NONLINEAR OPTICS

New strings to the optical bow

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NONLINEAR optics is the basis of all the fledgling photonics technologies, in which light works with, or even replaces, electrons in applications traditionally carried out by microelectronics. On page 47 of this issue, Kuwata-Gonokami, Peyghambarian and co-workers[1] add an entirely new form of nonlinear optical excitation to the list of those already observed — exciton strings, observed in an organic molecular solid of anthracene and pyromellitic dianhydride (anthracene–PMDA; see Fig. 1).

The prime candidates for technologically useful nonlinear materials — those whose refractive indices or absorption characteristics vary with light intensity — are high-performance conjugated organics and polymers[2], which show a remarkable range of ultra-fast, highly nonlinear optical excitations.

The origin of the outstanding nonlinear optical properties of organic systems is the relative ease with which light affects π-electron motions[3,4]. The π-electron paths, or orbitals, extend over long distances, spanning an entire molecule, or even a macroscopic solid. Delocalized in this way, the π-electrons are less tightly bound to the positive atomic nuclei of the molecule or solid than electrons in single atoms. As a result, to change paths, or equivalently, to promote a π-electron from its natural ground-state orbital S_0 to a nearby excited-state orbital S_1, requires much less light energy. In addition, when the electron is removed from the ground S_0, a positively charged hole is formed and left behind in S_0. Now when the π-electron moves in the excited state S_1, tagging along — coulombically attracted to the electron — is the oppositely charged hole in S_0. Bound together, they form a moving electron–hole pair, called an exciton. So much has been known for about 30 years, and researchers can directly detect single excitons in an organic, or polymeric, system by illuminating the system with intense light, then looking for characteristic absorption peaks.

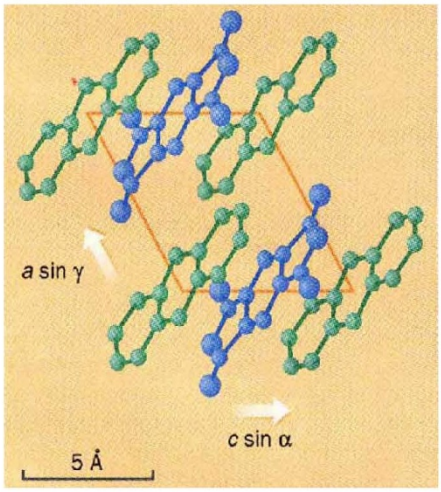

FIG. 1 Triclinic crystal structure of the quasi-one-dimensional charge-transfer complex anthracene–PMDA with anthracene donors (D) in green and PMDA acceptors (A) in blue. (Adapted from ref. 5.)

The organic solid that Kuwata-Gonokami, Peyghambarian and co-workers used for observing excitons is a one-dimensional charge-transfer complex[5]. They chose the complex for their experiments because S_0 is located in a linear stack of molecules on a donor site (D, the anthracene) while S_1 lies on an immediately adjacent acceptor site (A, the PMDA) in the same stack. In the measurements, the individual excitons created by the incident light are confined to move only in a straight line along the stack.

The effect of this one-dimensional confinement is profound. In moving up and down a molecular stack, the excitons cannot easily avoid one another; they bump together, spontaneously forming pairs, triplets and longer assemblies called biexcitons, triexcitons and longer n-strings. A schematic illustration of a bound biexciton is presented in Fig. 2. The exciton n-strings become more numerous and easier to observe as more and more individual excitons are created with increased incident light intensity, because the otherwise faint absorption peaks now become pronounced. The entire process is nonlinear, as the creation and number of exciton n-strings depend in a nonlinear way on the light intensity. Further, in describing the pulling apart of an exciton along a stack, the authors show that the stability of one string (say, $n = 2$) depends on the existence of the next longer string ($n = 3$). This general condition reflects the nonlinear behaviour that is inherent to exciton n-strings.

The exciton n-strings join other excitations in condensed phases classified as collective excitations[6]. The list is long: examples include plasmons, which are back-and-forth oscillations of all the conduction electrons together in a metal, and rotons, which are associated with vortex motions in superfluid helium. In another example, electron–hole liquids can form in semiconductors when exciton concentrations are allowed to get so high that the excitons literally condense into separate electron-and-hole droplets which then behave like ordinary metals. The observation and properties of such collective excitations, in general, have been the central focus of solid-state and condensed-matter physics for more than half a century.

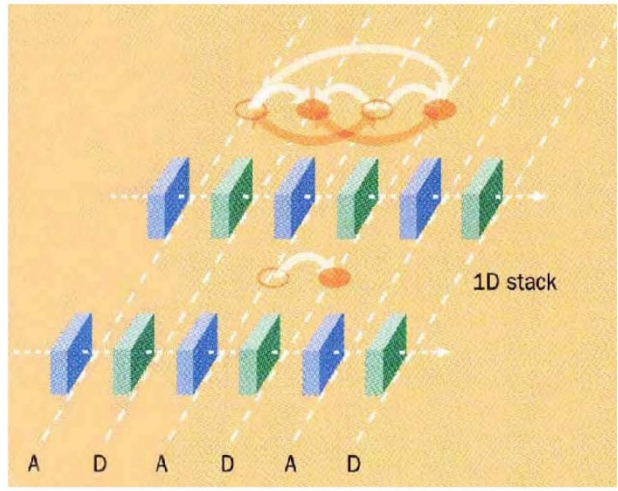

FIG. 2 Schematic illustration of the stability of exciton n-strings. The green and blue sites are donor (D) and acceptor (A) molecular sites, respectively. The white arrows indicate electron–hole Coulomb attractions (filled circles are electrons, open circles are holes). Orange arrows indicate electron–electron and hole–hole Coulomb repulsions. A single exciton is stabilized by the electron–hole attraction, and the biexciton is stable because the attractions outweigh repulsions. The stability of larger n-strings can be understood in a similar way.

Kuwata-Gonokami and co-workers' observation of the exciton n-strings extends our understanding of nonlinear optical processes in organic systems and points to the tasks as yet undone, which range from experimental measurements on new materials to the continued development of a comprehensive many-body theoretical description of the excitations. Their experimental discovery and its theoretical confirmation are fine examples of the beauty of fundamental nonlinear optical physics and the benefits of international scientific cooperation. □

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