

# Influence of molecular composition on H-aggregation in hemicyanine Langmuir-Blodgett multilayers

WANG Wen-jun\*, LI Shu-hong, HU Hai-quan, and BAI Cheng-lin

Department of Physics, Liaocheng University, Liaocheng 252059, China.

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Influence of molecular composition in hemicyanine Langmuir-Blodgett (LB) films on the aggregation features was investigated by using steady state and time-resolved photoluminescence spectroscopy. It was found that a lower degree of H-aggregation (smaller aggregate size) could be realized in hemicyanine LB films with larger donor groups, leading to a smaller photoluminescence peak blue shift with respect to their solution spectra and longer aggregate lifetime.

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Langmuir-Blodgett (LB) films have been receiving considerable attention due to the scientific and technological significance<sup>[1-2]</sup>. For a given type of molecules with specific functions, the macroscopic physical and chemical properties of LB films are determined by molecular assembly. Amphiphilic hemicyanine dyes have potentially wide applications in nonlinear optics because of their high hyperpolarizability  $\beta$  ( $10^{-28} - 10^{-27}$  esu) and possibility of constructing stable LB multilayers. However, these organic molecules often form aggregates in LB films, leading to change of their macroscopic optical characteristics<sup>[3]</sup>. Thus, molecular orientation, aggregation and their control in LB films become one of the key issues in their applications to microelectronics and photonics. The optical properties of hemicyanine molecules have been studied by using polarized UV-visible absorption spectra and second harmonic generation (SHG) technique. The frequency-doubling properties of LB films are sensitive to the choice of donor/acceptor group<sup>[4]</sup>, degree of molecular aggregation<sup>[5]</sup>, and type of packing<sup>[6]</sup>. In this paper, the aggregation behaviors of four kinds of hemicyanine dyes (HD) with the similar molecular compositions but different donor-acceptor groups in LB multilayers have been studied by steady state and time-resolved photoluminescence spectroscopy.

Following a procedure similar to that of I. R. Girling *et al.*<sup>[7]</sup>, four kinds of hemicyanine dyes have been synthesized by adjusting different donor-acceptor groups. The molecular structures of these hemicyanine dyes (abbreviated as HD1—HD4 respectively) are given in Tab. 1. They are composed of three parts: the donors (dimethylamine or diethylamine), the acceptor groups including a hydrocarbon ( $C_{18}H_{37}$  or  $C_{22}H_{45}$ ), and the central parts of the molecules (styrylpyridines). Spectroscopic-grade arachidic acid  $C_{19}H_{39}COOH$  (abbreviated as AA)

was purchased directly from Shanghai No. 1 Reagent Plant and used without further purifications.

The LB films were prepared on a KSV5000 Langmuir double trough made in Finland. The subphase was deionized, doubly distilled water at 20°C with  $CdCl_2$  of  $3 \times 10^{-4}$  mole  $l^{-1}$  and a pH value of 5.8~6.2. The hemicyanine dyes (HD1~HD4) and arachidic acid (AA) were spread from  $10^{-3}$  mole  $l^{-1}$  chloroform solution onto the subphase surface in two separate compartments respectively. The compression rate was 3 mm  $min^{-1}$ . Y-type interleaving multilayers of HD/AA were deposited on hydrophilically treated quartz plates of dimension 30 mm  $\times$  18 mm  $\times$  2 mm at a constant pressure of 25 mN  $m^{-1}$  (for HD) and 30 mN  $m^{-1}$  (for AA) respectively. Insertion of the AA layers not only insured the noncentrosymmetric structure of the HD multilayers, which was a prerequisite for nonvanishing macroscopic second-order optical nonlinearity, but also improved the degree of order and stability of the films. The HD layers were deposited during upstrokes with a dipping speed of 5 mm  $min^{-1}$  and AA during downstrokes with a dipping speed of 2 mm  $min^{-1}$ . The transfer ratio during the whole deposition process could be kept  $1 \pm 0.1$ . We prepared four Y-type interleaving samples of 15 bilayers (HD1/AA, HD2/AA, HD3/AA, HD4/AA) under the above conditions. The LB multilayer on one side of the samples was removed, while the other side was used for optical measurements.

