

Push–pull dithiole – fluorene acceptors as electron transport materials for holography

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Abstract

A comparative investigation of photoconductivity sensitisation of poly-N-(2,3-epoxypropyl)carbazole (PEPK) by push-pull acceptors of the fluorene series shows that intramolecular charge transfer (ICT) in these acceptors leads to a significant increase in the electrophotographic response. However, high stability of the radical anion of the acceptor is also a necessary requirement: lack of this stability for compounds 3 results in a poor response for these materials, in spite of their intense ICT bands.

Keywords: photoconductivity, semiconducting films, conjugated or conducting polymers, amorphous thin films, opto-electronic devices

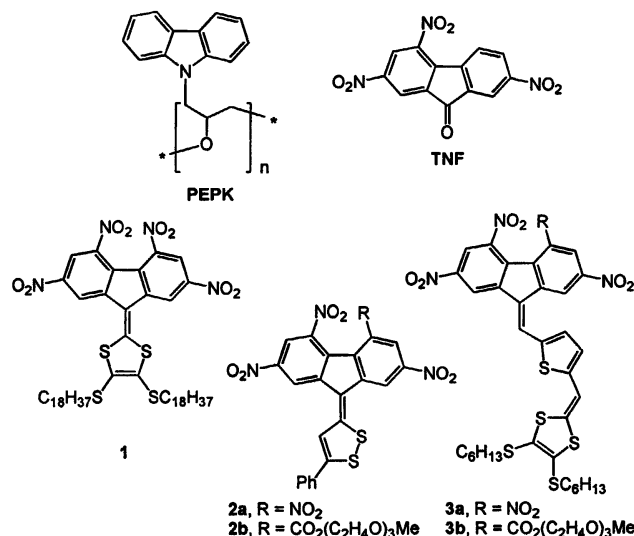
1. Introduction

Electron acceptors of the fluorene series with intramolecular charge transfer (ICT) have been recognised for the last decade as promising candidates for photoconductive materials [1,2], particularly as sensitisers of photothermoplastic storage media (PTSM), which can be used for hologram recording on a real-time scale. The PTSM in which they are used exhibit a substantial increase in the photoresponse in the ICT optical region of the acceptor and, thereby, their spectral response can be tuned. The best results have been obtained with the 1,3-dithiole heterocycle as the donor moiety: 1.5 μm films of PEPK doped with acceptor 1 display extremely high holographic sensitivity [3]. Herein we describe our investigation of the effect of the structure of the dithiole moiety and the conjugated bridge in D- π -A molecules on the photoconductive properties of PTSM.

2. Results and discussions

ICT transitions from the donor dithiole fragment onto the acceptor fluorene moiety in compounds 1–3 are manifested by two intense long-wavelength absorption bands in the region of 400 to 900 nm (Fig. 1). The change in the heteroatom position in the dithiole ring from 1,3 (1) to 1,2 (2) results in a red shift of both ICT bands and a

substantial increase in the intensity of the lowest energy band. A more pronounced effect was found when a thiophene ring was incorporated into the conjugation pathway (3): for the lowest absorption band the red shift $\Delta\lambda = 110$ nm.



The redox properties of compounds 1–3 were studied by cyclic voltammetry (CV). Compounds 1 and 2 display three reversible single electron reduction waves, yielding subsequently the radical anion, dianion and radical trianion.

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Reduction of compounds **3** possessing a hydrogen atom at the fluorene exocyclic double bond is electrochemically irreversible. Electron affinities estimated from their first reduction waves [2.14 eV (**1**), 2.13 eV (**2a**) and 1.98 eV (**2b**)] characterise them as moderate acceptors which are able to form semiconductive complexes with π -electron donors and, therefore, to sensitise the photoconductivity of PEPK and related hole transport polymers.

