Langmuir–Blodgett films of new amphiphilic electro-optically active charge-transfer dyes

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Abstract. Non-centrosymmetric Langmuir–Blodgett (LB) films have considerable potential for applications in second-order non-linear optics: the relevant lattice parameter, $\chi^{(2)}$, is non-zero in a non-centrosymmetric environment. The precision with which LB multilayers can be built up allows fine control over the thickness and geometry of the film. Non-centrosymmetric LB films can be obtained by X- or Z-type deposition using a single-trough regime, or by Y-type deposition using troughs incorporating two different amphiphilic molecules. Five new amphiphilic dyes were used in our study of multilayer deposition for the production of organic LB multilayers for non-linear optics.

1. Introduction

The interaction of light with matter may be characterized by phenomena such as absorption, refraction and scattering. These phenomena are functions of both wave-length and intensity, although a laser source is required to demonstrate the second of these. The induced dipole/unit volume (the polarization, P) arises from the separation of charge under the influence of the oscillating electric field, $E(w)$, and may be expanded as a power series in $E(w)$. We are particularly interested in the coefficient describing the quadratic dependence of P on $E(w)$. For bulk matter, this coefficient is $\chi^{(2)}$, the second-order non-linear electric susceptibility. For a single molecule, the equivalent coefficient is β, the first hyperpolarizability coefficient [1]. Both $\chi^{(2)}$ and β are third-rank tensors, quantum mechanical expressions for which involve triple products of matrix elements of the position operator r. This latter feature dictates that $\chi^{(2)}$ is zero for materials comprising centrosymmetric unit cells, and that β is zero for centrosymmetric molecules. The matrix-element triple-product involves terms describing the transition moment between the ground state and up to two excited states, and a term describing change in molecular electric dipole moment between two electronic states. Self-consistent field Pariser–Parr–Pople (SCFPPP) estimates of β [1–3] for many dyes indicate that having a well defined 'pseudo-linear' long molecular axis with strong electron donors at one end and strong electron acceptors at the other end are desirable prerequisites to enhance the transition moments, and usually give dyes exhibiting pronounced charge transfer and fluorescence. The principles of molecular design to obtain large changes in molecular dipole moment are not so clearly defined. We have shown [4] how the performance of dyes in second harmonic generation may

be calculated from experimental features in the absorption and fluorescence spectra in at least two solvents of very different dielectric constant.

In accord with the above remarks on molecular design, the dyes that we describe in this paper contain strong electron accepting groups such as nitro, N+ or cyano and hydrophobic regions usually associated with some electron-donating capacity as exemplified in -O-long-alkyl (figure 1). The juxtaposition of the two types of substituent has been selected to maximize the extent of the charge-transfer between them.
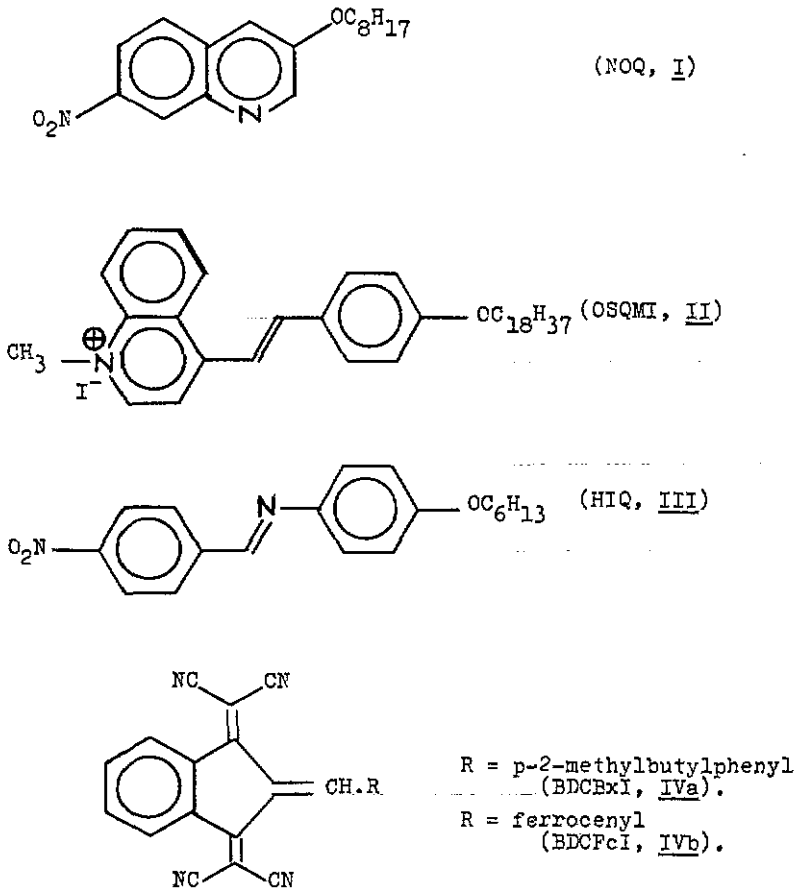

