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# π-Extended nitrofluorene-1,3-dithiole chromophore: enhancing the photoresponse of holographic materials through the balance of intramolecular charge transfer and electron affinity

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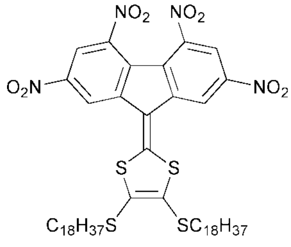
**The synthesis, electrochemistry, and electron absorption spectra of the novel push–pull type acceptor, 9-{[4,5-bis(hexylthio)-1,3-dithiol-2-ylidene]ethylidene}-2,4,5,7-tetranitrofluorene 3 is reported. A bathochromic shift and increased intensities of intramolecular charge transfer bands (compared to 1) are well-balanced with the electron affinity of the acceptor, which results in a pronounced increase of the photoresponse of carbazole-containing photothermoplastic optical information storage materials in the long wavelength visible and near infrared regions.**

Non-conjugated carbazole-containing polymers, *e.g.* poly-*N*-vinylcarbazole (**PVK**) and poly-*N*-(2,3-epoxypropyl)carbazole (**PEPK**) are gaining attention as hole transport materials for optical information storage,[1] photorefractive composites,[2] photovoltaic[3] and electroluminescent devices.[4] Among many compounds which are able to sensitise the photoconductivity of these polymers in the visible region of the spectrum, fluorene acceptors are the most promising, and photothermoplastic storage media elaborated on this basis can be used for hologram recording,[5] particularly in holographic interferometry (HI[6]), a very powerful method of non-destructive control of a wide range of processes and materials in real-time scale.[7]

The presence of both electron donating 1,3-dithiole and electron accepting nitrofluorene moieties in 9-(1,3-dithiol-2-ylidene)polynitrofluorenes (*e.g.* **1**[8]) results in strong intramolecular charge transfer (ICT) in these compounds, the energy of which depends substantially on the substituents in both fluorene and dithiole moieties and lies in the range of 2.53–2.03 eV ($\lambda_{\mathrm{ICT}} = 490$–$610$ nm).[8,9] In spite of the presence of the donor unit, compound **1** possesses a significant electron affinity ($\approx 2.1$ eV) and is able to form charge transfer complexes with electron donors and, hence, to increase the photoresponse of carbazole-containing polymeric photoconductors. One of the peculiarities in the mechanism of **PEPK** sensitisation by this push–pull type of acceptors is an initial triplet state of the photogenerated electron–hole pair, whereas for conventional fluorene acceptors like 2,4,7-trinitro-9-fluorenone (**TNF**) it is a singlet.[10] A marked increase in the photoconductivity was observed in the ICT region of such push–pull fluorene acceptors, which lies around 600 nm allowing the design of extremely efficient materials for hologram recording {with a He–Ne laser ($\lambda = 632.9$ nm) as the source, the holographic response of $S_{\eta=1\%} = 100$–$300\ \mathrm{m^2\ J^{-1}}$ and the maximal diffraction efficiency of plane wave holograms of $\eta_{\max} = 15$–$25\%$ were achieved}.[8,11,12] Tuning the ICT energies in backbone 9-(1,3-dithiol-2-ylidene)-polynitrofluorene fragments of polythiophenes has also been suggested as an approach to control the bandgap of the polymer.[13]

Recently we demonstrated that increasing the length of the bridge between the donor and the acceptor units in compounds of type **1** lowers the ICT energy (bathochromic shift of $\lambda_{\mathrm{ICT}}$) and increases the intensity of this band.[8,11] This effect should be reflected in the electrophotographic response of the materials based on such acceptors, resulting in a red shift of the photoresponse maximum.[14] However, tuning the photoconductive properties of the materials requires precise control



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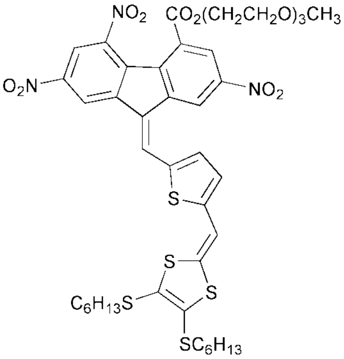

