Nonlinear Optical Phenomena due to Donor–Acceptor Interfaces Created in Langmuir–Blodgett Films

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Langmuir–Blodgett films consisting of two-dimensional interfaces between corbiene donor and quinone acceptor molecules show a significant nonlinear optical property (second-harmonic generation) that can be attributed to the intermolecular contact across the interface between the donor and acceptor molecules in the film.

In the last decade Langmuir–Blodgett (LB) films have played an important role as a means of organizing materials at the molecular level. Multilayer films on suitable substrates have been considered for application in the fast growing fields of molecular electronics, nonlinear optics (NLO), conducting organic thin films, *etc.*[1] Significant nonlinear optical properties have been achieved using the LB technique to arrange molecules with high molecular hyperpolarizabilities in a way that avoids cancellation of the molecular effects. Molecules possessing high molecular hyperpolarizabilities typically consist of a donor group (*e.g.*-NH_2) connected *via* an aromatic system to an acceptor group (*e.g.*-NO_2).[2]

We report experimental evidence for a significant nonlinear optical effect in an LB film, which differs from the abovementioned films as it does not contain individual molecules of the donor–acceptor type. Instead, we provide evidence that the NLO effect is due to an intermolecular interaction created in the LB film by depositing first a layer of donor molecules followed by a layer of acceptor molecules thereby creating a two-dimensional interface between donors and acceptors (Fig. 1).[3]

Monolayers at the air/water interface of the acceptor (octadecylthiobenzoquinone,[4] **1**) and the donor {7-(*N*-octadodecylaminomethyl)-8-16-dioxadibenzo[*f,g*]perylene,[5] **2**} were created by spreading a $CHCl_3$ solution of the molecules followed by compression (dA/dt = 30 cm^2 min^{-1}) until a surface pressure of 20 mN m^{-1} and 15 mN m^{-1} was reached for the acceptor and donor respectively [Fig. 2(*a*) and (*b*)]. Both molecules exhibit smooth isotherms that rise steeply at mean molecular areas, which agree well with the dimensions of the molecules as estimated from spacefilling models ($\approx$0.25 nm^2 for the acceptor, and $\approx$0.5 nm^2 for the donor molecules. These areas lead roughly to a 2 : 1 stoichiometry of the resulting two-component film on the substrate). Possible molecular orientations in accordance with these areas are indicated in Fig. 2.

Alternate layers of the donor and acceptor molecules were transferred to trimethyl silanized quartz substrates[6] (Suprasil 1) using a double LB trough (KSV Instruments, Finland, Model 5000-3). The downstroke occurred through the donor layer and the upstroke through the acceptor layer. The entire experiment was conducted in darkness in order to prevent photoinduced endoperoxide formation from **2**.[7] The films transferred smoothly with a transfer ratio of 1 ± 0.1 for both up- and downstroke. UV absorbance at 250 nm increases linearly with the number of bilayers [Fig. 3(*b*)]. The UV–VIS absorption spectrum of the donor–acceptor films corresponds roughly to the sum of the spectra of Y-type films of the donor and acceptor, respectively. The NLO data, however (*vide infra*), show that through-space-charge transfer does take place. As the charge-transfer transition is not clearly seen in the absorption spectrum, it is likely to be hidden under the strong absorption bands arising from local excitations in the donor. A more detailed study of this aspect is under way.[8]

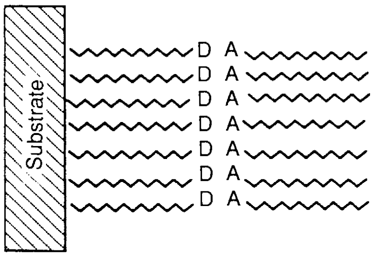

Fig. 1 Interface of donor (D) and acceptor (A) molecules in an LB film with alternating layers of donor and acceptor molecules

