Fluorescence Investigations of Pure and Mixed Evaporated Dye Layers

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Fluorescence spectroscopy is used to investigate energy transfer processes in evaporated layers consisting of several different dyes. In this study films of N,N'-dimethylperylene-3,4:9,10-bis-di-carboximide (methylperylene pigment, MPP), coevaporated with copper phthalocyanine (CuPc) at varying ratios, and double layers of MPP and CuPc with different thicknesses are investigated. It is shown that energy transfer from MPP to CuPc occurs in both mixed and double layers. The energy transfer leads to a strong quenching of the MPP fluorescence and sensitized CuPc emission in the NIR region. The concentration dependence of the fluorescence quenching in mixed layers can be described by a Stern–Volmer plot. A simple model based on exciton diffusion between MPP molecules toward active quenching centers is used to determine the diffusion length.

KEY WORDS: Dyes; fluorescence; energy transfer; thin films.

INTRODUCTION

Evaporated dye layers can be easily prepared with high-vacuum evaporation techniques. Many neutral and cationic dyes with simple anions are evaporable and form thin homogeneous films of high optical quality. Technical applications are emerging as xerographic charge generation layers and gas sensors. Great efforts are made to use evaporated dye layers for low-cost solar cells and electroluminescence devices.

For such applications, dye layers will be arranged as double or mixed layers in order to extend the spectral range of absorption and to improve the photoelectrical properties [1]. In this respect, a frequently discussed problem is the dynamics of the excitation energy in a dye layer system. Of special interest are the mechanisms of charge carrier generation and the interactions between different solid dyes. The matter is complicated by the fact that the light absorption of solid dyes does not directly produce free charge carriers but singlet or triplet excitons of the Frenkel type. These are capable of rapid molecule-to-molecule migration by energy transfer in competition with other deactivation processes like recombination or charge generation [2]. The migration of excitons in solid dyes is generally described as a diffusive process.

In order to investigate directly the exciton diffusion and the electronic interactions between two differently arranged solid dyes, the fluorescence behavior of N,N'-dimethylperylene-3,4:9,10-bis-dicarboximide (MPP) and copper phthalocyanine (CuPc) in mixed and double layers is studied in this work.

EXPERIMENTAL

Sample Preparation. The dyes were obtained from BASF Farbenlaboratorium Ludwigshafen/FRG and used without further purification. The evaporation is accomplished in vacuum (10^{-3} Pa) from two indirectly heated quartz crucibles onto cellit foil (140 μm) at room temperature. Film thickness and evaporation rate are con-

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trolled during the evaporation using quartz thickness monitors. A detailed description of the vacuum system is given elsewhere [3]. Mixed layers are produced by coevaporation at varying rates (CuPc, 0.001–0.2 nm/s, MPP, 0.2–0.75 nm/s). The total amount of MPP in the layer is kept constant (300 nm). Double layers are produced without breaking the vacuum by use of several masks, which allow a partial covering of the MPP layer by CuPc. Thus, a direct comparison between the single MPP layer and the corresponding double layer is possible for the MPP layer from the same evaporation process.

The exact mole concentration of CuPc [$C_{CuPc} = N_{CuPc}/(N_{CuPc} + N_{MPP})$; N is the number of molecules] in the layers is determined spectrophotometrically after dissolution of the layers in conc. H_2SO_4. All thickness values refer to quartz monitor readings. The quartz monitors are calibrated by comparison to optical interferences from *in situ* absorption measurements.

Luminescence in the Visible Range. A commercial fluorescence spectrometer (FluoroMax, SPEX) with a red sensitive photomultiplier (Hamamatsu R928P) in the photon-counting mode is used. The samples are measured by means of a special front-face illumination geometry with perpendicular incidence of the excitation light and detection at an angle of 22.5°. With this geometry and an additional edge filter (500 nm), scattered excitation light can be effectively suppressed.

Luminescence in the NIR Region. For the luminescence measurements in the NIR region we use a setup consisting of an Ar–Kr ion laser as the light source (perpendicular incidence; excitation wavelengths 488 nm and 30 mW for MPP and 647 nm and 11 mW for CuPc, resp.; excited area, 0.2 cm²), an emission monochromator, and a nitrogen cooled Germanium detector (EO-817L, North Coast Scientific Corporation) using lock-in amplification. Emission is measured at an angle of 40°.

