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Mendeleev Commun., 2017, **27**, 366–367

Mendeleev Communications

Nonradiative energy transfer in planar systems based on structurally different fluorophores

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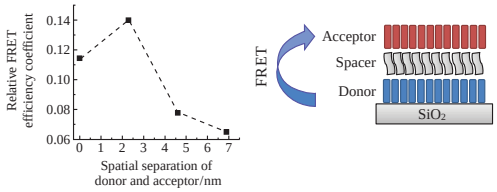
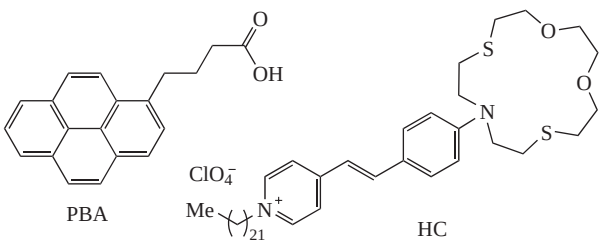
DOI: 10.1016/j.mencom.2017.07.015

In the multilayer systems where monolayers of donor and acceptor fluorophores of different chemical structure are separated by an inert layer, the dependence of nonradiative energy transfer efficiency on the distance between the planar components of a donor–acceptor couple has a maximum at a finite nonzero thickness of the separating layer.



The Förster resonance energy transfer (FRET) attracts attention due to its potential applications in solar energy collection systems,[1–3] biomedical studies,[4,5] sensorics,[3,6–10] organic electronics,[3,11,12] *etc*. The efficiency of FRET in highly organized planar systems can be significantly higher than that in bulk systems of the same composition.[3,13] Moreover, in multilayered Langmuir–Blodgett films (LBFs) based on naphthalimide derivatives,[14] the spatial separation of donor and acceptor layers by an ultrathin inert spacer can increase this process efficiency. The dependence of FRET efficiency in such systems on the distance between fluorophore layers exhibits a maximum at about 7 nm. Most probably, the efficiency boost upon distancing the active layers is owing to an increased probability of reverse energy transfer from acceptor to donor. Such a behavior of the system can be associated with the similarity of the chemical and electronic structures of the fluorophores and their identical orientation in the monolayers, which directly affects FRET efficiency.

The aim of this work was to study the effect of the chemical composition of a donor–acceptor couple on the nature of FRET efficiency dependence in multilayer planar supramolecular systems on the spatial separation of donor and acceptor. For this purpose, we studied the photophysical properties of a system analogous to that described previously[14] (single-layer LBFs of a donor and an acceptor of energy are separated by several monolayers of an inert spacer) but based on flourophores of different chemical classes: an amphiphilic pyrene derivative (1-pyrenebutanoic acid, PBA, energy donor) and a functionalized hemicyanine dye (4-{(*E*)-2-[4-(1,4-dioxa-7,13-dithia-10-azacyclopentadec-10-yl)-phenyl]vinyl}-1-docozylpyridinium perchlorate, HC, energy acceptor).



PBA HC

These compounds were chosen because of relatively high fluorescence quantum yields and photostability,[15–17] a high degree of overlap of donor emission and acceptor absorbance spectra (Figure 1), and the ability to form stable monolayers on a water surface to be transferred onto solid substrates by the Langmuir–Blodgett technique. Note that the long-wavelength part of PBA fluorescence (Figure 1, above 420 nm) is associated with excimer emission;[18,19] therefore, the excimer fluorescence was maximal under the conditions of monolayer film formation, due to the aggregation state of the monolayer, as controlled by *in situ* measurements of the optical reflection–absorption spectra of the precursor monolayer.[20] As previously,[14] we used stearic acid as an inert spacing layer material, which is a classic surfactant that can form densely packed monolayers on solid substrates and does not have absorbance or emission in the visible range.

Using the Langmuir–Blodgett technique, we prepared a series of multilayer planar supramolecular systems based on the test compounds according to previously described procedures.[21–24] Figure 2 shows the structure of such systems. Each LBF multilayer consists of energy donor (PBA) and energy acceptor (HC) monolayers separated by an inert spacer of various thickness (from 0 to 3 layers of stearic acid).

