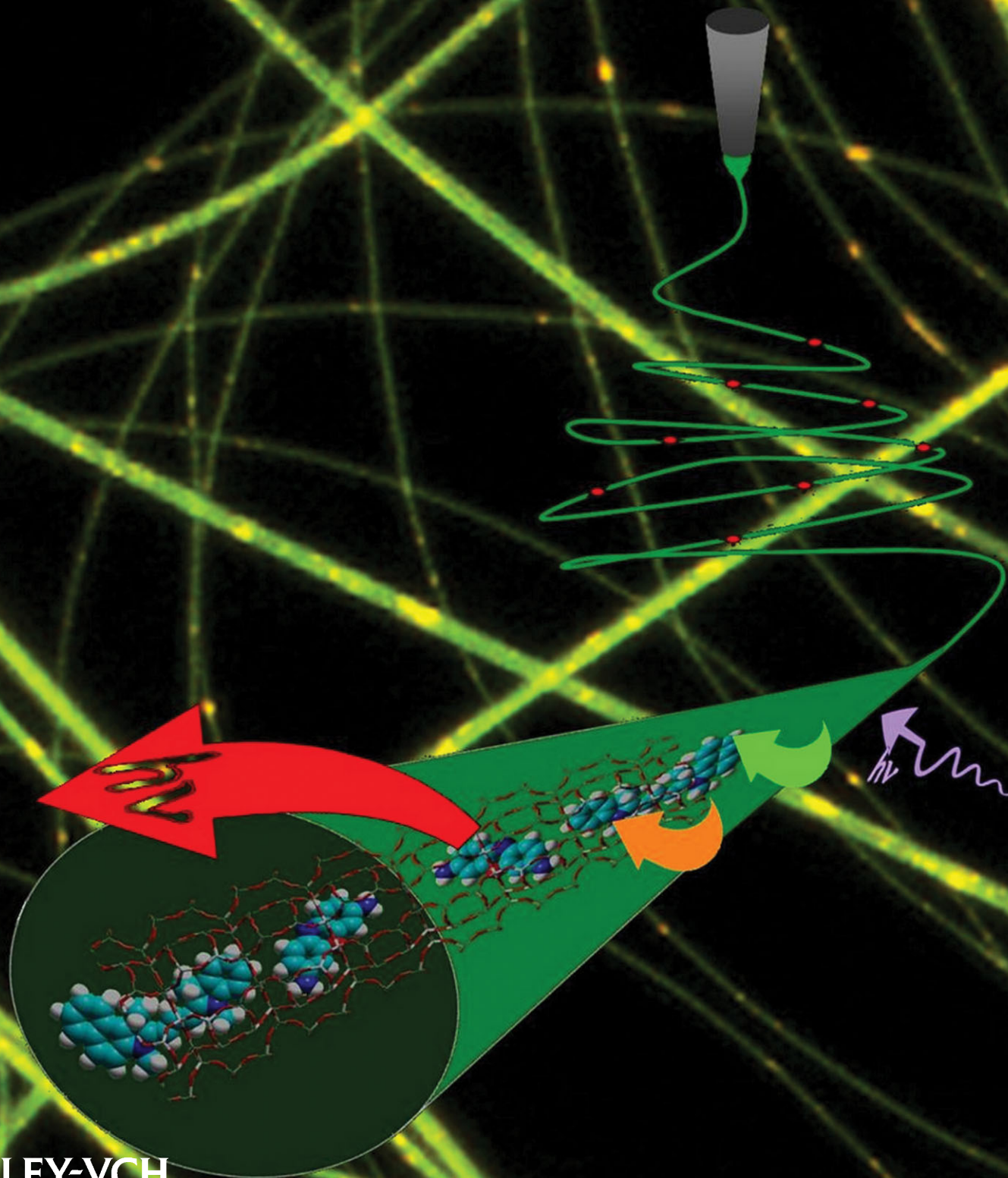
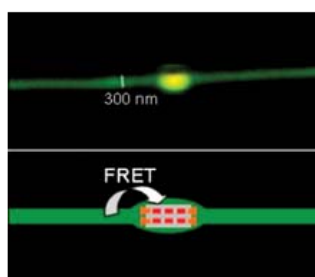


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**Electroluminescent polymeric nanofibers embedding dye-loaded zeolite L crystals** are prepared. By exciting the polymer nanofiber, the energy is transferred to the fluorescent dyes inside the zeolite L channels through a two-step Förster resonant energy transfer process. This study opens new perspectives in the field of low-cost fabrication technology of flexible nanoscale OLEDs.

