversible and reproducible over many illumination cycles. In addition, the hole mobility remained high even with blend films containing 40 wt% of DAE molecules.

The decrease in the transistor current after illumination with ultraviolet light demonstrates that energy-level tuning is responsible for the transistor current modulation. Analogous transistors made only with P3HT exhibited a 10% increase in transistor current after illumination with ultraviolet light, in agreement with previously reported results. The response time, defined as the time between the pulse of laser light (about 3 ns long) and the instant at which a variation in transistor current is measured before a decay takes place, corresponded to a few microseconds, on irradiation with light of wavelength  $\lambda = 313$  nm.

The DAE–P3HT blend is all the more remarkable because of its stability: transistor operation was found to be unaltered after two-month-long storage of the OTFTs under nitrogen atmosphere. The importance of the strategy proposed by Orgiu *et al.*<sup>5</sup> relies on the programmability of the energy levels of diarylethenes, which offers a broad repertoire of solutions for combinations of organic semiconductors that can be p type or

even ambipolar. Finally, the blending strategy is extremely versatile and is applicable to both pure organic systems and organic–inorganic hybrids, as in both cases the presence of photochromic molecules gives an optical functionality to the device. Integrating new organic building blocks with DAE molecules will allow the creation of blend films with novel multiple functionalities. This could lead to sensors and biosensors with higher sensitivities and better selectivities, as well as to organic photovoltaic devices with improved solar energy conversion efficiencies, owing in particular to the photo-tunable energy levels. □

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