Since the absorbance bands of PBA and HC are located quite far from each other, and the fluorescence spectra of all the samples are identical in the positions of emission bands of the individual components of a donor–acceptor couple, the FRET efficiency in

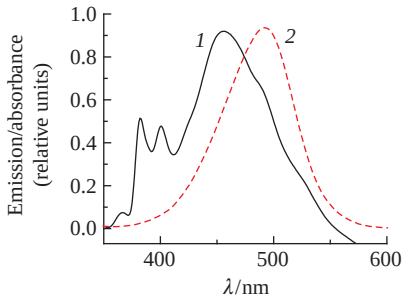


Figure 1 Normalized spectra of (*1*) single layer PBA LBF emission and (*2*) single layer HC LBF absorbance.

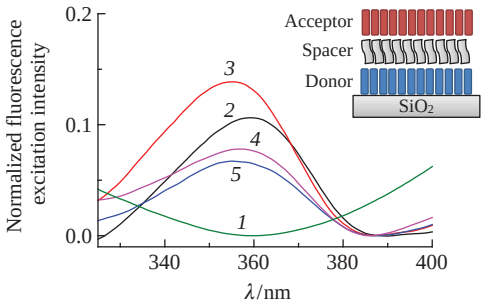


Figure 2 Normalized fluorescence excitation spectra for (*1*) the individual single-layer HC LBF and multilayer systems consisting of PBA and HC monolayers separated by inert spacers containing (*2*) 0, (*3*) 1, (*4*) 2, and (*5*) 3 stearic acid layers. Inset: schematic diagram of the test structures.

the described systems can be compared using the acceptor fluorescence excitation (576 nm) spectra.

The spectrum of fluorescence excitation by this emission band for the individual single LBF layer of hemicyanine acceptor has only one band that corresponds to the position of HC absorbance in the film. Excitation spectra of multilayer systems containing both donor and acceptor, as was expected, exhibit two excitation bands, one of which characterizes excitation of acceptor fluorescence directly by its absorbance band, and the other corresponds to the absorbance of the donor in densely packed monolayer (about 360 nm),[18] and it is associated with nonradiative energy transfer from donor to acceptor. The energy transfer efficiency can be estimated using the ratio $k_{rel} = I_{492}/I_{360}$, where k_{rel} is the relative coefficient of FRET process efficiency, and I_{492} and I_{360} are the excitation spectra intensities (emission at 576 nm) at 492 and 360 nm, respectively.

For a graphic comparison of the relative coefficients of FRET efficiency in the test films, it is convenient to normalize the excitation spectra of multilayer system to the excitation band intensity corresponding to the absorbance of the acceptor (492 nm) and to compare the values of normalized intensities of short wavelength bands of the excitation spectra corresponding to the system fluorescence *via* nonradiative energy transfer.

An analysis of the excitation spectra of multilayer films (Figure 2) shows that a maximum FRET efficiency ($k_{rel} = 0.140$) is observed upon the separation of donor and acceptor monolayers by one layer of stearic acid, which corresponds to 2.3 nm. The value of k_{rel} for such a system is greater than k_{rel} for the film without a spacer interlayer ($n = 0$) by a factor of 1.23. Further spatial separation leads to a sharp decrease in the energy transfer efficiency ($k_{rel} = 0.078$ and 0.065 for 2 and 3 layers of stearic acid, respectively), which is quite explicable in terms of classical concepts of FRET process.

Thus, in contrast to classical 3D-systems, in which FRET efficiency monotonically decreases with raising the distance between energy donor and acceptor, a maximum energy transfer efficiency in the planar supramolecular system occurs upon the spatial separation of donor and acceptor layers, as in the previously described naphthalimide-based fluorophore couple. The replacement of the donor–acceptor couple of similar fluorophores by a couple in which the composition and structure of its components drastically differ affects only the position of the maximum, and it does not change the nature of the dependence of FRET efficiency on the thickness of the separating layer. In the system based on pyrene and hemicyanine derivatives, the optimal distance is 2.3 nm.

This work was supported by the Russian Foundation for Basic Research (grant nos. 16-03-00538_a, 16-29-05284_ofi_m and 16-33-60024_mol_a_dk).

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Received: 5th December 2016; Com. 16/5111