Figure 1. New amphiphilic dyes.

One means by which non-centrosymmetric molecules may be formed into a non-centrosymmetric ensemble is the LB multilayer technique [5]. Care must still be exercised in overcoming the tendency for the highly polar molecules to form, under the influence of electrostatic forces, an overall centrosymmetric structure. Thus, although Z- and X-type depositions (see figure 2) are satisfactory because all the dipole moments point in the same direction, Y-type deposition (with a single molecular species) is not, because all vectorial properties along the long molecular axis cancel to give a centrosymmetric ensemble. However, skilful design of the organic molecules [5, 6] can enable Y-type films to be constructed out of two classes of molecules (the so-called AB layers). One molecular class has, say, β parallel to the molecular dipole moment,

whereas the other class has β anti-parallel to the molecular dipole moment. Thus, the vectorial properties of all layers are additive (see figure 3). Less efficient means for achieving a similar end are either for A and B to have β coefficients of the same sign, but with different magnitudes, or for one molecular class to have a virtually zero value of β (e.g. stearic acid). It is the last of the foregoing three techniques to give Y-type films that has been used in our work.
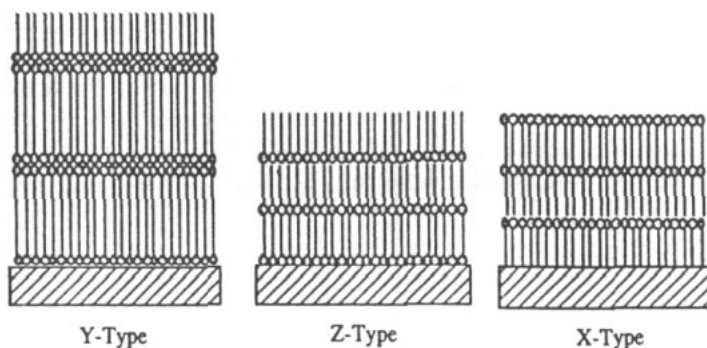

Y-Type   Z-Type   X-Type

Figure 2. Types of Langmuir–Blodgett multilayers.

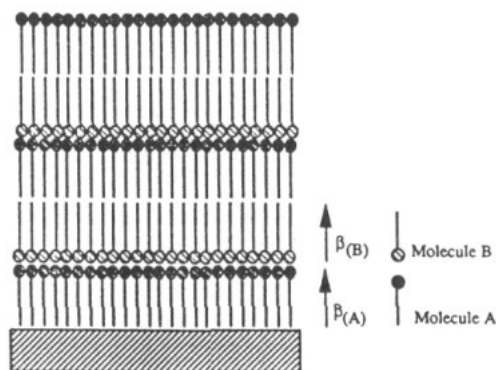$\beta_{(B)}$ Molecule B

$\beta_{(A)}$ Molecule A

Figure 3. Alternate-layer non-centrosymmetric Langmuir–Blodgett film.