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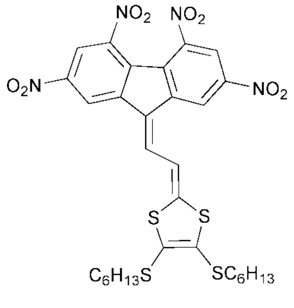

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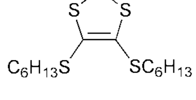

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of several parameters such as the electron affinity of the acceptor (which, generally, decreases as ICT becomes stronger), the planarity and topology of π–π donor–acceptor overlap, stability of the excited state of CTC, $(D^{+\bullet}\cdots A^{-\bullet})^*$, and solubility and chemical/thermal stability of the acceptor.

Thus, we recently reported[11] the thiophene-bridged compound **2**, which showed a bathochromic shift in $\lambda_{ICT}$ of 100 nm and 2.5-fold increase in the molar extinction coefficient (from 10000 to 25000 $M^{-1}\,cm^{-1}$) compared to **1**. However, this structural change resulted in a decrease of the electron affinity, irreversibility of its radical anion formation in cyclic voltammetry (CV) experiments and, as a result, the photoresponse of the materials based on acceptor **2** was lower than that for **1**. Moreover, the stability of the acceptor **2** also decreased which substantially reduced the cycling ability of the materials in HI applications.

Herein we report chromophore **3**, a new, stable π-extended analogue of the efficient sensitiser **1**. We demonstrate changes in the electrochemical and spectral behaviour of the molecule due to this π-extension which significantly improve its ability to sensitise the photoconductivity of polymeric carbazole-based hole-transport materials.

Compound **3** was prepared by condensation of aldehyde **4** (obtained similarly to previous analogues[15]) with 2,4,5,7-tetranitrofluorene in DMF (room temperature, 2 h).[16]

A solution electrochemical study shows that compound **3** is capable of both reversible reduction and oxidation processes. As seen from Fig. 1, there are three single-electron reduction waves: two closely-spaced reversible reductions resulting in the radical anion and dianion, respectively, followed by a third quasi-reversible wave resulting in the radical trianion ($E_{1red}^{1/2} = -0.89$ V, $E_{2red}^{1/2} = -1.04$ V, $E_{3red}^{1/2} = -1.78$ V *vs.* Fc/Fc$^+$). Scanning anodically a reversible single-electron oxidation resulting in the radical cation ($E_{1ox}^{1/2} = +0.57$ V) and a second single-electron oxidation wave ($E_{2ox}^{pa} = +1.05$ V, irreversible) are observed.[17] The CV of **TNF**, a widely used sensitiser of photoconductive polymers, measured under the same conditions, shows three single electron reductions at $E_{1red}^{1/2} = -0.88$ V, $E_{2red}^{1/2} = -1.15$ V, and $E_{3red}^{1/2} = -1.79$ V, indicating the very similar electron affinities of these two acceptors.

The additional vinylene unit between the donor and the acceptor moieties in **3** [compared to predecessor **1**] results in a bathochromic shift of the ICT bands ($\Delta\lambda_{ICT-1} = 95$ nm and $\Delta\lambda_{ICT-2} = 33$ nm) and an increase in their intensities ($\approx 1.5$ and $\approx 3$ times for ICT-1 and ICT-2, respectively) (Fig. 2). A further bathochromic shift of these bands is observed in the solid state for the "**PEPK–3**" film ($\lambda_{max} = 546$ and 658 nm), partly arising from a charge transfer complexation between the carbazole units of the polymer and acceptor **3** (Fig. 2).

