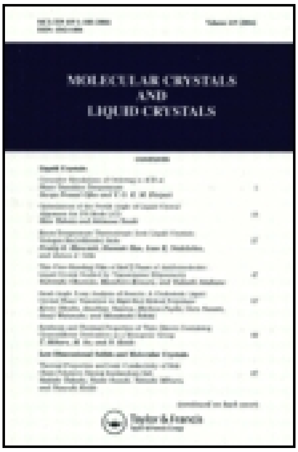

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Photophysical and Transport Properties of a Novel Soluble Conjugated Polymer Based on Zn-Porphyrin Units Edge-Linked by Acetylenic Spacers

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PHOTOPHYSICAL AND TRANSPORT PROPERTIES OF A NOVEL SOLUBLE CONJUGATED POLYMER BASED ON Zn-PORPHYRIN UNITS EDGE-LINKED BY ACETYLENIC SPACERS

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Abstract We present preliminary results on various transport and photophysical properties of a novel soluble conjugated polymer based on Zn-porphyrin units edge-linked by acetylenic spacers. The basic optical transitions of the porphyrin unit are retained in the polymer and the lowest-lying absorption is strongly red-shifted, indicating substantial extended conjugation in the system. $\chi^{(3)}(-\omega;0,0,\omega)$, as assessed from electroabsorption measurements, is very large. Charged and neutral excited states are investigated by doping studies, photoluminescence, photoinduced absorption, and spectroscopy of electric field-injected charges in metal-insulator-semiconductor devices. Field-effect transistors with the porphyrin polymer as the active semiconductor are used to investigate the conductivity and mobility of charge carriers and the influence of oxygen and solvents on the transport properties.

INTRODUCTION

Porphyrin-based molecules and derivatives have been extensively studied over many years, mainly in order to understand their functionality in biological/biochemical processes; hemoglobin, myoglobin, chlorophyll, vitamin B_{12}, to name but a few, all contain a porphyrin unit in their molecular structure. The porphyrin-unit is usually involved in the light-harvesting and charge generation process and, as in the case of hemoglobin, the central metal atom is responsible for complexation to other moieties, such as oxygen.[1]

The extended π-electron system, low-lying electronic transitions, and the stability of porphyrins and phthalocyanines, a related class of molecules, also bring about other very interesting material science aspects. The molecules have been widely investigated for artificial photosynthesis and photovoltaic applications. Also, extended conjugated systems tend to have a large and very fast non-linear optical response. For this reason, porphyrin- and phthalocyanine-based molecules have been investigated for their non-linear optical properties, see [2] and references therein.

We have recently started to investigate the non-linear optical response of a novel, soluble, stable and fully conjugated polymer containing Zn-porphyrin units in the backbone, bridged by acetylenic links. The non-linear optical response of this material is very large; [2,3] in order to understand and exploit this phenomenon, we have also been looking at other photophysical and transport properties, as well as short-chain analogues of this polymer. We present here a preliminary account of this work.

EXPERIMENTAL

The porphyrin polymer investigated here is shown in figure 1; details of the chemical synthesis are published elsewhere.[3,4] The degree of polymerisation is rather low ($n < 20$). The polymer is readily soluble in chloroform containing pyridine, which acts as a ligand and co-ordinates to the Zn atom; therefore, films of the polymer may contain some pyridine if they are not annealed (see below). Spin-coating gives uniform, homogeneous films. The polymer can be easily blended with poly(methyl-methacrylate), PMMA, which was also used as a matrix studies on the monomer and dimer, $n = 1$ and 2, respectively (see figure 1).

Further experimental details and parameters are given below where necessary; more specialised experimental techniques were employed as described in the literature (electroabsorption/Stark spectroscopy[2,5], electrical characterisation and spectroscopy in metal-insulator-semiconductor, MIS, devices[6-8], field-effect transistors[6]).

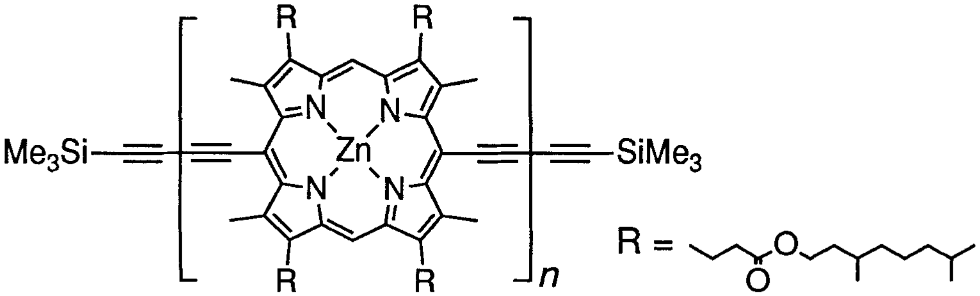

FIGURE 1: Chemical structure of the porphyrin polymer.