2. Thin-film preparation and deposition

A Nima mini-trough (from Nima Technology) controlled by a BBC microcomputer was used for assessing the suitability of a representative selection of amphiphilic, charge-transfer dyes for deposition by the LB technique. The monolayer-spreading area was defined by a circular PTFE fixed barrier supported within a circular glass trough. Compression into a sector of a circle of gradually decreasing area was by means of a mobile PTFE beam. The position of the beam responded to the surface pressure (tension) measured by a Wilhelmy plate attached to a linear voltage transducer. The subphase consisted of distilled and deionized water (mQ with resistivity of 18 MΩ cm). However, in some cases, the subphase also contained cadmium chloride (2.5×10^{-4} M). The spreading phase consisted of 25–50 μl of dye (1 mg ml^{-1}) in ARISTAR chloroform.

Surface area–pressure isotherms were obtained by compressing the monolayer (a Langmuir film) at a constant rate of 50 cm^2 min^{-1}. The stability of the compressed monolayer was assessed by monitoring the surface area as a function of time whilst maintaining a constant surface pressure: a stable film occupies a constant area at constant pressure.

Hydrophilic glass substrates (for LB film deposition) were prepared by cleaning with chromic acid [7] and washing with mQ water. Hydrophobic glass slides were prepared by washing the foregoing slides with HPLC-grade propan-2-ol using a Soxhlet apparatus, and then allowed to dry before treating with dichlorodimethyl silane. The efficiency of LB monolayer deposition was assessed by the ratio of the area of monolayer removed to the area of the immersed substrate (the 'transfer ratio'). Improvements in the transfer ratio were sought by optimizing the surface pressure and substrate and by the inclusion of cadmium chloride in the subphase when appropriate.
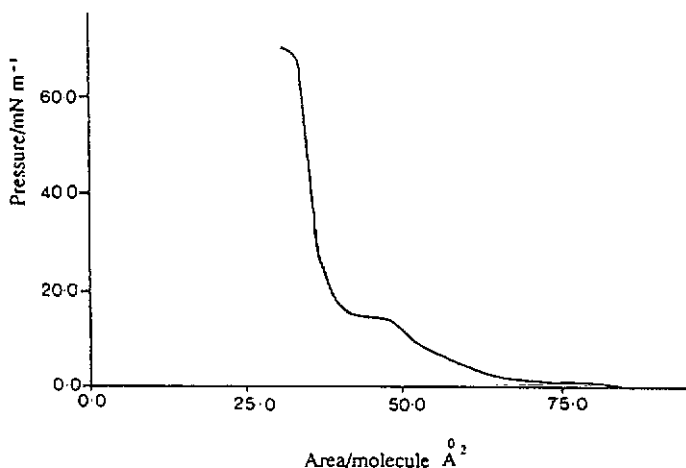

Figure 4. Isotherm of Langmuir monolayer of OSQ-MI (II).

3. Results

3.1. Langmuir monolayers

Molecule I gave poor isotherms indicative of the occurrence of stacking or aggregation. The inclusion of either 1,3,5-trimethylbenzene or stearic acid in the spreading phase did not give films of improved quality. These results suggest that a true Langmuir film was not obtained due, we suggest, to the poor hydrophilicity of the nitro-group [8]. We also suggest that the dual lack of a compact electron-accepting group, and of a distinctly hydrophilic region, caused the pronounced instability of compressed monolayers of III. Reproducible isotherms and a stable compressed film were observed for II under almost all of the conditions utilized (see table 1). An extended liquid phase was observed for a compressed film of pure II (see figure 4), which is consistent with reorientation of the dye molecules during the compression process. On an alkaline subphase, the monolayers of II were not stable, due, we assume, to interactions between iodide and hydroxyl ions leading to disruption of the film.