All spectra (VIS and NIR) are corrected for the spectral response of the system and display relative intensities as photons per second. Pure and mixed layers are investigated from the layer side; sandwich systems (substrate/MPP/CuPc), from the substrate side. All luminescence measurements are carried out at room temperature.

RESULTS AND DISCUSSION

Mixed Layers

Absorption and emission spectra of pure MPP and CuPc layers are shown in Fig. 1. The two dyes absorb

and emit in different spectral regions so that they can be excited separately and their emission signals can be distinguished as well. The fluorescence of MPP stems from an excimer state [4], while the CuPc emission originates from a triplet state (phosphorescence) [5].

The emission spectra of mixed layers for excitation of MPP are shown in Fig. 2 (MPP emission) and Fig. 3 (CuPc emission). The concentration dependence of the emission intensities can be seen in Fig. 4. The MPP emission strongly decreases with increasing CuPc ratios, without significant changes in the emission spectrum itself. The excitation of the MPP simultaneously causes emission of CuPc. This CuPc emission increases up to a certain concentration and then decreases again.

The MPP emission data can be linearly approximated using a Stern–Volmer plot $\varphi_0/\varphi = A + B \cdot C_{CuPc}$, where φ_0 and φ are the fluorescence quantum yields of the pure layer and the mixed layers, respectively. In order to obtain φ from the measured emission intensities I the peak values are corrected for real absorption and for reabsorption:

$$I_{corr} = I \cdot \frac{k_{reabs}}{1 - R - T} \qquad (1)$$

(R, reflection; T, transmission). The reabsorption correction factor is calculated on the basis of a simplified model using Beer's law: $k_{reabs} = 1 + \alpha(\lambda_{emission})/\alpha(\lambda_{excitation})$, where α is the absorption coefficient.

The CuPc emission clearly reveals that energy transfer from MPP to CuPc takes place. The decrease of the CuPc emission intensity at high CuPc concentrations can be explained by aggregation of the CuPc molecules. The efficiency φ_T of the energy transfer process can be estimated by comparing the intensity I_{sens} of the sensitized CuPc luminescence with the CuPc luminescence intensity for direct excitation of CuPc I_{dir}. To do this, the same layer is measured with excitation both at $\lambda_{dir} = 647$ nm (direct excitation of CuPc) and at $\lambda_{sens} = 488$ nm (excitation of MPP, detection of sensitized CuPc luminescence). Considering the different excitation rates r_{dir} and r_{sens} at the corresponding wavelength, the transfer efficiency becomes

$$\varphi_T = \frac{I_{sens}}{I_{dir}} \cdot \frac{r_{dir}}{r_{sens}} \qquad (2)$$

The fraction of the excitation rates includes the incident light power P, the excitation wavelength λ, and the absorption A of the layers (indices for excitation at λ_{dir} and λ_{sens}, resp.):

