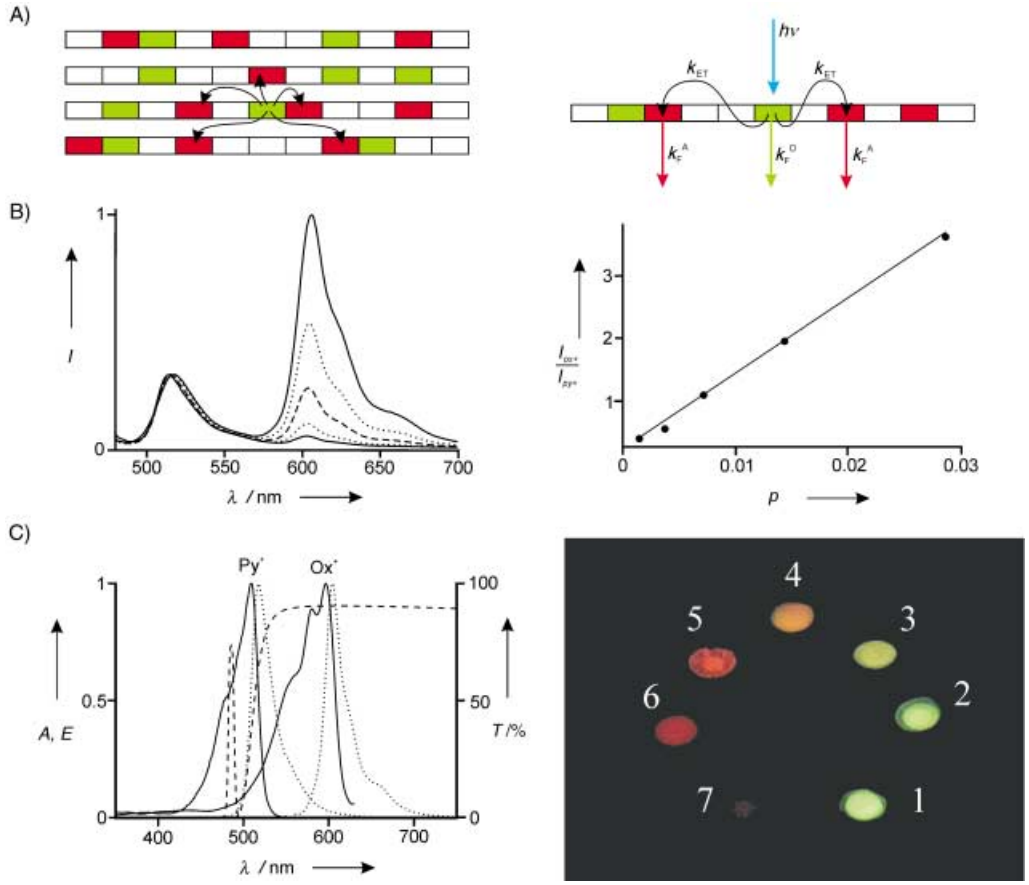

Figure 21. Energy-transfer experiment. A) Scheme of a zeolite L crystal containing acceptors A (red rectangles) and donors D (green rectangles). Each rectangle marks a dye site. The main processes taking place after excitation of a donor are indicated on the right. k_{ET} is the rate constant for energy transfer. k_F^A and k_F^D are the rate constants for fluorescence. B) Fluorescence of five suspensions with equal loading $p_{Py^+} = p_{Ox^+}$ (expressed in units of $p = 0.0014$: p, $2.5p$, $5p$, $10p$, and $20p$) after specific excitation of Py^+ at 465 nm. Left: fluorescence spectra, scaled to the same peak height for the Py^+ emission at approximately 520 nm. The intensity of the Ox^+ emission (band at around 600 nm) increases with increasing loading p. Right: ratio of the fluorescence intensity I_{Ox} of Ox^+ and I_{Py} of Py^+ as a function of the loading p. C) Visual demonstration of energy transfer; left: absorption (solid line) and emission spectra (dotted line) of Py^+ and Ox^+ in zeolite L. The dashed lines show the transmission T of the Schott DAD 8-1 interference filter and the Schott OG 515 cut-off filter we have used. Right: photograph of the fluorescence of dye-loaded zeolite L layers upon monochromatic irradiation at 485 nm and observation through a 500-nm cut-off filter. Probes 1 and 7 are references loaded with Py^+ and Ox^+. Probes 2 to 6 contain a 1:1 mixture of Py^+ and Ox^+ with the following loading for each dye: 2) p, 3) $2.5p$, 4) $5p$, 5) $10p$, and 6) $20p$.

The seven luminescent samples shown in Figure 21 C consist of zeolite L crystals of 300-nm average length filled with different amounts of Py^+ (donor D) and Ox^+ (acceptor A). In all the cases Py^+ was selectively excited at 485 ± 5 nm, a wavelength at which the absorption of Py^+ is strong and that of Ox^+ very weak (see Figure 21 C, left side). The two reference probes 1 and 7 are loaded with 5×10^{-3} M Py^+ and 5×10^{-3} M Ox^+, respectively. The other samples contain a 1:1 mixture of Py^+ and Ox^+ of the following concentrations: probe 2) 5.3×10^{-4}, 3) 1.3×10^{-3}, 4) 2.6×10^{-3}, 5) 5.2×10^{-3}, 6) 1.00×10^{-2} M. A rough estimate of the mean donor to acceptor distance R_{DA} (in Å) can be obtained, assuming isotropic conditions and equal concentrations of donors and acceptors, from Equation (28) where N_A is the Avogadro number and c_A is the concentration of Ox^+ in the zeolite nanocrystal.

$$R_{DA} = \left[\frac{3}{4\pi}\frac{10^{-3}}{c_A N_A}\right]^{1/3} \times 10^{10} \qquad (28)$$

From Equation (28) we obtain the following mean donor–acceptor separations: probe 2) 91, 3) 68, 4) 54; 5) 43, 6) 34 Å. The Förster radius for $Py^+ \rightarrow Ox^+$ energy transfer in a medium of refractive index of 1.4 is about 70 Å, based on the Py^+/Ox^+ spectral overlap which is 1.5×10^{-13} $cm^3 M^{-1}$. We observe in probe 2 mainly the green luminescence of Py^+, which indicates that energy transfer is insignificant. But the yellow color of probe 3 is due to a mixture of green and red luminescence which means that energy transfer is significant in this sample. It becomes more and more important with increasing concentration so that from probe 5 on, the red luminescence stemming from Ox^+ is dominant.

The same experiment can be carried out quantitatively. A linear relationship between the fluorescence intensity of the acceptor I_{Ox^+} and that of the donor I_{Py^+} as a function of the occupation probability (p_{Ox^+}) of the acceptor is expected to hold [Eq. (29) where C is a constant].[43]