The photoluminescence experimental setup has been described in detail elsewhere<sup>[8]</sup>. Photoluminescence was excited by a laser beam of pulse width 80 ps, repetition rate 82 MHz, and average power 40 mW at 532 nm generated from an actively mode-locked Nd:YAG laser. The diameter of the pump beam focused on the samples was about 1 mm. The photoluminescence signals were dispersed by a monochromator, detected and analyzed by a synchro-scan streak camera system of resolution 10 ps. Both steady state (integrated) and time-resolved photo-

\* E-mail: phywwang@163.com

luminescence spectra could be measured simultaneously.

All experiments were performed at room temperature.

Tab. 1 The chemical structure of the four hemicyanine dyes

NO	Chemical name	Chemical structure
HD1	E-N-octadecyl-4-[2-(4-dimethylaminophenyl) ethenyl]pyridinium Bromide	
HD2	E-N-octadecyl-4-[2-(4-diethylaminophenyl) ethenyl]pyridinium Bromide	
HD3	E-N-docosyl-4-[2-(4-dimethylaminophenyl) ethenyl]pyridinium Bromide	
HD4	E-N-docosyl-4-[2-(4-diethylaminophenyl) ethenyl]pyridinium Bromide	

Consider a dimer formed from two molecules with their transition dipole moments parallel to each other. According to the simple theory on aggregations by Wagner *et al.*<sup>[9]</sup>, the excited energy level splits into two sublevels when molecules approach each other and form a dimer due to the electric dipole interactions. The sign and size of the excitation splitting  $2\Delta E$ , as well as the selection rules for optical transitions were essentially determined by the inclination angle  $\theta$  between the molecular transition moments and the connecting lines of the

two molecules. For larger  $\theta$  as in the case of H-type aggregation ( $\theta=90^\circ$ ), the lower sublevel is optically forbidden and the transition between the ground state and upper sublevel leads to an absorption band which is blue-shifted from original absorption band of monomeric molecules. It was also found that the photoluminescence spectra would be blue-shifted when molecules formed H-aggregates, which was similar to the shift behavior observed in the absorption spectra<sup>[8]</sup>.

Fig. 1 gives the steady state photoluminescence spec-

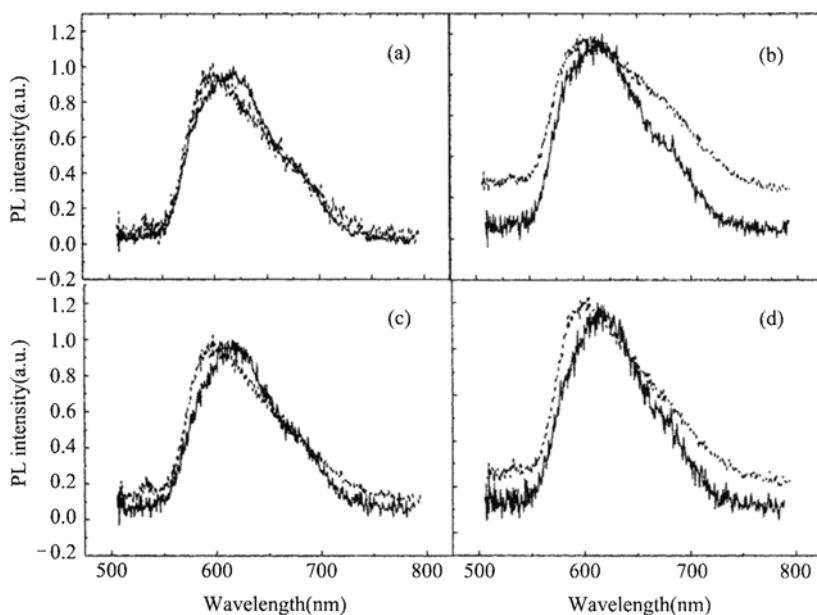


Fig. 1 The steady state photoluminescence spectra of the LB films (dash line) and the solutions (solid line) for (a) HD1, (b) HD2, (c) HD3 and (d) HD4.