$$\frac{r_{dir}}{r_{sens}} = \frac{P_{dir}\lambda_{dir}A_{dir}}{P_{sens}\lambda_{sens}A_{sens}} \qquad (3)$$
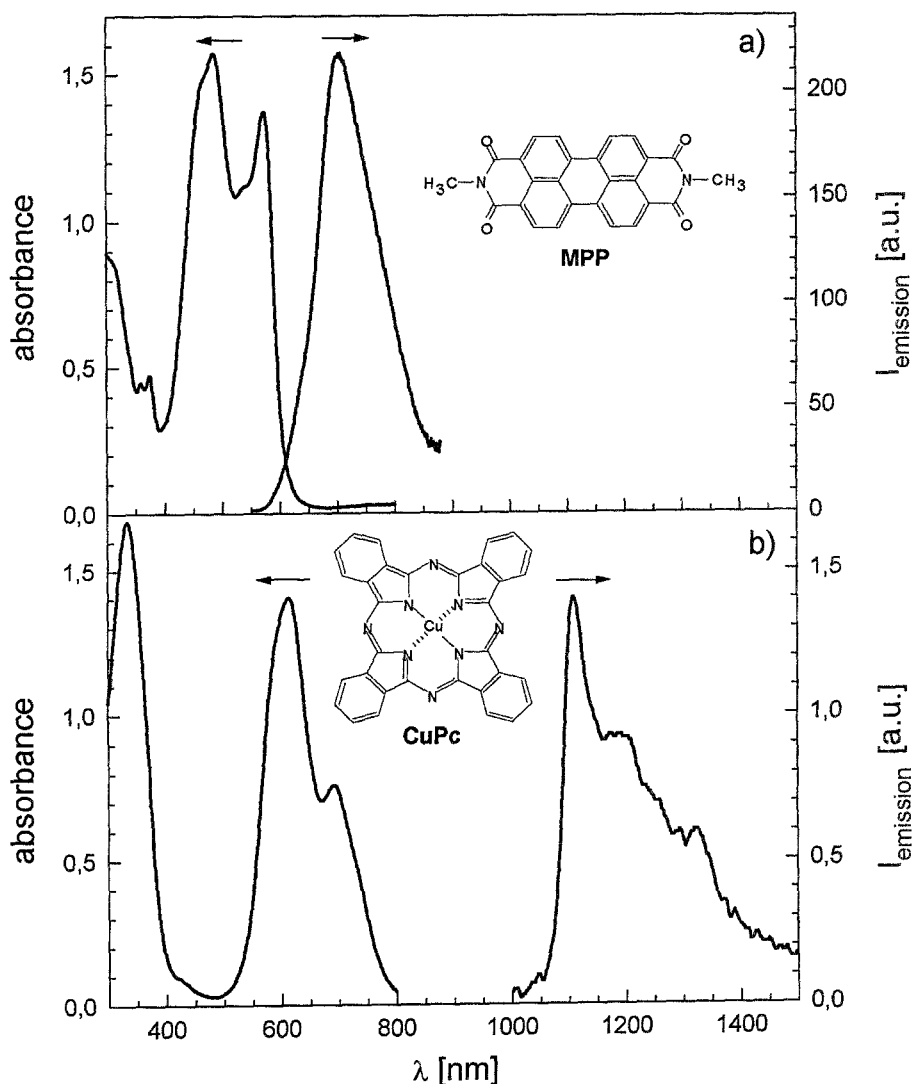
Fig. 1. Absorption and emission spectra of the pure dye layers. (a) MPP layer ($d=300$ nm), emission spectrum for excitation at 488 nm. (b) CuPc layer ($d=200$ nm), emission spectrum for excitation at 647 nm.

Furthermore, the superposed absorption A_0 of a pure MPP layer was subtracted from A_{dir}. With these considerations one obtains a maximum energy transfer efficiency of $\varphi_T=86\%$ at $C_{CuPc}=8.8$ mol%. At lower CuPc concentrations φ_T becomes smaller and the numerical values become very uncertain due to the small absorption. At high CuPc concentrations (≥ 8.8 mol%) the error in φ_T is estimated to be of the order of several percent. Despite this uncertainty it is obvious that a very efficient energy transfer to CuPc occurs, which is the main factor of the fluorescence quenching. Additional quenching processes (e.g., electron transfer) cannot be completely excluded. A trivial reabsorption process would not explain the observed sensitized CuPc emission because the

CuPc emission increases at higher CuPc concentrations, although the MPP emission is strongly quenched. The effect of the reabsorption on the quenching data is taken into account by the correction described in Eq. (1).

The linear Stern–Volmer plot describing the fluorescence quenching can be interpreted by the following model, which is analogous to diffusion-controlled reactions in solutions.