Both IVa and IVb gave stable compressed monolayers, although several initial compressions were needed before a reproducible isotherm was given by IVb. Once

Table 1. Characteristics of isotherm of II.

Subphase and pH	Molecular area ($Å^2$)	Collapse pressure (mN m^{-1})	Film stability and target pressure (mN m^{-1})	
Film OSQ-MI				
Water (pH 3.4)	34	70	Stable	18
Water (pH 5.1)	34	71	Stable	18
Water (pH 9.4)	35	70	Unstable	18
CdCl$_2$ (pH 5.5)	39	65	Stable	30
Film 1.1 Mixture of OSQ-MI with stearic acid				
CdCl$_2$ (pH 5.1)	21[a]	59	Stable	15
			Stable	30
Film 1:2 mixture of OSQ-MI with stearic acid				
CdCl$_2$ (pH 5.1)	24[a]	65	Stable	15

[a] Calculated for pure OSQ-MI contained in the mixture.

Table 2. Conditions for LB film deposition of OSQMI (II).

Substrate	Surface pressure (mN m^{-1})	Deposition speed (mm min^{-1})		% deposition and type
		Up	Down	
Film OSQ-MI				
Hydrophobic	30	10	5	Inconsistent
Hydrophilic	30	10	5	Inconsistent
Film 1:1 mixture of OSQ-MI with stearic acid				
Hydrophobic	15	10	5	< 10% X-type
Hydrophobic	30	10	5	< 10% X-type
Hydrophilic	30	10	5	Inconsistent[a]
Hydrophilic	30	10	—	Inconsistent[a,b]
Hydrophilic	30	10	5	> 76% Z-type[a]

Alternate layer LB film —Hydrophobic substrate Molecule and layer	Surface pressure (mN m^{-1})	Deposition speed (mm min^{-1})	% deposition
First			
Stearic acid	30	5	> 86%
Second			
1:1 mix OSQ-MI	30	10	< 56%

[a] Film appeared wetted.
[b] Z-type deposition was encouraged by compression of the film during the upstroke only. The film was relaxed during the downstroke.

assembled, the ordered monolayer of IVb gave a very rigid film because a high residual pressure was exhibited once the compression was relaxed.

Table 3. Conditions for LB film deposition of BDCBxI(IVa).

Substrate	Surface pressure (mN m^{-1})	Deposition speed (mm min^{-1})		% deposition and type
		Up	Down	
Film BDCB*I				
Hydrophobic	10	10	5	> 67% Z-type
Hydrophilic	10	10	5	> 47% Z-type
Film 1:1 mixture of BDCB*I with stearic acid				
Hydrophobic	7	5	5	0%
Hydrophobic	7	10	5	0%
Hydrophobic	12	10	5	∼ 88% Y-type
Hydrophilic	12	10	5	> 50% Z-type
Hydrophilic	18	10	5	> 90% Z-type[a,b]
Hydrophilic	12	10	5	100% Z-type[a]

Alternate layer LB film —Hydrophobic substrate Molecule and layer	Surface pressure (mN m^{-1})	Deposition speed (mm min^{-1})	% Deposition
First			
Stearic acid	40	5	> 94%
Second			
1:1 mix BDCB*I	12	10	< 34%

[a] Z-type deposition was encouraged by compression of the film during the upstroke only. The film was allowed to relax during the downstroke.
[b] Evidence for removal of the film during the downstroke.

3.2. Langmuir–Blodgett films

Only molecules II, IVa and IVb were studied in this context. For convenience, fresh aqueous solutions of 2.5×10^{-4} M cadmium chloride in mQ water were used as the subphase at 20 °C and pH 5.6 (due to dissolved carbon dioxide). Each class of molecule was applied to the subphase and partially compressed until the isotherm became reproducible. An area–time plot was recorded for 10 min prior to the immersion and withdrawal of the substrate through the film. When required, alternate-layer (AB) films were prepared by the use of two separate spreading phases (i.e. dye and stearic acid) and repetition of the sequence, 'spreading, compression and substrate removal'.