tra of the hemicyanine dyes (HD1~HD4) in LB films and in solutions. The solutions were  $10^{-5}$  mole  $l^{-1}$  chloroform diluted solution so that the photoluminescence spectra of the monomeric molecules could be obtained. The photoluminescence intensity of AA was at least one order of magnitude smaller than that of the HD layers, so the influence of AA in the samples could be neglected. It is clear that the photoluminescence peaks are blue-shifted in the LB film compared with that of the molecules in the solution, which demonstrated that all hemicyanine dyes formed H-aggregation.

Tab. 2 gives the photoluminescence peak positions of these molecules in the LB films and in the solutions, respectively. As shown in Tab. 2, the molecules with the same acceptor but different donor groups would have different photoluminescence peak positions (HD1 compared with HD2 or HD3 compared with HD4). However the molecules HD1 and HD3 (or HD2 and HD4) with the same donor groups  $-N(CH_3)_2$  (or  $-N(C_2H_5)_2$ ) but different acceptor groups ( $N^+-C_{18}H_{37}$  or  $N^+-C_{22}H_{45}$ ) nearly have the same photoluminescence peak position. In the solutions, the monomeric molecules have also the same behaviors as in LB films. So the donor groups  $-N(CH_3)_2$  and  $-N(C_2H_5)_2$  play a main role to determine the photoluminescence properties of these hemicyanine dyes.

**Tab. 2 The photoluminescence peak positions of the hemicyanine dyes**

No	LB $\lambda_{max1}$ (nm)	Solution $\lambda_{max2}$ (nm)	Blue shift(nm)
HD1	599	616	17
HD2	603	612	9
HD3	597	615	18
HD4	603	612	9

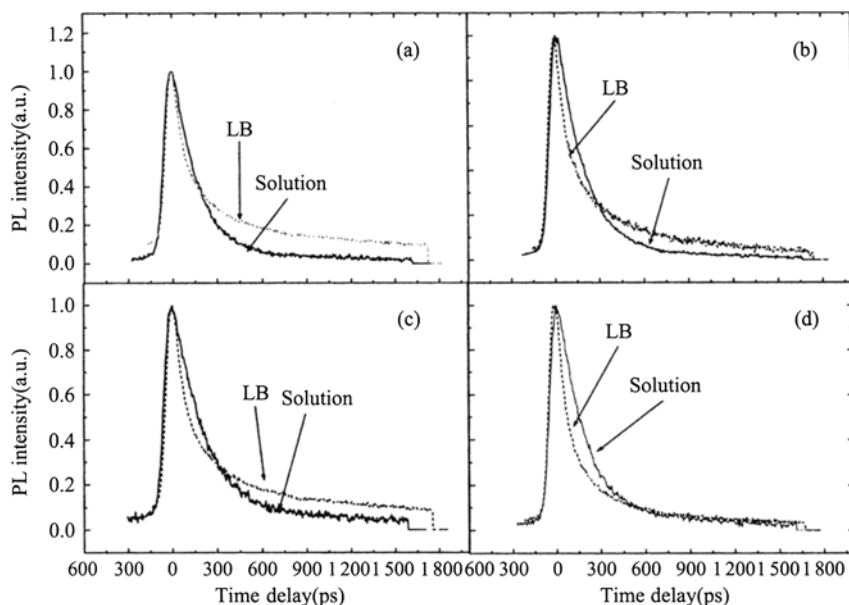
Notice that the photoluminescence peak positions of the HD1 and HD3 have a much larger blue-shift (17 nm and 18 nm) than those of HD2 and HD4 (9 nm), because the hydrophilic donor groups  $-N(CH_3)_2$  of HD1 and HD3 molecules take up smaller area than the groups  $-N(C_2H_5)_2$  of HD2 and HD4 molecules, the intermolecular interaction between adjacent donor groups for HD1 and HD3 is stronger than that for HD2 and HD4, leading to a higher degree of aggregation. This agrees with the results of Ma *et al.*<sup>[4]</sup> deduced from their UV-visible absorption spectra.