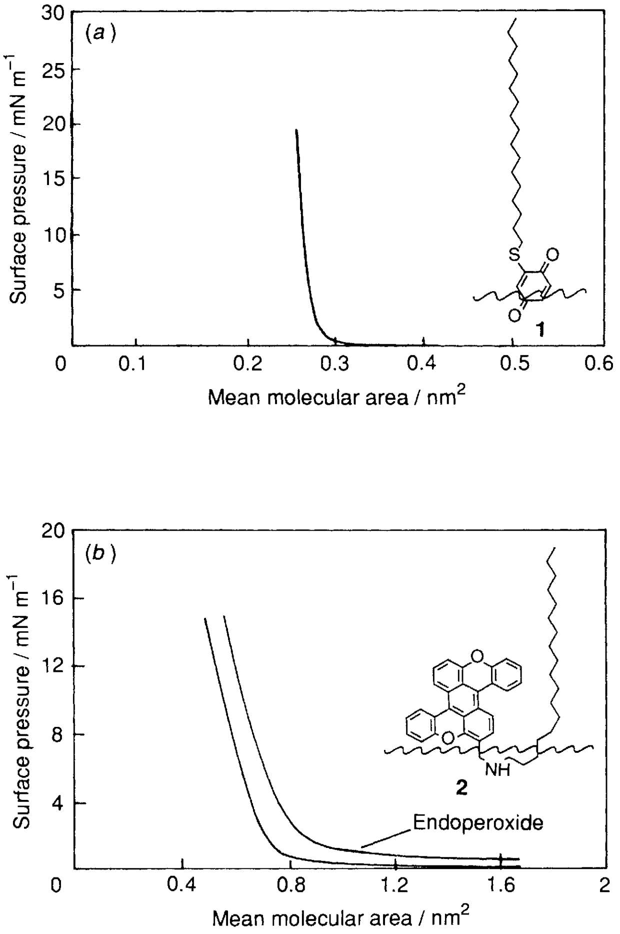

Fig. 2 Isotherms at $T = 20$ °C of (*a*) acceptor, and (*b*) donor molecules. Collapse occurs at 40 mN m^{-1} and 20 mN m^{-1} for the acceptor and donor, respectively. (*a*) $E^{\frac{1}{2}} = -0.6$ V and (*b*) $E^{\frac{1}{2}} = +0.6$V. $E^{\frac{1}{2}}$ values refer to oxidation potentials measured in CH_2Cl_2 *vs.* a standard calomel electrode (SCE) using tetra(n-butyl)ammonium hexafluorophosphate (0.1 mol dm^{-3}) as electrolyte.

The NLO properties of the films were probed by measuring the optical second-harmonic generation (SHG).[9] In the SHG measurements a linearly polarized Q-switched Nd : YAG laser beam (λ = 1064 nm) was incident on the sample. After filtering off the fundamental, the transmitted second-harmonic signal (λ = 532 nm) polarized in the plane spanned by the normal to the substrate and the wave vector of the incident light (*p*-polarized) was detected by a photomultiplier tube situated after a monochromator. The films possessed in-plane isotropy. By far the largest signal was obtained for a *p*-polarized fundamental beam at high angles of incidence [Fig. 3(*a*)]. This is in agreement with the major NLO-component being perpendicular to the donor–acceptor interface. The SHG intensity generated by a *p*-polarized fundamental beam plotted as a function of the angle of incidence shows, in addition, a fringe pattern due to interference between the signals generated in the films at the front and back of the substrate.[10] The good fringe contrast together with a less than 5% variation in the SHG intensity, when different areas of the sample were irradiated, shows that the film quality was good.† The SHG intensity increases quadratically with the number of bilayers [Fig. 3(*b*)], in agreement with theory.[9] A 20 bilayer sample gave rise to a SHG intensity comparable with a monolayer of a hemicyanine fatty acid derivative, which has a very high hyperpolarizability, mixed with stearic acid in a 1 : 1 ratio.[11] By comparing these values with literature values[3,11] we estimate $\chi_{zzz} \approx 0.5$ pV m^{-1} for one bilayer. This value is two to three orders of magnitude lower than the highest values obtained in LB films so far.[3] As the NLO effect arising at the donor–acceptor interface critically depends on the details of the electronic contact (overlap) between the donor and acceptor molecules, the prospects for improving the NLO effect by trying other donor–acceptor pairs should be good.