(i) 4-[2-(4'-octadecyloxy)styryl]-1-methylquinolinium iodide known as OSMQI,II. Table 2 summarizes the conditions used to examine the preparation of LB films of II. This quinolinium dye was found to deposit more efficiently on hydrophilic substrates, which is consistent with the observations noted by other workers for the closely related hemicyanine dyes [9]. It did prove possible to initiate the simple Z-type non-centrosymmetric deposition as itemized later.

The spreading phase consisted of a 1:1 mixture of II and stearic acid in chloroform. If the mixed Langmuir film was permitted to relax during the downstroke and therefore only compressed during the upstroke, a minimum-transfer ratio of 76% was observed during the upstroke. A uniform bilayer could be deposited in this way. However, attempts to produce further layers in Z-type deposition led to gradual dissolution of the film from the substrate due, perhaps, to the weak cohesive forces at the interlayer

Table 4. Conditions for LB film deposition of BDCFcI(IVa).

Substrate	Surface pressure (mN m^{-1})	Deposition speed (mm min^{-1})		% deposition and type
		Up	Down	
Film BDCFcI				
Hydrophobic	12	10	5	< 10% Y-type
Hydrophobic	30	10	5	< 10% Y-type
Hydrophilic	30	10	5	< 20% Y-type
Film 1:1 mixture of BDCFcI with stearic acid				
Hydrophobic	7	10	5	< 10% Y-type
Hydrophobic	12	10	5	< 10% Y-type
Hydrophobic	30	10	5	< 35% Y-type
Hydrophilic	30	10	5	> 88% Z-type[a]
Hydrophilic	30	10	5	> 70% Z-type[a,b]

Alternate layer LB film —*Hydrophobic substrate* Molecule and layer	Surface pressure (mN m^{-1})	Deposition speed (mm min^{-1})	% Deposition
First			
Stearic acid	40	5	> 88%
Second			
1:1 mix BDCFcI	30	10	> 70%

[a] Evidence for removal of the film during the downstroke.
[b] Z-type deposition was encouraged by maintaining the surface pressure during the upstroke only and by expanding the film during the downstroke.

contact that is a characteristic of Z-type films.

Attempts were made to circumvent this difficulty by preparing Y-type films in which the dye monolayer was spaced with a monolayer of stearic acid, giving the higher-stability Y-type films with conventional philic–philic and phobic–phobic contacts. It was possible to obtain a transfer ratio of 56% for a dye layer deposited on to a stearic acid layer. Efforts to produce extra layers on this bilayer again led to gradual dissolution of the film.

(ii) 1,3-bisdicyanovinyl-2-[(4-(S)-(+)-2-methylbutoxy)benzylidene]indane known as BDCB*I,IVa. Details of the deposition conditions for IVa are summarized in table 3. Using only IVa in the spreading phase, and keeping the Langmuir film under continuous compression, a 'partial' Z-type deposition was observed, with a minimum of 67% transfer on the downstroke, and less than 35% on the upstroke. However, when the spreading phase contained a 1:1 mixture of dye and stearic acid, a minimum of 88% transfer was observed, with the formation of a centrosymmetric, Y-type LB film.

In contrast, an almost 100% transfer ratio was observed in the formation of a Z-type film using the foregoing mixed-composition spreading phase, by successively compressing and relaxing the film during the upstroke and downstroke respectively. The film was allowed to dry between each stroke. In a study of the deposition of alternate layers, no more than 34% of dye was transferred on to a film of stearic acid.

