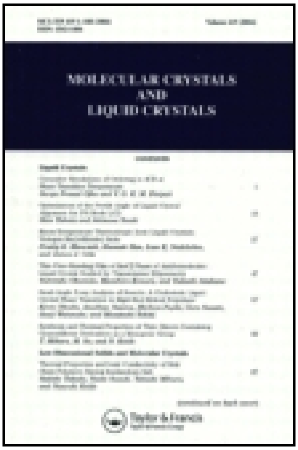

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Influence of the Interlayer Interactions on Aggregates in Organic Molecular Films

Jianhua Xu [a] , Wenjun Wang [a] , Xingze Lu [a] , Gongming Wang [a] , Wencheng Wang [a] , Zhigang Cai [b] , Peiqing Yang [b] & Jianying Zhou [b]

[a] Department of Physics, Fudan University, Shanghai, 200433, China

[b] State Key Laboratory of Ultrafast Laser Spectroscopy, Zhongshan University, Guangzhou, 510275, China

Version of record first published: 24 Sep 2006

To cite this article: Jianhua Xu, Wenjun Wang, Xingze Lu, Gongming Wang, Wencheng Wang, Zhigang Cai, Peiqing Yang & Jianying Zhou (1999): Influence of the Interlayer Interactions on Aggregates in Organic Molecular Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 337:1, 389-392

To link to this article: http://dx.doi.org/10.1080/10587259908023459

Mol. Cryst. and Liq. Cryst., 1999, Vol. 337, pp. 389-392
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Influence of the Interlayer Interactions on Aggregates in Organic Molecular Films

JIANHUA XU[a], WENJUN WANG[a], XINGZE LU[a],
GONGMING WANG[a], WENCHENG WANG[a], ZHIGANG CAI[b],
PEIQING YANG[b] and JIANYING ZHOU[b]

[a]*Department of Physics, Fudan University, Shanghai 200433, China and* [b]*State Key Laboratory of Ultrafast Laser Spectroscopy, Zhongshan University, Guangzhou 510275, China*

Influence of the interlayer interactions on aggregates in Langmuir-Blodgett films has been investigated by using the steady-state and time-resolved fluorescence techniques.

Keywords: Langmuir-Blodgett (LB) multilayers; aggregate; time-resolved fluorescence

INTRODUCTION

In LB multilayers, the organic molecules have a strong tendency to from aggregates and the existence of aggregation can change the optical and electronic properties of LB films significantly[1,2]. The molecular interlayer or intralayer interactions in multilayers would not only cause different aggregates and spectral behaviors but also become one of the key problems in the design of organic molecular optoelectronic devices.

EXPERIMENT

The hemicyanine dye, E-N-docosyl-4-[2-(4-diethylaminophenyl) ethenyl]-pyridinium bromide, (abbreviated as DAEP), and spectroscopic-grade arachidic acid, $C_{19}H_{39}COOH$, (abbreviated as AA), were spread from 10^{-3} mol l^{-1} chloroform solutions onto aqueous subphase in two separate compartments of a KSV5000 Langmuir trough made in Finland. We prepared two Y-type DAEP/AA interleaving samples A and B with different bilayer numbers 10 and 20, one pure 15 layers Y-type DAEP sample C, and one pure 10 layers AA sample respectively, at a surface pressure of 30 mN $m^{-1}$and dipping speed of 3 mm min^{-1}.

The experimental setup for steady-state and time resolved fluorescence measurement has been described in Ref. 2.

RESULTS AND DISCUSSION

According to the simple theory of exciton splitting [3], the sign and size of the exciton splitting $2\Delta E$ as well as the selection rules for optical transitions are essentially determined by the inclination angle θ between the molecular transition moments and the connecting lines of the molecules. For larger θ's as in the case of H-type aggregation, the lower level is optically forbidden and the transition between the ground state and upper level leads to a blue-shifted fluorescence spectra with respect to the original fluorescence spectra of monomeric molecules. However, for small inclination angle θ, the upper level is optically forbidden, leading to red-shifted as well as J-aggregation. On the other hand, if the radiative decay rate of an isolated two-level single molecule is γ and the size of an aggregate involving N identical molecules is much smaller than the wavelength associated with the optical transition, the radiative decay rate of an aggregate is $N\gamma$[4].