1. The incident light creates localized excitons MPP*, which diffuse freely in the solid MPP with a diffusion constant D.
2. If an MPP exciton comes into the vicinity of a fixed CuPc molecule (distance R), it will be deactivated: MPP* + CuPc → MPP + CuPc*.
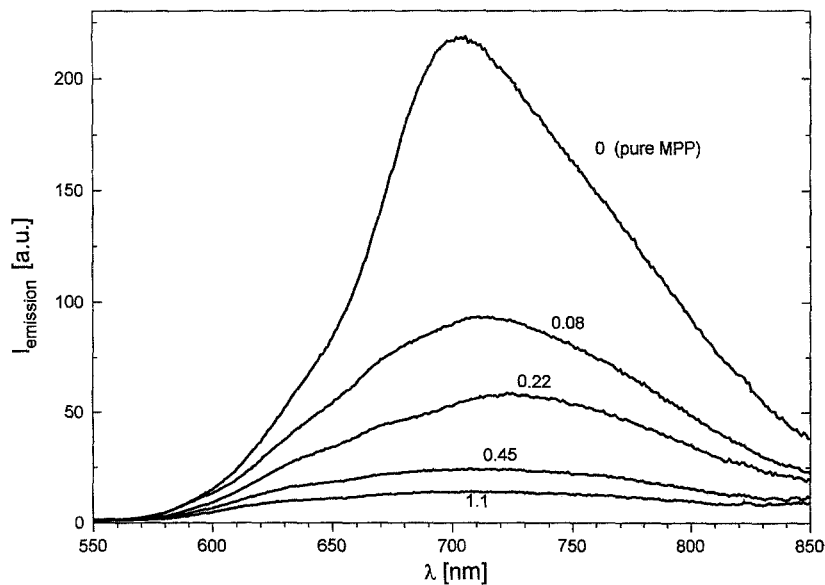
Fig. 2. Emission spectra of a pure MPP layer (d=300 nm) and of corresponding mixed layers with increasing concentration of CuPc (mol%); excitation at 488 nm.
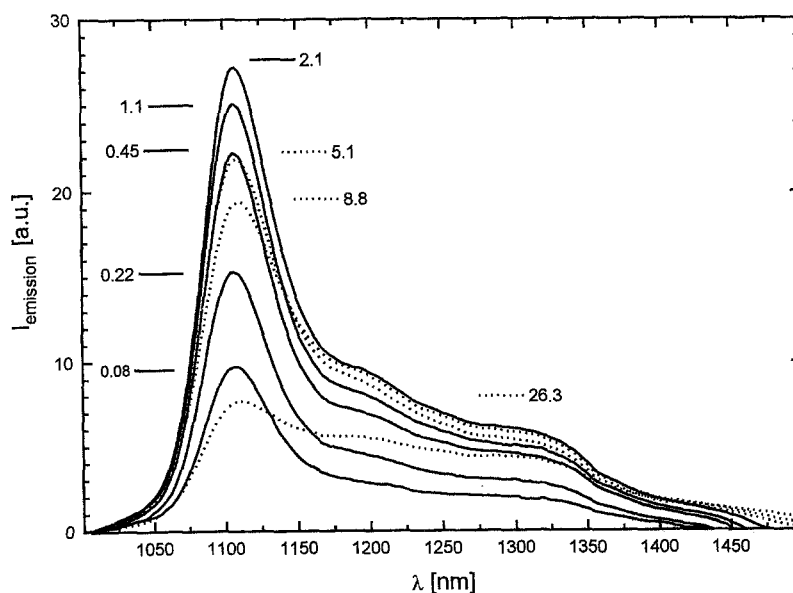

Fig. 3. CuPc emission spectra of mixed layers (300 nm MPP with increasing concentration of CuPc), excitation at 488 nm (MPP absorption band), corrected for the long wave tail of the MPP emission.

The Stern–Volmer equation for such a process is φ_0/φ = $1 + \tau_0 k C_{CuPc}$. With the rate constant k for a diffusion-controlled reaction ($k = 4\pi RDN_A$), the experimental data allow the calculation of the exciton diffusion length L_{Diff} = $\sqrt{\tau_0 D}$ (τ_0, unquenched exciton lifetime) as