RESULTS AND DISCUSSION

Optical Absorption

Figure 2 shows the optical absorption of the porphyrin monomer, dimer and polymer in solution and the polymer film (undoped and iodine-doped). There is a very pronounced red-shift of the lowest lying optical transition with a concomitant increase in oscillator strength on going from the monomer to the polymer. Exciton-coupling between the porphyrin units and polarisation effects do not seem to be sufficient to account for this pronounced red-shift, which suggests that extended delocalisation of the π-electron system through the porphyrin units and the acetylenic links occurs;[4] consequently we assume that the individual polymer chains are linear and highly ordered along the chain. The spectra also show that the principal features of the molecular transitions, including the narrowness of the absorption bands, are preserved in the polymer. Details of the large red-shift and, in particular, the large increase of oscillator strength in the lowest-lying transition are currently under investigation.

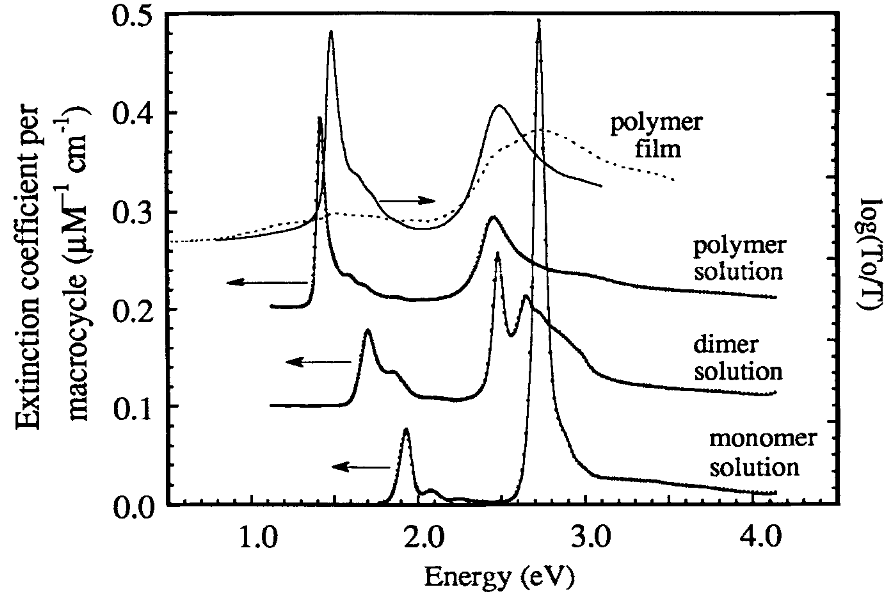

FIGURE 2: UV-VIS-NIR absorption spectra of the monomer, dimer and polymer in chloroform/pyridine solution and the polymer film (undoped - full line, doped - dotted line) on glass, all at room temperature. The film spectra are measured as $\log(T_0/T)$; T_0 and T are transmissions through the substrate without and with the polymer film, respectively. Reflection is not corrected. All spectra are displaced for clarity in the diagram (the dimer and polymer spectra are shown with an offset of 0.1 and 0.2 $\mu M^{-1}cm^{-1}$ absorbance units respectively, with respect to the monomer). The solution spectra are normalised to obtain the absorbance per porphyrin ring. The undoped polymer film has an absorbance of 1.3 at the peak at ≈ 1.5 eV. The doped polymer spectrum was obtained after 32 minutes exposure of the sample to saturated iodine atmosphere at room temperature.