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# Energy Transfer in Fluorescent Nanofibers Embedding Dye-Loaded Zeolite L Crystals

By Varun Vohra,\* André Devaux, Le-Quyen Dieu, Guido Scavia, Marinella Catellani, Gion Calzaferri, and Chiara Botta

Host-guest systems based on zeolite L crystals have drawn a lot of attention in the past few years in the fields of artificial antennae and color converters, as they exhibit enhanced emission efficiency (in the solid state) and chemical stability. The peculiar structure of the zeolite L crystal provides an hexagonal network of parallel nanochannels. Due to size restrictions both at the channel entrances and inside the channels, the organic guest molecule included in those inorganic hosts will have to maintain a specific spatial organization to be able to adjust to the particular geometry of the zeolite L crystal.<sup>[1]</sup> Being organized in such a way, the quenching of the emission from the organic dyes due to aggregation is avoided even at very high dye concentrations. By designing the molecule shape and size, the organization within the zeolite L crystal can be tuned.<sup>[2]</sup> Considering this, molecules reported as stopcock molecules,<sup>[2,3]</sup> which stay at the channel entrances, were synthesized. The interesting aspect of these molecules is that they provide a link between the dyes loaded inside the crystal and its environment.

As previously reported, the organization can be led to another level by imposing a specific orientation to the zeolite crystals on a substrate, through self-assembly<sup>[3,4]</sup> or by embedding them in a polymeric nanofiber.<sup>[5]</sup> These polymeric nanofibers are obtained by electrospinning, a well-known technique that allows one to obtain polymeric fibers on both micro- and nanoscale, using a high-voltage electric field to spin a polymer melt or a polymer solution into oriented fibers, which will be collected on a metallic screen.<sup>[6–8]</sup> This simple and efficient process is used in many different fields, such as membranes and tissue engineering,<sup>[9]</sup> composite materials,<sup>[10]</sup> sensors and electronics,<sup>[11]</sup> photovoltaics,<sup>[12]</sup> and photonics.<sup>[13]</sup> The electrospun fiber can also be spatially oriented by using a specifically shaped collector screen,<sup>[14]</sup> which opens the path to obtaining innovative devices

based on a single fiber of active material. Fibers containing zeolites could be easily obtained with different colors, by blending an organic dye with a polymer that also embedded dye-loaded zeolites.<sup>[5]</sup> However, with this technique it was not possible to create a link between the fiber and the dye-loaded zeolites, which would be necessary for the fiber to be used as active material for a nanodevice.

In this paper, we report the preparation of nanofibers with electroluminescent properties embedding dye-loaded zeolite L crystals, as well as the study of the Förster resonant energy transfer (FRET) from the polymer to the host-guest system. The aim of the work is to obtain a hybrid nanofiber that can emit in different regions of the visible spectrum. The different emissions should be obtained by excitation of the polymer and through energy transfer from the polymer to the dye-loaded zeolite L crystals.

In the literature, only a few examples are given of electrospinning of conjugated polymers, and, in most cases, an elaborated set up (using a double spinneret) is needed.<sup>[15,16]</sup> In order not to use a sophisticated set up for the spinning but avoiding the loss of the electroluminescent properties of the conjugated polymer, the conjugated polymer was blended with another polymer with good viscoelastic properties.<sup>[17,18]</sup>

Aiming for multichromic fibers, different sets of dye-loaded zeolites were prepared using disk-shaped zeolite L crystals with a mean height of 80 nm and a mean diameter of 300 nm. The crystals were loaded either with oxonine (ZL1), with both oxonine and, in a second step, with a stopcock molecule called Cy02702 (ZL2), or with oxazine 1 and Cy02702 (ZL3, Fig. 1).<sup>[3]</sup>

To obtain materials for innovative devices, it is necessary to have an energy transfer from the electroluminescent polymer in the fiber to the dyes inside the zeolites. The stopcock molecule is composed of two parts: a head, which cannot enter the zeolite channels due to its size, and a tail, which can fit in those channels (Fig. 2). Having such a structure, the molecule will stay at the channel entrances, thus creating a “link” between the surrounding environment (the polymer, in the case of fibers) and the dyes inside the crystals.

The function of the stopcock molecule Cy02702 is not only to be an acceptor for energy transfer from the polymer fiber, but also a donor toward the dye molecules inside the zeolite channels. The oxonine and oxazine 1 are two potential acceptors for this second energy transfer. The spectral overlap between the Cy02702 stopcock molecule as donor and those two organic molecules is almost equivalent in both cases. The difference between the two systems comes from the specific orientation of the molecules inside the zeolite L channels. Oxazine 1’s electronic-transition

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