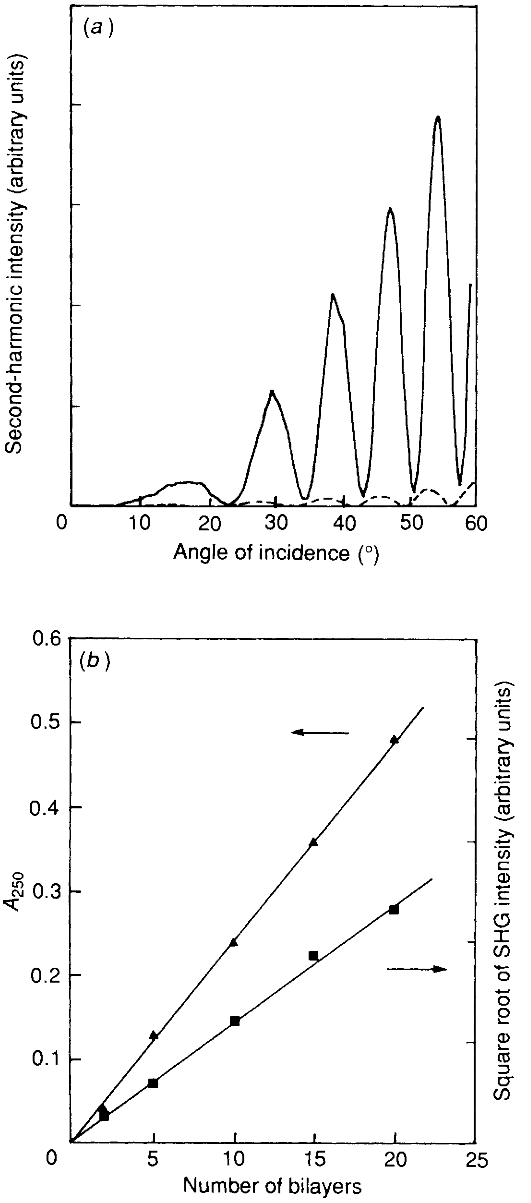

Fig. 3 (*a*) Second harmonic intensity of 20 bilayers of acceptor **1** and donor **2** *vs.* angle of incidence of laser light. (*b*) Dependence of the optical absorbtion at 250 nm, and the square root of the second harmonic intensity on the number of bilayers.

In order to demonstrate that the second-harmonic generation is due to the intermolecular interaction between donor and acceptor, we prepared LB double layers containing the endoperoxide[7] of **2** instead of the donor **2** itself. This change gives rise only to a small structural perturbation but a very large increase of the redox potential of the donor. Formation of the endoperoxide was accomplished by irradiating a monolayer of **2** in air for 1 h with a green spotlight (40 W)

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† Preliminary experiments on the stability in time of the films show that the NLO activity of films exposed occasionally to light dropped by 20% over a period of 2 weeks. Direct irradiation of the films with green light degrades the activity rapidly, and we therefore attribute the degradation of the NLO effect primarily to the endoperoxide formation of the corbiene molecule resulting in a deactivation of the donor.

before compression of the monolayer. Investigations on Y-type deposition of such monolayers show complete conversion to the colourless endoperoxide.[8] The isotherm of the endoperoxide resembles that of the unoxidized species **2**, except that the area per molecule has increased by 0.1 nm^2 in agreement with the addition of one O_2 molecule per donor molecule [Fig. 2(*b*)]; transfer occurred as for the unoxidized species.

The second harmonic intensity for 20 bilayers of such films is approximately 40 times lower than the signal from films with unoxidized donors [data are shown with dotted lines in Fig. 3(*a*)]. In addition we have measured the SHG signal from a number of films in which behenic acid replaces either the donor or the acceptor molecule. All of these show similar low values of the SHG intensity. This demonstrates that the SHG signal is not due to an intramolecular effect in either the donor or the acceptor layer.

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References

1 See for example, Proceedings from the fifth International Conference on LB films, Paris, 1991; to appear in *Thin Solid Films*, 1992.

2 See for example, L. J. Oudar and D. S. Chemla, *J. Chem. Phys.*, 1977, **66**, 2664.

3 An enhancement of the intrinsic nonlinear optical properties of dye molecules has been achieved by creating similar alternating LB films; D. B. Neal, M. C. Petty, G. G. Roberts, W. J. Feast, I. R. Girling, N. A. Cade, P. V. Kolinsky and I. R. Peterson, *Electronic Lett.*, 1986, **22**, 460.

4 M. Jørgensen, PhD Thesis, University of Copenhagen, 1990.

5 J. Larsen, I. Johannsen and K. Bechgaard, unpublished work; H. Decker and T. v. Fellenberg, *Liebigs Ann.*, 1907, **356**, 329. See also ref. 7.

6 M. R. Buhaenko, M. J. Grundy, R. M. Richardson and S. J. Roker, *Thin Solid Films*, 1988, **159**, 253.

7 The endoperoxide forms in a Diels–Alder reaction in which O_2 adds to the central ring of the corbiene molecule; S. Tokita, S. Suge, M. Toya and H. Nishi, *Nippon Kagaku Kaishi*, 1988, 97.

8 T. Bjørnholm, unpublished work.

9 Y. R. Shen, *The Principles of Nonlinear Optics*, Wiley, 1984.

10 F. Kajzar, J. Messier, J. Zyss and I. Ledoux, *Opt. Commun.*, 1983, **45**, 133.

11 I. R. Girling, N. A. Cade, P. V. Kolinsky, R. J. Jones, I. R. Petersen, M. M. Ahmad, D. B. Neal, M. C. Petty, G. G. P. Roberts and W. J. Feast, *J. Opt. Soc. Am. B*, 1987, **4**, 950.