Exposure of the polymer films to iodine vapour results in bleaching of the optical transitions and the emergence of a broad band peaking at ca. 1.2 eV and one at ca. 2.7 eV. The bleaching is particularly strong for the low-lying absorption at ≈1.5 eV. Another weak doping-induced band appears below 0.5 eV (not shown). Monitoring the spectra during increased doping indicates the presence of two isosbectic points (at about 1.95 and 2.6 eV), though they are not very well defined. More detailed studies and interpretations of the optical spectra are presented elsewhere.[2-4]

Electroabsorption/Stark Spectroscopy: Non-Linear Optics

In figure 3 we show the measured electroabsorption spectrum in the region of the lowest-lying optical transition. This spectrum is related to the electric field-induced (Stark) shift of the molecular transitions, which relates to the $\chi^{(3)}(-\omega;0,0,\omega)$ non-linear optical susceptibility and the non-linear refractive index $n_2(I)$. $\chi^{(3)}(-\omega;0,0,\omega)$ is calculated from the electroabsorption spectrum and the complex dielectric function[2,5].

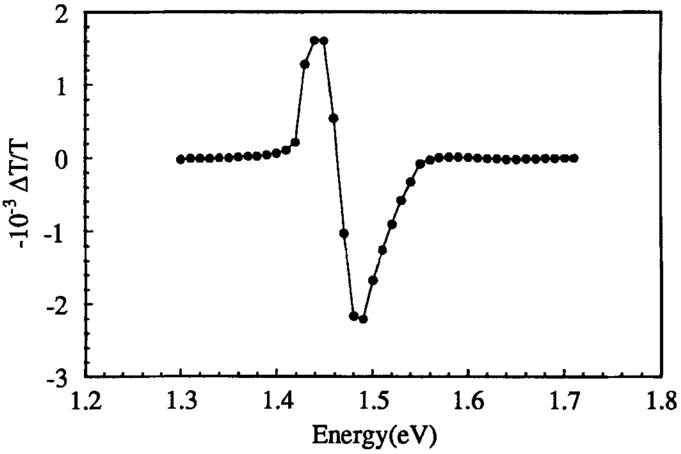

FIGURE 3: Measured electroabsorption spectrum of a porphyrin polymer film. The electroabsoption spectrum was taken at 77 K and 35 kV/cm applied electric field at 5 kHz.

$\chi^{(3)}(-\omega;0,0,\omega)$ of this porphyrin polymer, calculated from figure 3, is very large, regardless of the fact that it is in resonance. The peak value of ca. 7×10^{-8} esu is appreciably larger than that for other conjugated polymers[2] and this is of considerable interest for applications in non-linear optics (e.g. optical switches), see [2] and references therein. Note also that the strong response is in the near infrared close to the 1 μm region relevant to telecommunication applications.

The increased extent of conjugation on going from the monomer to the polymer (see figure 2) is also reflected in the non-linear response; the response in the electroabsorption measurements increases by a factor of ca. 30 from the monomer to the dimer and by another 20 from the dimer to the polymer (all measurements in PMMA matrix).[2,3]

Photoinduced Absorption and Spectroscopy of Electric Field-Induced Charged States

Charge separation and subsequent non-uniform charge distributions may act to establish electric fields within materials and such fields, as we showed above, lead to non-linear optical processes. It is therefore necessary to establish the level diagram of charged - as well as neutral - ground and excited states and their dynamic behaviour.

Figure 4 shows spectra of induced absorptions due to charged states and the applied electric field in a metal-insulator-semiconductor, MIS, device in which a thin film of the porphyrin polymer acts as the semiconductor. It has been shown that this is a powerful technique to investigate charged excited states in conjugated polymers.[7-9]

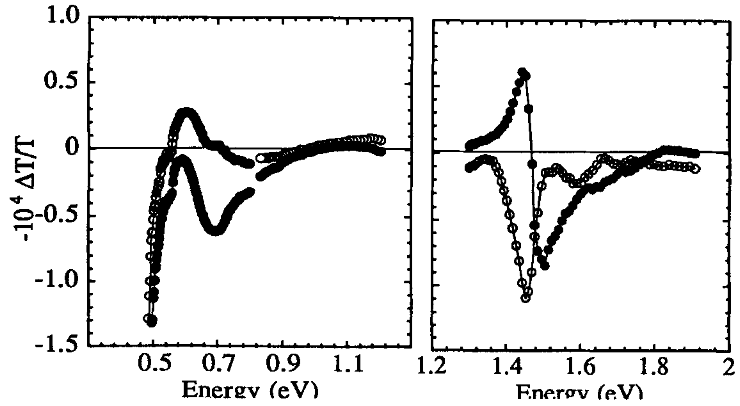

FIGURE 4: Modulated transmission of a semi-transparent MIS device. Room temperature, 0 V bias voltage, 2 V peak-to-peak AC modulation at 127 Hz. The two spectra show the in-phase and quadrature response of the two-phase lock-in amplifier and both signals are not yet fully phase-analysed. Device structure: glass substrate coated with indium-tin-oxide, ITO, as top-electrode - spin-coated polymer - ca. 1000 Å of evaporated SiO as insulator - evaporated semi-transparent gold as gate-electrode.

