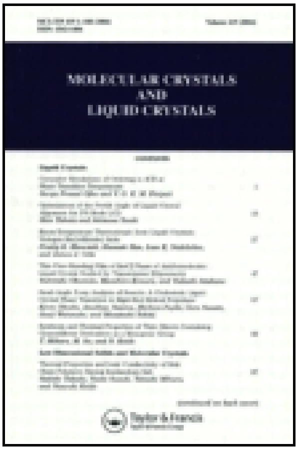

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THE ROLE OF PHOTOCHROMISM IN MOLECULAR ENGINEERING

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Introduction Photochromic materials are interesting components as functional groups in Molecular Engineering; they often involve a major reorganization of their electronic structure, which provide a number of useful mechanisms in the design of electronic or optical functions. Once integrated in a molecular system, their contribution is not limited to the original photochromism, i.e. change in absorption spectrum but, due to the interaction with the other molecules of the system, new properties can be generated allowing the performance of new functions for molecular design.

Photoisomerization in spiropyrans can be initiated by charge transfer. This can take place within a polymer structure with crosslinked polymers containing a spiropyran molecule in the link (Fig. 1), between spiropyran and oligomer molecules dispersed in a binder or between closed spaced Langmuir-Blodgett films.

Crosslinked Polymers The condition for intrinisic charge transfer is that there is conjugation between the donor part of the polymer and the spiropyran molecule. In that case charges can be generated by absorption of light in the spectral range of the polymer (donor) and be transferred to the spiropyran that will open providing the absorption band of the open form and a change of dichroism (i.e. elliptic to linear).

Fig. 2 shows the relative change in intensity of light transmitted through cross-polarizers (dichroism) as a function of infrared exposure in the absorption band of the polyacetylene in the structure of Fig. 1, [1].

Mixed Components Ring opening by charge transfer has been demonstrated on the spirooxazine shown on Fig. 3 using a sexithiophene with alkyl substitution as a donor (Fig. 4). The composition of the film was 5:1. Spiropyran 2.5 10^{-4}. Sexithiophene 5 10^{-5}.

The films were deposited by spin coating on a microscope slide. A spectral analysis (UV-visible) is represented on Fig. 5 where (1) corresponds to the spirooxazine alone and (2) the spirooxazine - sexithiophene mixture where the absorption band of the sexithiophene can be seen (λ_{max} = 480 nm).

Both films: spiropyran alone and the mixture spiropyran - thiophene were irradiated with a Xenon lamp using a filter blocking radiations under 400 nm. a) With the spiropyran alone no modification is observed. b) With the mixture spiro-thiophene, the absorption band (3) appears characteristic of the open form of the spiropyran.

Excitation with a 1 p sec. laser pulse at 1.06 μ has provided the response of Fig. 6, clearly indicating a ring opening by charge transfer from the thiophene moiety of the polymer. The measurement was made at 600 nm corresponding to the maximum of absorption of the open form of the spiropyran.

This behavior confirms the mechanism of ring opening by charge transfer initiated by absorption of light in the absorption band of the sexithiophene. These experiments were first conducted by Dr. Francis Garnier (CNRS - Thiais, France).

Langmuir Blodgett Films The Langmuir Blodgett film deposition technique provides two methods for arranging two different types of molecules in a thin film. One results in the layerwise heterogeneous structure, where each monomolecular layer contains molecules of both kinds, while the second method results in the alternate layer heterogenous structure, with alternate monomolecular layers composed of the same material. Figure 7 shows the expected configurations in the macroscopic structure. In all cases, it can be observed that the spiropyran chromophores are in close proximity to the polymer donor. In LB films, charge transfer can take place by physical means, through a configuration where the polymer and spiropyran molecules are in close proximity to each other.

For the purpose of investigating intermolecular charge transfer, the film assembly will contain alternate layers of polymer and spiropyran. This arrangement increases the probability of acceptor-donor interaction by sandwiching each donor layer with two acceptor layers and vice versa.

Spiropyran Diacetylene Films The diacetylene 4BCMU (Fig. 8) was used as a donor with the spiropyran represented on Fig. 9. The diacetylene and spiropyran mixed together in chloroform in a molecular ratio of 1:1 were spread on an aqueous subphase containing 9.09 x 10^{-4} M cadmium chloride. The diacetylene was polymerized by exposure to UV radiation for 30 minutes. The polymerized Langmuir layer was transferred to hydrophobically treated glass substrates with good deposition ratios. Investigation of different experimental variables indicated that the best diacetylene-spiropyran LB films were obtained when the Langmuir layer is compressed slowly, at a rate of about 20 sq. cm/min and is exposed to UV radiation for long periods, and when deposition is conducted at temperatures below 20°C.