Here we consider an aggregate involving  $N$  identical molecules. If the size of the aggregate is much smaller than the wavelength associated with the optical transition, we can use the dipole approximation<sup>[10,11]</sup>. According to the theory of aggregate decay dynamics, the radiative decay rate of the aggregate will be  $N\gamma$ , i. e.  $N$  times as large as that of an isolated two-level single molecule due to the coherent interaction between all molecules in the aggregate and the radiation field. In other word, the lifetime of an aggregate is  $N$  times smaller than that of a single molecule<sup>[12,13]</sup>.

The temporal photoluminescence profiles of the HD's in LB films and solutions at room temperature are shown in Fig. 2. The solid and dash lines are the decay profiles of the hemicyanine derivatives in the solutions and the LB films respectively. After analyzing the data, we found that the data could be well fitted by an exponential model (in the solutions) and a bi-exponential model (in the LB films):

$$I(t) = A_1 e^{-t/T_1} + A_2 e^{-t/T_2}$$

The decay time ( $T_1$  and  $T_2$ ), relative amplitudes of the



**Fig. 2 Temporal photoluminescence profiles of the LB films (dash line) and the solutions (solid line) for (a) HD1, (b) HD2, (c) HD3 and (d) HD4.**

components ( $A_1$  and  $A_2$ ) and molecular numbers ( $N$ ) in an aggregate were deduced and listed in Tab. 3. Different components with different decay time could be attributed to different molecular species (monomer or aggregate, etc.) in LB films<sup>[14]</sup>. Since the intermolecular coupling in aggregates should shorten the excited state life-

time<sup>[15]</sup>, we could attribute the component with longer decay time ( $T_1$ ) to the contribution from the monomers, and another one with shorter decay time ( $T_2$ ) to the contribution from the aggregates in the LB films. The aggregate size  $N$  was then deduced from the ratio  $T_1/T_2$ .

Tab. 3 Time-resolved photoluminescence proportions of HD1~ HD4 multilayers films

Dyes	Samples	$T_1$ (ps)	$T_2$ (ps)	$A_1$	$A_2$	$N(T_1/T_2)$
HD1	Solution	168		1		0
	LB film	1115	92	0.32	0.68	11
HD2	Solution	202		1		0
	LB film	688	87	0.33	0.67	8
HD3	Solution	204		1		0
	LB film	1084	96	0.30	0.70	11
HD4	Solution	179		1		0
	LB film	728	79	0.23	0.77	9

Tab. 3 indicates that all HD molecules exist with the monomer formation in the solutions, but form aggregates with different numbers  $N$  in the LB films. Notice that the average aggregate size  $N$  for HD1 and HD3 is 11 which is larger than that for HD2 (8) and HD4 (9), indicating that the molecules of HD1 and HD3 perform a stronger aggregation behavior than that of HD2 and HD4. It proves once again that the donor groups would mainly influence aggregation properties of hemicyanine dyes, which agrees well with our result from the steady state photoluminescence spectra.

Notice that the monomer lifetimes of HD's are much shorter in solutions compared with those in their respective LB films due to collisional quenching. This is because the probability of collisions in a solution is larger than that in LB films leading to a larger damping coefficient and a smaller radiative lifetime.

Four kinds of hemicyanine dyes were synthesized by selecting different donor-acceptor groups, and the aggregation behavior of these molecules in LB multilayers were investigated by using steady state and time-resolved photoluminescence spectroscopy. It was shown that the degree of H-aggregation in LB films was essentially affected by the type of donor groups due to different intermolecular interaction between adjacent donor groups. The molecules with the donor  $-\text{N}(\text{CH}_3)_2$  showed stronger aggregation properties than that with  $-\text{N}(\text{C}_2\text{H}_5)_2$ , leading to larger blue shift of photoluminescence spectroscopic peak with respect to their solution spectra, greater aggregate size and shorter aggregate

lifetime.

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