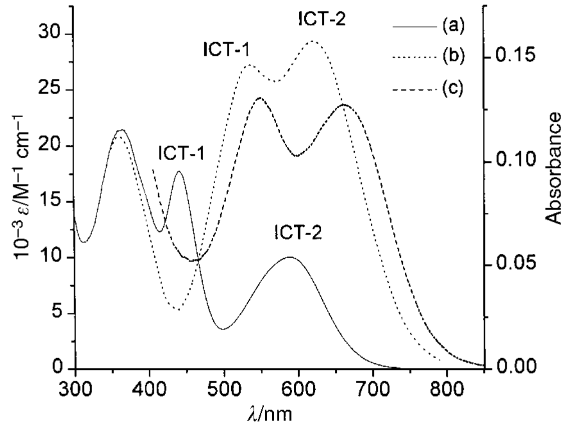

**Fig. 2** Electronic absorption spectra for solutions of compounds **1** in $CH_2Cl_2$ (a) and **3** in acetone (b) and for the film of **PEPK** with 2 wt% of **3** (c).

Consequently the good balance between the electron affinity and the ICT energy in acceptor **3** resulted in its excellent ability to sensitise the photoconductivity of carbazole-containing polymers. The increased photoresponse of **PEPK** films sensitised by acceptor **1**, as compared to **TNF**, in the ICT region of the acceptor (Fig. 3)[8] is further enhanced with the novel acceptor **3**: the maximum and red limit of the photoresponse is further bathochromically shifted, and the photoresponse in its maximum is raised. Moreover, due to two close-spaced ICT bands of similar intensity (Fig. 2), the peak of the photoresponse becomes wider resulting in a high level of electrophotographic response ($S_{\Delta V}$) in the 500–700 nm region. Electrophotographic response under He–Ne laser radiation ($\lambda = 632.9$ nm) increased from $S_{\Delta V} = 10\ m^2\,J^{-1}$ (0.5–1.1 mol% of **1**) to $S_{\Delta V} = 15\ m^2\,J^{-1}$ (0.3–0.5 mol% of **3**) (Table 1). A more pronounced difference in $S_{\Delta V}$ is observed at longer wavelengths, where acceptor **3** is 3–4 times more efficient than **1** (Fig. 3), at $\lambda = 700$ nm: $S_{\Delta V} = 0.2$ (**TNF**), 1.2 (**1**) and 5.0 (**3**) $m^2\,J^{-1}$; at $\lambda = 750$ nm: $S_{\Delta V} = 0.3$ (**1**) and 1.0 (**3**) $m^2\,J^{-1}$.

"**PEPK–3**" films show good rheological characteristics allowing the attainment of maximal diffraction efficiency for plane wave holograms of $\eta_{max} = 22\%$. The maximal holographic response of "**PEPK–3**" film (He–Ne laser) is $S_\eta = 150$–$210\ m^2\,J^{-1}$ which is comparable to that for "**PEPK–1**",[8] but it is reached at lower concentrations of the acceptor. It should also be noted that a decrease of the photoresponse is observed at high concentrations of **3** which partly arises from its limited solubility in the polymer matrix.

In conclusion, we have demonstrated that lengthening the conjugated linker in fluorene–dithiole acceptors, together with a precise control of the balance between the electron affinity and the ICT energy in the chromophore, can tune efficiently the level and the spectral distribution of the photoresponse of