$$L_{Diff} = \sqrt{\frac{\tau_0 k}{4\pi RN_A}} \qquad (4)$$

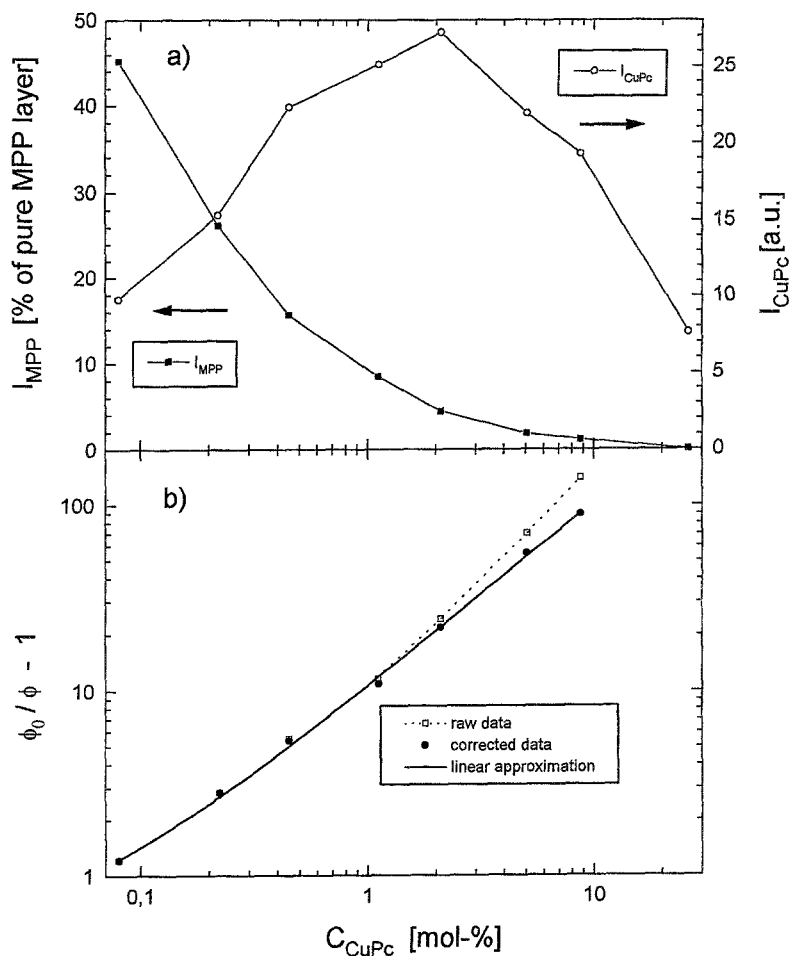The quenching distance R was estimated as follows:

Fig. 4. (a) Emission intensities of mixed layers (300 nm MPP + varying content of CuPc) vs CuPc concentration; excitation at 488 nm, detection at 696 nm for I_{MPP} and at 1106 nm for I_{CuPc}. I_{MPP} and I_{CuPc} are not comparable as absolute values. (b) Quenching of MPP emission I_{MPP} on a Stern–Volmer plot. The peak emission intensity is corrected for reflection and reabsorption.

Every quenching process will be most efficient for the excited MPP molecules which directly surround the CuPc molecule. With the assumption that single CuPc molecules are incorporated into the MPP crystal like substitutional impurities, the active quenching region is only determined by the MPP lattice parameters. This assumption is justified by the absorption spectra of the mixed layers. At low CuPc concentrations, they do not show the spectra of crystalline CuPc, but a single absorption peak similar to the absorption of dissolved CuPc [4]. For simplification the quenching region is assumed to be a sphere of volume $V = V_{uc}/Z$ (unit cell volume $V_{uc} = 873.2$ Å³, $Z=2$ [6]). It then follows that $R = 2r_{quenching\ sphere} = 1.5$ nm and the experimental data from Fig. 4 give $L_{Diff}=9$ nm. This result is in good agreement with literature values for the diffusion length of

excitons in several other evaporated dye layers, most of them between 5 and 20 nm [7,8].

The model of diffusion controlled dynamic quenching is supported by lifetime measurements, which show a decrease in the MPP emission lifetime with rising CuPc concentrations. Reliable evaluation was not yet possible because the lifetimes are too short (140 ps in the pure MPP layer and accordingly less in mixed layers) and the decay curves are multiexponential.