(iii) 1,3-bisdicyanovinyl-2-(ferrocenylidene) indane known as BDCFcI,IVb. Details of the conditions used in the deposition of IVb are given in table 4. Z-type LB films of

a 1:1 mixture of IVb with stearic acid were obtained with greater than 88% deposition using a hydrophilic substrate. The film was allowed to dry between each stroke, and four molecular layers were deposited without difficulty.
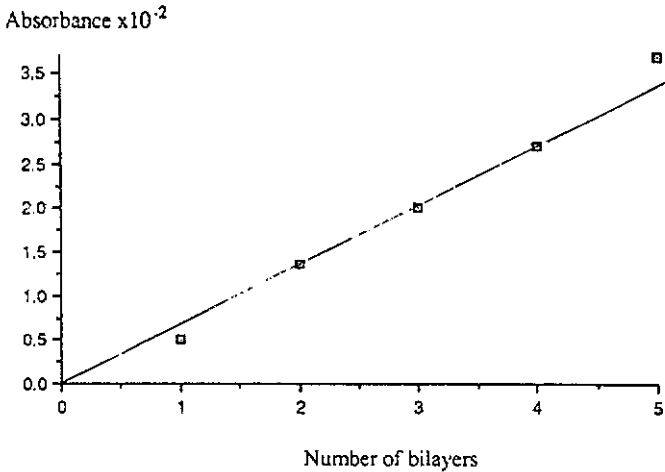
Absorbance x10^{-2}

Figure 5. Optical absorbance against number of LB bilayers for an AB film of BDCFcI (IVb) and stearic acid.
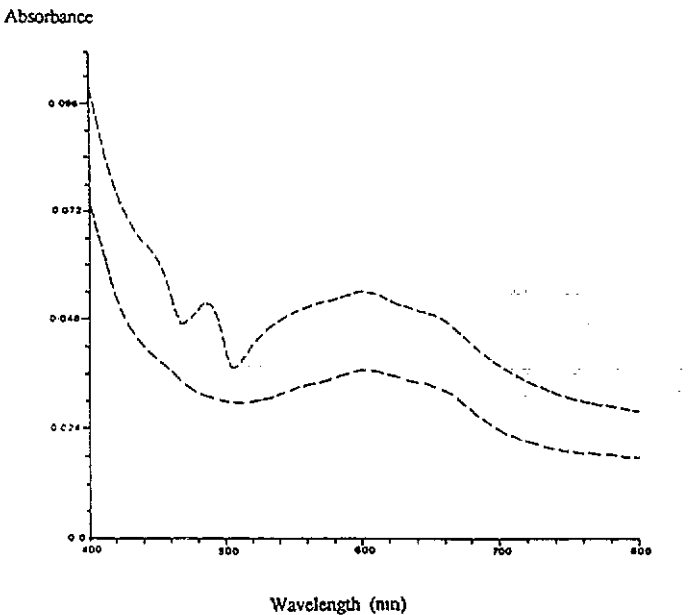
Absorbance

Wavelength (nm)

Figure 6. Polarization dependence of the optical absorbance of an AB film of BDCFcI (IVb) and stearic acid.

4. Conclusion

Only one of the dyes studied (i.e. IVb) showed the capacity for deposition as non-centrosymmetric films of acceptable quality. Films consisting of IVb are worthy

of further investigation, particularly with regards to obtaining multilayer ensembles thick enough for active wave-guiding and non-linear optical experiments.

The fabrication of a non-centrosymmetric Y-type film was achieved by spacing a monolayer consisting of a 1:1 mixture of dye and stearic acid with a monolayer of pure stearic acid. A minimum of 88% stearic acid was transferred onto the hydrophobic substrate on the first downstroke. The spreading phase of pure stearic acid was removed and replaced by a compressed layer of IVb + stearic acid, an upstroke through which gave a transfer ratio of at least 70%. Five such non-centrosymmetric bilayers were deposited in this way without difficulty to yield a non-patchy film of good quality, as substantiated by visible spectroscopy: the deposition was found to be uniform (figure 5), and the spectroscopic absorption intensity was polarization dependent (figure 6). This latter observation showed that there was a (desirable) degree of ordering within the film.

References

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