Integrated and Time Fluorescence of Y-type interleaving DAEP/AA Multilayers

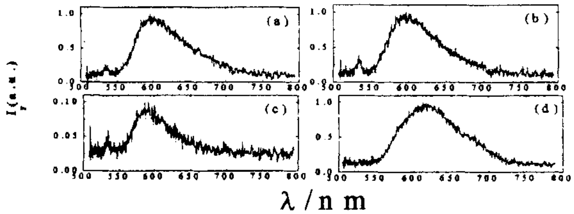

FIGURE 1 The steady-state fluorescence spectra of (a) Sample A; (b) Sample B; (c) AA; (d) DAEP solution

We measured the steady-state fluorescence spectra of sample A, B as shown in Fig.1 (a) and (b), respectively. The fluorescence peaks are both at 598nm, displaying a significant blue shift with respect to that of DAEP (615nm) in solution given in Fig. 1(d). The fluorescence intensity of AA sample (Fig. 1(c)) was at least one order of magnitude smaller than that of the samples, so the influence of AA in the samples could be neglected. It was confirmed again that the aggregation in interleaving multilayers was H-type. The effective distance of intermolecular interaction was about 1nm[5], and the thickness of AA layer in sample A and B was about 2.5nm, so they could screen the interlayer interaction of DAEP molecules in the samples. Therefore, the degree of aggregation would be independent of the bilayer numbers.

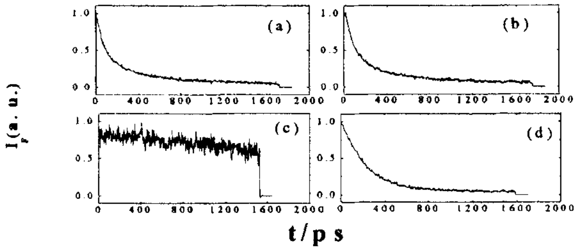

FIGURE 2 The temporal fluorescence profiles of (a) Sample A; (b) Sample B; (c) AA; (d) DAEP solution

The temporal fluorescence profiles of sample A, B, AA film and DAEP in solution are shown in Fig.2. The influence of AA in sample A and B could be ignored because of the above reason, and the other reason was that its fluorescence decayed very slowly. After analyzing the data, we found that all data in Fig.2 (a, b, d) could be well fitted by a bi-exponential model[1]. The lifetime, relative amplitudes of the components and molecular numbers in an aggregate were deduced and listed in Table 1. The deduced values of sample A and B in Table 1 were almost same, confirming again that the interlayer interaction didn't affect the aggregation of the molecules in interleaving multilayers.

TABLE I Fluorescence lifetimes and proportions of DAEP monomer and aggregate in Y-type interleaving DAEP/AA LB films

Sample	T_1/ps	T_2/ps	A_1	A_2	$N(T_1/T_2)$
Solution	204	1353	0.97	0.03	0
A	821	91	0.30	0.70	9
B	875	97	0.35	0.65	9

Integrated and Time Fluorescence of Y-type pure DAEP Multilayers

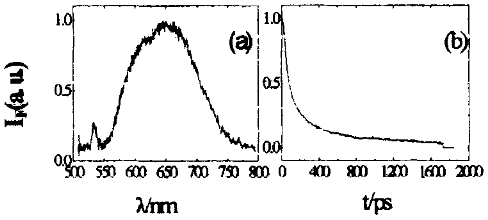

FIGURE 3 (a) steady-state fluorescence spectra and (b) temporal fluorescence profiles of Sample C

As shown in Fig.3 (a), the fluorescence spectra (peak at 645nm) of sample C exhibited a distinct red shift relative to that of DAEP in solution. It indicated the interlayer interaction would be stronger than the intralayer interaction because of the lack of the screening of AA and the inclination angle θ would be reduced (close to 0), which caused J-type aggregation. The temporal profile could also be well fitted by the model as shown in Fig. 3. Notice that the molecular numbers of the aggregates in the sample C was larger than that of LB interleaving films.

CONCLUSION

In interleaving multilayers, since the AA molecules screened the interlayer interaction of DAEP molecules, the DAEP molecules would form H-type aggregates and the bilayer numbers didn't affect the degree of aggregation. However, the strong interlayer interaction would cause J-type aggregation in Y-type pure DAEP multilayers, displaying a significant red-shift of fluorescence spectra and a larger scale of aggregates.

References

[1] Shihong Ma, Xingze Lu, Jianhua Xu, et al., Chem. Phys. Lett., **280**, 308(1997).
[2] Jianhua Xu, Xingze Lu, Guangpeng Zhou, et .al., Thin Solid Films, **312**, 295(1998).
[3] G. H. Wagniere, J. B. Hutter, J. Opt. Soc. Am. B, **6**, 693(1989).
[4] J. Grad, G. Hernandez, S. Mukamel, Phys. Rev. A, **37**, 3835(1988).
[5] L. M. Hayden, Phys. Rev. B, **38**, 3718(1988).