Double Layers

For the application of dyes, e.g., in organic solar cells the arrangement as double layers of different dyes offers several advantages: (i) with suitable dyes an optimum adaptation to the solar emission spectrum is pos-
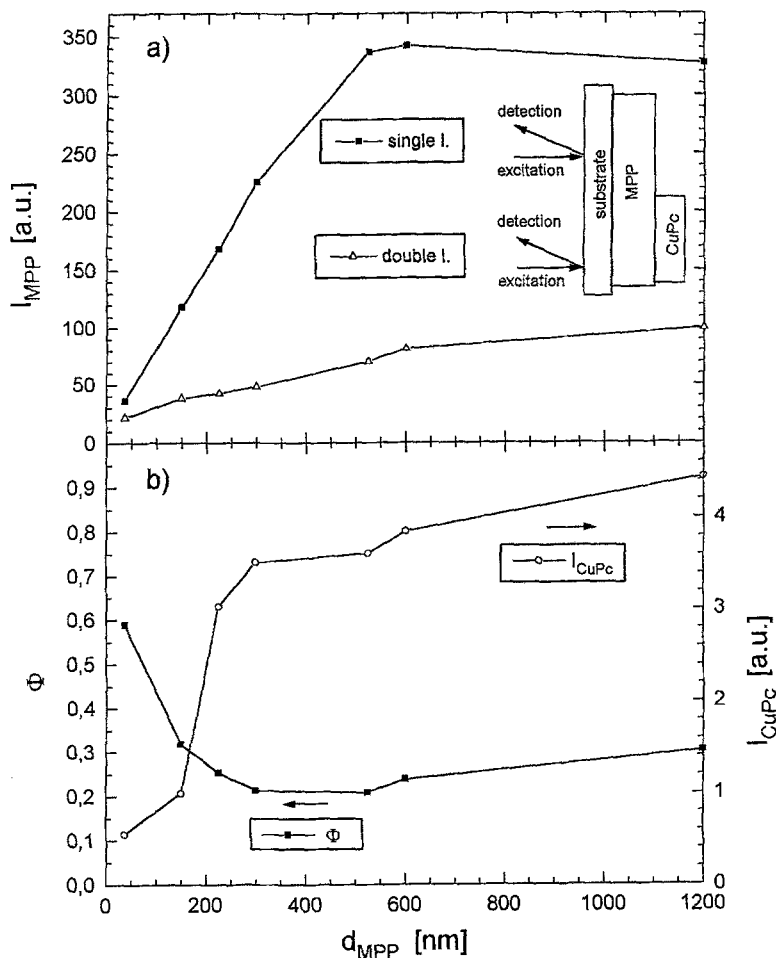
Fig. 5. Fluorescence quenching of MPP/CuPc double layers. (a) MPP emission intensity of single layers (substrate/MPP) and corresponding double layers (substrate/MPP/100 nm CuPc). (b) Quenching $\Phi = I_{\text{double layer}}/I_{\text{single layer}}$ of MPP emission and sensitized CuPc emission I_{CuPc}. Excitation at 488 nm.

sible; (ii) efficient transport of excitation energy can be realized by exciton migration and energy transfer to the second dye; and (iii) efficient charge generation could occur at the dye interface due to charge transfer. Therefore, it is important to investigate to which extent energy migration, energy transfer, and electron transfer processes occur between two sandwich-arranged dye layers. Due to the efficient energy transfer in mixed layers MPP and CuPc are ideal components for fluorescence investigations of double layer systems.

In Fig. 5a, MPP emission intensity vs MPP layer thickness d is shown for a single MPP layer and a double-layer system (substrate/MPP/100 nm CuPc). The ratio $\Phi = I_{\text{double l}}/I_{\text{single l}}$ is given in Fig. 5b. Φ is less than 1 and stays constant at large thicknesses. The MPP excitation causes CuPc emission with a thickness depend-

ence also shown in Fig. 5b. Like Φ it levels off for very thick layers. Thus, MPP fluorescence quenching and energy transfer to CuPc are detectable similar to mixed layers. The thickness dependence of both Φ and I_{CuPc} cannot be described by a diffusion process to the quenching layer. Assuming exciton diffusion and energy transfer ranges of the order of magnitude of 10 nm, any influence of the CuPc layer should vanish if d becomes very large compared to the penetration depth of the excitation light (about 100 nm in this case). Then Φ should approach 1 (no quenching) and the sensitized CuPc luminescence should also disappear.

The experimental results are in strong contrast to these expectations and to the described results from the mixed layers. Trivial optical effects like reabsorption can be excluded since the effects do not occur if the two

layers are separated by an additional transparent spacer layer of NaF. Although we do not understand this long-range energy transfer between evaporated double layer systems, it might be relevant for the design of similarly prepared organic solar cells.

CONCLUSIONS

We have studied the energy transfer from the per-ylenimide dye MPP to CuPc in both mixed and double layers using fluorescence quenching. The CuPc concentration-dependent quenching in mixed layers is well described by a Stern–Volmer relation, indicating an exciton diffusion process to the quencher molecules. Using a simple model for the quenching radius, we obtain a diffusion length of $L_{Diff}=9$ nm.

In double layers, we observe quenching of the MPP fluorescence and energy transfer to CuPc even for film thicknesses orders of magnitude above the diffusion length determined in mixed layers. The mechanism of this apparent long-range effect is not known at present.

The observed efficient energy transfer between two dyes in the solid state is comparable with results from other fixed dye compositions, e.g., LB layers [9], polymers [10], membranes [11], vesicles [12], and other biological systems [13].

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