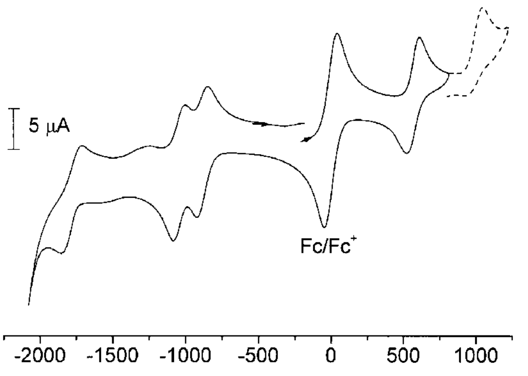

**Fig. 1** Cyclic voltammogram of compound **3** (*ca.* $10^{-3}$ M) in $CH_2Cl_2$, 0.2 M $Bu_4NPF_6$, 25 °C.

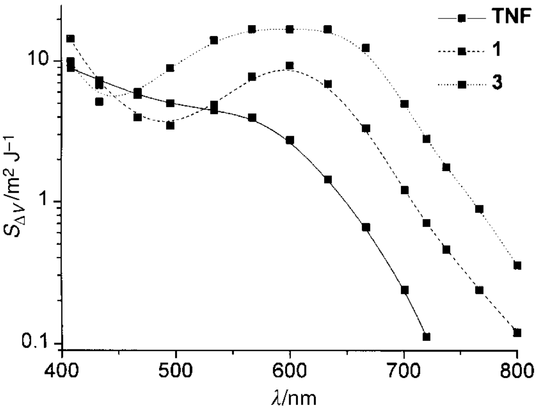

**Fig. 3** Spectra of the electrophotographic response of **PEPK** films sensitised by **TNF** (5 wt%), **1** (5 wt%) and **3** (1.5 wt%).

**Table 1** Comparative results of photophysical measurements of **PEPK** films sensitised by acceptors **TNF**, **1**, and **3**[a]

| Acceptor | Concentration | | $V_0$/V | $\Delta V/V_0$ (%) | $\lambda = 632.9$ nm | | $\eta_{max}$ (%) |
|---|---|---|---|---|---|---|---|
| | Wt% | Mol% | | | $S_{\Delta V}$/m$^2$ J$^{-1}$ | $S_\eta$/m$^2$ J$^{-1}$ | |
| **3** | 1.0 | 0.32 | 170 | 5 | 15 | 200 | 22 |
| **3** | 1.5 | 0.48 | 160 | 6 | 15 | 210 | 20 |
| **3** | 3.0 | 0.95 | 150 | 10 | 10 | 150 | 15 |
| **3** | 10.0 | 3.2 | 120 | 15 | 9 | 100 | 5 |
| **1** | 2.0 | 0.44 | 170 | 10 | 8 | 210 | 25 |
| **1** | 5.0 | 1.1 | 160 | 10 | 10 | 250 | 25 |
| **TNF** | 5.0 | 3.5 | 210 | 14 | 1.9 | 9 | 15 |

[a] $V_0$ is the surface potential of the film, charged in the dark; $\Delta V/V_0$ is the dark decay of the surface potential for 30 s; $S_{\Delta V}$ is the electrophotographic response of the film estimated by latent electrostatic image by 20% decay of the surface potential under illumination; $S_\eta$ is the photoresponse estimated by visualised image at the level of 1% diffraction efficiency of the hologram; $\eta_{max}$ is the maximal diffraction efficiency of the film for plane wave hologram.

holographic materials for optical information storage, allowing a substantial increase of the photoresponse in the long wavelength visible and near IR regions.

More soluble analogues of **3** may allow the introduction of 3–5 mol% of acceptor into the films without lowering the diffraction efficiency of the hologram and, thereby, increase the photoresponse of the materials and improve further their rheological characteristics.

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14 Achieving a high photoresponse in the near-IR region is of great importance for HI offering more compact and cheap solid state lasers as radiation sources.

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16 Black solid, 57% yield, mp 217–220 °C; $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 8.99 (1H, d, $J = 2$ Hz), 8.87 (1H, d, $J = 2$ Hz), 8.77 (1H, d, $J = 2$ Hz), 8.71 (1H, d, $J = 2$ Hz), 7.70 (1H, d, $J = 13$ Hz), 7.24 (1H, d, $J = 13$ Hz), 3.01 (2H, t, $J = 7$ Hz), 2.94 (2H, d, $J = 7$ Hz), 1.80–1.55 (4H, m), 1.55–1.40 (4H, m), 1.40–1.10 (4H, m), 0.90 (6H, m); MS (EI) $m/z$ 704 (100%); $\lambda_{max}$/nm (log $\varepsilon$) = 361 (4.32), 536 (4.43), 622 (4.46) (in acetone).

17 Redox potentials of compound **1** measured under the same conditions are: $E_{1red}^{1/2} = -0.91$ V, $E_{2red}^{1/2} = -1.10$ V, $E_{3red}^{1/2} = -1.91$ V, $E_{1ox}^{1/2} = +0.86$ V and $E_{2ox}^{pa} = +1.22$ V (irreversible) *vs.* Fc/Fc$^+$.