The spectra in figures 4 show the two signals from our two-phase lock-in measurement (not yet fully phase-analysed). The derivative response in the region from ca. 1.3 to 1.8 eV (full circles) is fast and likely due to electroabsorption (see figure 3); the other component (open circles) shows a slow response and is presumably due to bleaching of the π-π^* states; In the low-energy region we observe a double-peak feature at 0.65 and 0.71 eV; the response of the peak at 0.65 eV is slow and that of the 0.71 eV fast. We note that these two low-energy features are shown as measured and that we are not yet able to assign them definitely to either induced absorptions or bleaching. Slow response in the figures 4 (open circles) corresponds to a lifetime in the range of ms; the fast response (full circles) is instantaneous with respect to the modulation frequency up to several kHz.

Figure 5 shows a typical spectrum of photoinduced absorption of a film of the porphyrin polymer. The spectrum shows induced absorptions at ca. 1.2 eV and a broad band peaking at ca. 1.4 eV, as well as a strong negative signal (bleaching) peaking at 1.47 eV and another at ca. 1.65 eV. We note that we have also observed (not shown here) a weak double-peak photoinduced absorption at low energies (below ca. 0.8 eV, i.e. in close agreement with the low-energy features shown in figure 4). All features in the photoinduced absorption spectrum have similar temperature and frequency dependencies. The transitions can be observed up to ca. 250 K and the lifetime is high (the signals are still increasing at chop frequencies as low as 10 Hz), which indicates lifetimes of the order of several ms.

There are various possible assignments to the observed peaks in photoinduced absorption and the electromodulation of the MIS device. First, we point out that we have looked for signs of photoluminescence, both long- and short-lived, in the polymer films; although our results are preliminary, we have not been able to detect any luminescence. Fluorescence, phosphorescence and even fluorescence from higher excited singlet states have been observed in porphyrin-based compounds.[1,10] Porphyrin-based compounds tend to aggregate[4], and such aggregation as well as the presence of side-chains may act to quench luminescence. The photoinduced absorption experiments showed only signals with very long lifetimes and these were readily detectable up to elevated temperatures. We suggest that this excludes photoinduced absorption due to triplet-triplet transitions as assignment for the peaks in figure 5; note that we have not observed phosphorescence.

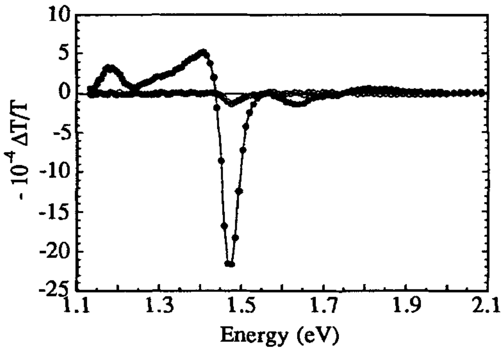

FIGURE 5: Photoinduced absorption of a porphyrin polymer film. Spectra taken at 50 K, 67 Hz, ca. 50 mW/cm^2 excitation intensity at 2.7 eV. The two curves show the in-phase (full circles) and quadrature (open circles) response of the two-phase lock-in amplifier.

Thus, it seems most likely that the observed transitions are due to photoinduced charge separation and the concomitant presence of internal electric fields; this causes transitions arising from charges residing on the polymer chains: The doping-induced broad band in the region from ca. 1 to 1.5 eV in figure 2 coincides with the positive features in photoinduced absorption (figure 5); the response in the MIS device in this spectral range is under closer investigation. The same MIS spectrum shows peaks below ca. 0.8 eV which are due to charged states by nature of the experiment, and for which we have also some evidence in photoinduced absorption (not shown here). The long-lived separated charges build up an internal electrical field which gives rise to the electroabsorption-like features around 1.5 eV in the figures 2-5; such processes are known for conjugated polymers, see [11] and references therein. Obviously, there must be some component in the negative feature around 1.5 eV in photoinduced absorption which arises from bleaching of the low-lying π-π^* transition. The pronounced photorefractive effect may be of some interest. In support of this interpretation, there is clear evidence for photoconductivity, i.e. photoinduced charge separation, as we show below.