Ring opening was investigated by ellipsometry using the dichroic properties of the closed form and the change in index of refraction resulting from the isomeric transformation. Fig. 10 shows the variation of the indices at 632.8 nm as a function of infrared irradiaton in the absorption band of the diacetylene.

In position 1, the substrate was positioned in the ellipsometer such that the direction of dipping is parallel to the plane of incidence, and in position 2 the direction of dipping was oriented perpendicular to the plane of incidence.

Spiropyran - Thiophene Films While the oligomer sexithiophene is known to deposit in an ordered fashion on a substrate, it does not dissolve in organic solvents. This precludes casting films by the Langmuir-Blodgett method. The hexylthiophene oligomer dissolves in organic solvents because of the presence of the hexylchain, and thus is better suited for LB deposition. A polymerized version of the hexylthiophene was also used as the donor molecule. In effect, this is a three-dimensional organic crystal. Hetero-structures can be constructed by preparing two monolayers comprising different materials on two different water surfaces, and then cycling a substrate through the two interfaces.

To facilitate formation of a uniform Langmuir (pre-deposition) film at the air-water interface, the thiophenes and spiropyran were prepared as mixtures in eicosanoic acid with molecular ratios of about 1:1. Eicosanoic acid forms well-ordered Langmuir-Blodgett layers. Microscope glass slides made hydrophobic by treatment with octadecyltrichlorosilane were used as substrates. Films of thiophene-eicosanoic acid and spiropyran-eicosanoic acid were assembled by using the one-molecule configuration of the trough. Also, alternating layers of the thiophene and spiropyran were assembled by using the two-molecule configuration. About 24 monomolecular layers of each material were assembled on substrates, with deposition conducted at a surface pressure of 20 mN/m and speed of 10 mm/min.

Evidence of charge transfer was obtained by observing the shift in the absorption band of the spiropyran as it converts itself to the open form from the closed form. This change can also be monitored as before by observing the change in refractive index of the film.

To ensure that the visible light (514 nm) used to excite the thiophene does not affect the spiropyran, an LB film containing the indoline spiropyran in eicosanoic acid matrix was exposed to visible light while the refractive index of the film was measured by ellipsometry. No significant change in the index was observed. The process was repeated by exposing a Langmuir-Blodgett film of polyhexylthiophene to blue light. Again, no change in index was observed.

When alternate layers containing spiropyran and thiophene were exposed to visible light, a change in refractive index was observed. When the visible light was turned off, the index gradually changed to its original value. The change in index was reproducible with successive cycles of exposure to blue light. Figure 11 shows the change in index with time as a function of exposure to blue light. The light source emitted radiation with an intensity of 7.8 mW/sq. cm. measured at the sample. Figure 12 shows the change over three cycles. The reversal of refractive index in the absence of excitation suggests that the open form of the spiropyran now becomes a donor and the thiophene the acceptor. The charge transfer is reversed and the spiropyran would return to its closed form.

Conclusion Molecular engineering is a fast growing interdisciplinary area of research in Materials Science. The concept of interacting different parts of molecules to perform specific functions has been inspired from integrated circuits in electronics. Photochromic materials because of their multi-facets can become useful building elements in molecular engineering. In building macromolecules containing photochromic entities new devices and processes are becoming possible and will contribute largely to this new science. Infrared detection and imaging as well as optical switching are early examples of such devices [2].

References

[1] J. Robillard, U.S. Patent No. 5,098,806.
[2] H. Kuhn and J. Robillard. Non Linear Optical Materials. CRC Press. Boca Raton, Florida (1992).

Acknowledgement We are grateful to Dr. Francis Garnier of the CNRS in Thiais, France for useful discussion and communication of his early results on ring opening by charge transfer. We thank Prof. Guglielmetti for the preparation of spiropyrans used in our experiments. We also thank Professor Cabanese from the University of Texas at El Paso and Dr. Jorge Buenostro of New Mexico State University for the synthesis and polymerization of the polydiacetylene samples.