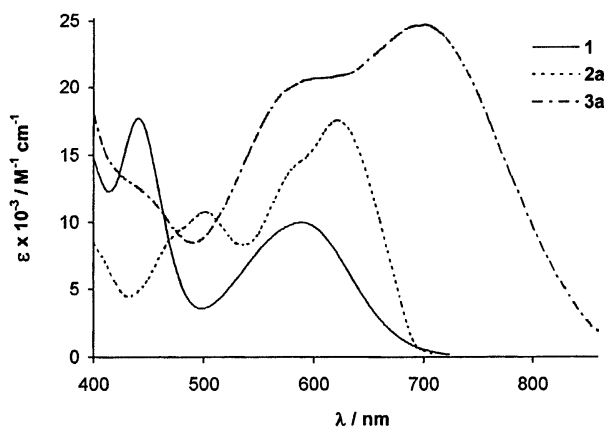


Figure 1. Electronic spectra of compounds **1–3** in CH_2Cl_2 .

A solubility problem which was encountered with tetranitro derivatives **2a** and **3a** was solved by introduction of a long-chain alkoxy carbonyl substituent (**b**) into the fluorene ring and acceptors **2b** and **3b** were tested as sensitizers of PEPK (Fig. 2).

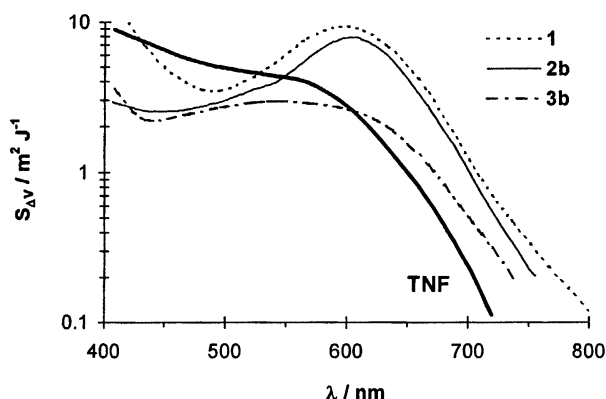


Figure 2. Spectral response of S_{AV} for PEPK films sensitised by electron acceptors **1** (5 w%), **2b** (1 w%), **3b** (2 w%) and TNF (5 w%).

In accordance with the observed spectral change from 1,3-dithiole **1** to 1,2-dithiole **2**, the response maximum of the PTSM with acceptor **2b** is slightly red-shifted compared to **1**, in spite of a reduction in the electron affinity and blue shift of the ICT band, observed with transition from compounds (**a**) to (**b**). This clearly indicates a high potential of 1,2-dithiole derivatives for PTSM. In contrast, PTSM doped with the thiophene-bridged acceptor **3b** showed a rather poor response, although some increase in S_{AV} is still observed in the ICT region. We explain this by

the electrochemical irreversibility of radical anion formation, and by the low photochemical stability of this compound. PTSM with acceptors **1** and **2b** showed excellent rheological characteristics allowing the attainment of diffraction efficiencies $\eta = 20\text{--}27\%$ for planar light wave holograms ($\lambda = 632.9\text{ nm}$, He–Ne laser), so the real response estimated by a visualised image was $S_{\eta} = 100\text{--}300\text{ m}^{-1}\text{ J}^{-1}$ (at $\eta = 1\%$).

In conclusion, investigating the effect of the donor moiety on the ICT in fluorene acceptors, we found a new highly efficient sensitizer of PEPK photoconductivity, namely compound **2b**, and showed that 1,2-dithiole derivatives are promising candidates for the design of new optoelectronic materials.

3. Experimental

Compounds **1** [3], **2a,b** [4] were prepared as described earlier. Compounds **3a,b** were obtained from the corresponding fluorenes and the 5-substituted thiophene-2-carbaldehyde under the same conditions as for **1** and **2** and characterised by ^1H NMR, MS, and elemental analyses (details will be reported elsewhere).

Photoconductive films of PEPK and a corresponding amount of the acceptor (**1–3** or TNF) were drop-deposited from toluene solution onto an ITO-coated glass base (the final thickness was $1.5 \pm 0.1\ \mu\text{m}$). The surface of the film was charged in the dark by positive corona discharge grid ($100\text{--}120\text{ V}\ \mu\text{m}^{-1}$). Dark decay for 30 s was found to be 10–15 % of the initial potential. The electrophotographic response was estimated at the level of 20% decay of the initial potential under illumination at 400–900 nm.

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