It is clear from the figures presented above that the correspondence of the various peaks in different experiments is not entirely unambiguous. Photoluminescence and photoinduced absorption experiments of the monomer, dimer and the polymer in solution and in films in PMMA are in progress, in order to obtain a definite assignment of the discussed optical transitions.

Transport properties

Figure 6 shows qualitatively some effects of the ambient conditions on the conductivity of a porphyrin polymer film. Clearly, the conductivity is strongly influenced by the presence of air (moisture and/or oxygen) and solvent. Photoconductivity is readily observed, albeit small.

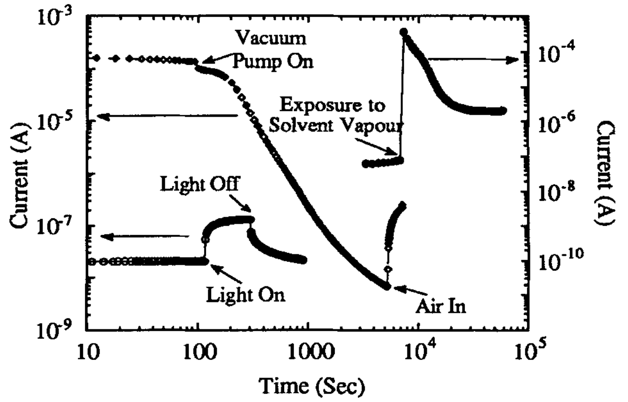

FIGURE 6: Current versus time at constant voltage (field strength 40 kV/cm) in order to qualitatively show the influence of air, solvent and light on the conductivity of the porphyrin polymer.

In addition to these effects, we noticed the presence of mobile charged species - even in films annealed in vacuum - through hysteresis in the capacitance versus voltage characteristics in MIS devices (not shown here), see for example[12]. This strong hysteresis prevented us from obtaining a reliable value for the charge carrier concentration in the porphyrin polymer. The nature of these mobile dopants is not yet identified.

The temperature dependent conductivity does not fit common transport models over a reasonably large temperature range. Limited fits to Arrhenius-type behaviour at temperatures from ca. 50 to 150°C give values of ca. 0.4 eV for the activation energy; this is well below half the energy-gap and indicates the presence of deep trap states, possibly associated with the mobile dopants which we observed in the MIS devices and which could not be fully removed by annealing.

Finally, figure 7 shows the behaviour of the porphyrin polymer as the active semiconductor in a metal-insulator-semiconductor field effect transistor, MISFET (details of the device fabrication as indicated in the figure caption). These measurements show very clearly that the polymer behaves as a p-type semiconductor. The mobility, however, is rather low; the analysis of the MISFET characteristics gives mobilities of ca. 1×10^{-7} cm^2/Vs at room temperature and ca. 2×10^{-6} cm^2/Vs at 175°C; these values are lower limits due to the presence of mobile dopants which compensate the applied gate voltage to some extent.

We associate the low mobility with the presence of the long side-chains[13] and note that we are presently attempting to modify the chemical synthesis of the porphyrin polymer in a way to be able to remove the side chains.

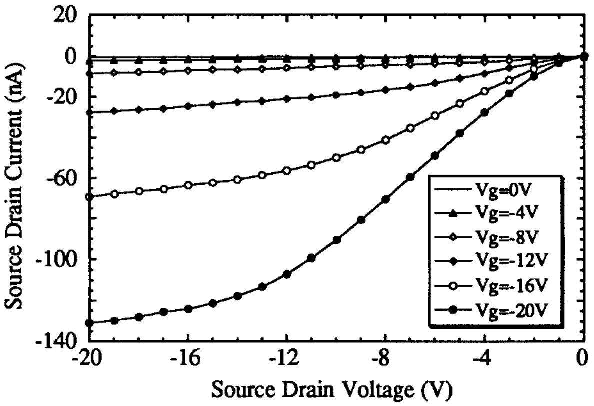

FIGURE 7: Field effect characteristics of the porphyrin polymer in a MISFET transistor. Gate - highly doped silicon, insulator - 1500 Å thermally grown SiO_2, source/drain separation - 5 μm, source/drain electrode width - 90 cm, polymer thickness - ca. 500-600 Å. Measurements in vacuum at room temperature after ca. 5 hours annealing in high vacuum at ca. 170°C.

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