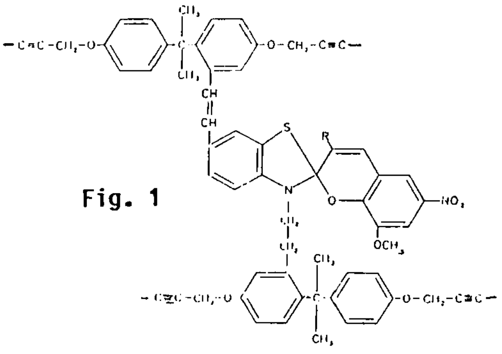
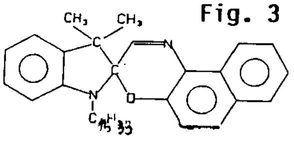


Fig. 1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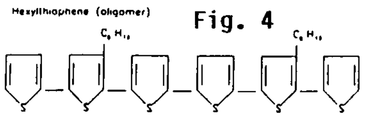
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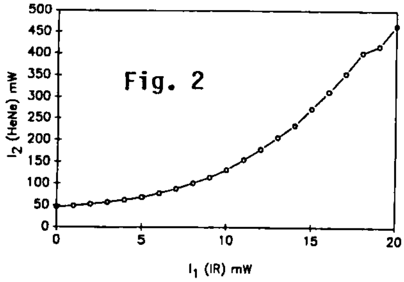
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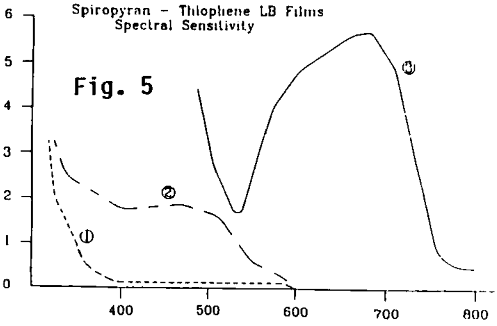
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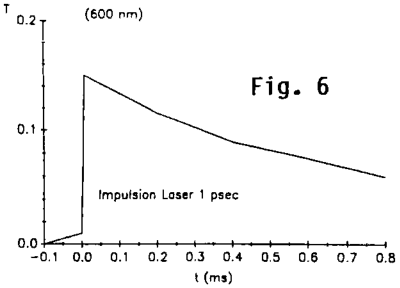
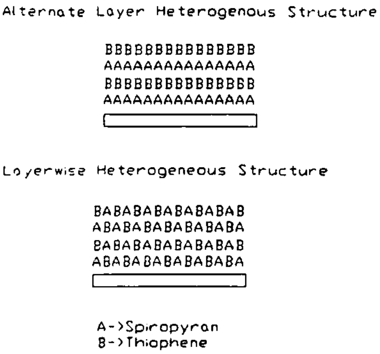


Fig. 6



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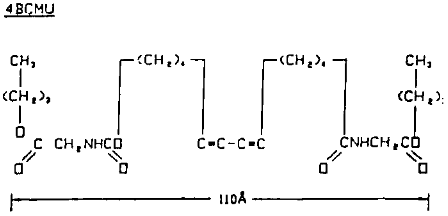

Fig. 8

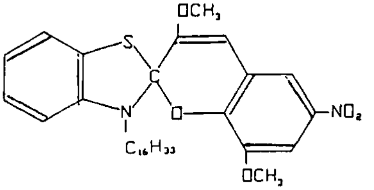

Fig. 9

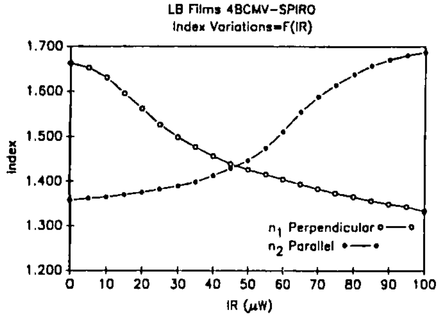

Fig. 10

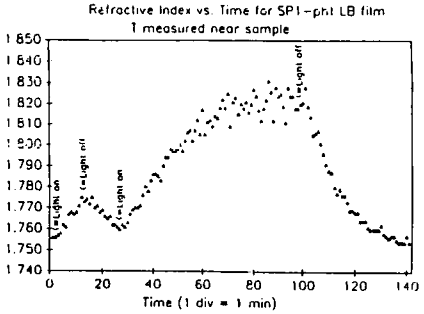

Fig. 11

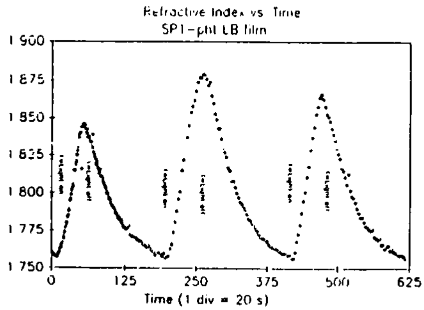

Fig. 12