Synthesis, Intramolecular Charge-transfer Interaction, and Electron Transport Properties of 9,9-Bis(alkylthio)nitrofluorenes

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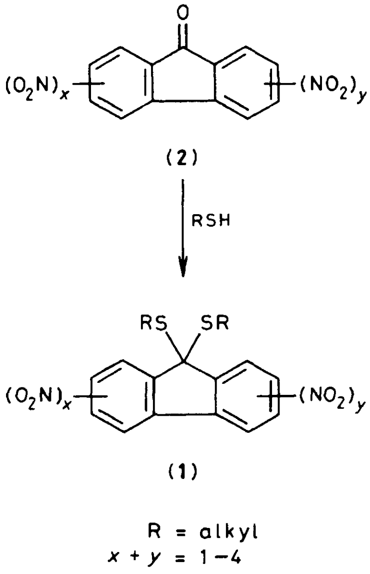
9,9-Bis(alkylthio)nitrofluorenes (**1**), obtained by thioacetalization of the corresponding nitrofluoren-9-ones with $AlCl_3$ in nitromethane, exhibit intramolecular charge-transfer characteristics and electron transport properties.

There is growing interest in molecularly dispersed electron donors or electron acceptors in dielectric binders as molecular charge transport systems.[1–5] The transport characteristics of these molecules, particularly those of the acceptor-type, often display a dramatic enhancement in the presence of proper charge-transfer (CT) interactions.[3–5] Although this phenomenon has been attributed to a better dispersion of the transport molecules in the matrix through CT interactions, recent findings from our laboratory suggest a definite role of the latter in the transport process. The study of CT interactions in this respect is however adversely complicated by the sensitivities of these intermolecular interactions to stoicheiometry and concentration, and to the morphology of the matrix polymer and its guest–host stereochemical relationship with the transport molecules. Accordingly, the significance of CT interactions in the charge transport process cannot be readily recognized. We report here the synthesis, CT interaction, and electron transport properties of 9,9-bis(alkylthio)nitrofluorenes (**1**): a novel class of intramolecular CT complexes which exhibit electron transport properties solely by virtue of their CT character.

The thioacetal (**1**) could not be effectively obtained by thioacetalization of the corresponding nitrofluoren-9-one (**2**)



Scheme 1

Table 1. Yields and physical and electron transport characteristics of 9,9-bis(alkylthio)nitrofluorenes (**1**).

Thioacetal (**1**)	Yield[a] (%)	M.p./ °C	EA[9]/ eV	μ_d[b]/ $cm^2 V^{-1} s^{-1}$
a R = Et; 2,4,5,7-tetranitro-	85	222 (decomp.)	2.16	2.5×10^{-7}
b R = Bu^n; 2,4,5,7-tetranitro-	93	74.75	2.16	2.5×10^{-7}
c R = Bu^n; 2,4,7-trinitro-	87	Viscous oil	1.82	5×10^{-8}
d R = Bu^n; 2,7-dinitro-	89	73—74	1.61	2×10^{-8}
e R = Bu^n; 3-nitro-	70	71—73	1.47	—

[a] Isolated yield of pure (**1**); all compounds display only one peak in their h.p.l.c. chromatograms, and have satisfactory spectroscopic data and elemental analysis. [b] μ_d = electron drift mobility in the (**1**)/PVK systems (1 : 1 by weight) under an applied field of 2×10^5 V cm^{-1}; values are estimates only as the transit signals cannot be accurately resolved.

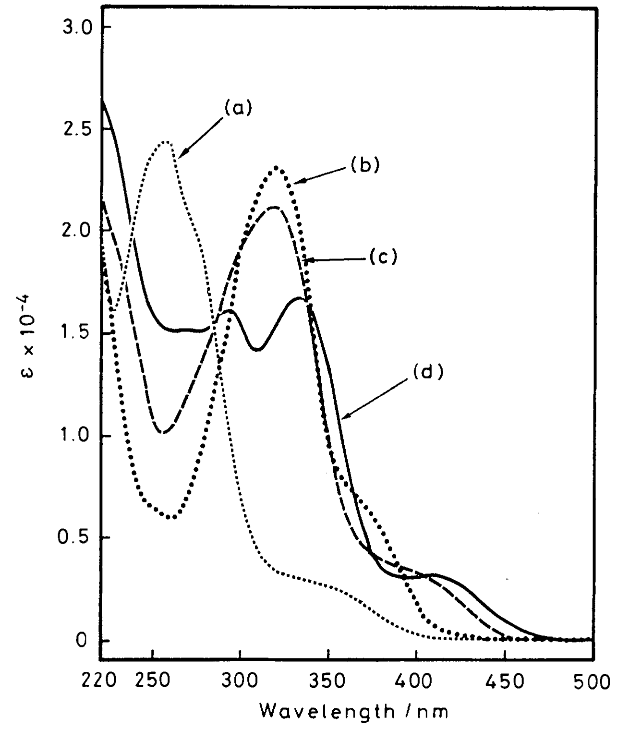
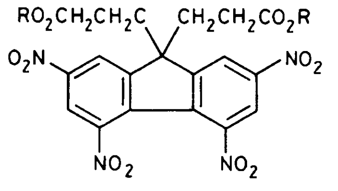


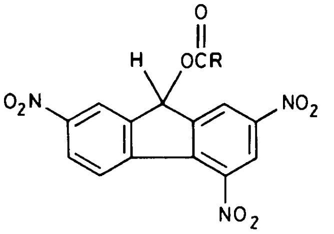
Figure 1. Electronic absorption spectra of 9,9-bis(n-butylthio)- (a) 3-nitro-, (b) 2,7-dinitro-, (c) 2,4,7-trinitro-, (d) 2,4,5,7-tetranitrofluorenes (**1**) (acetonitrile, 25 °C).

under the standard conditions[6] (Scheme 1); the over-ridingly strong CT interaction between (**2**) and the alkanethiol hampered the otherwise simple condensation. However, this difficulty was overcome by employing a stoicheiometric excess of $AlCl_3$ as a mediating agent in a polar medium such as nitromethane; a modification of our previously reported thioacetalization procedure.[7] Thus, when a partially dissolved mixture of a nitrofluoren-9-one and an alkanethiol in nitromethane was treated with a stoicheiometric excess of $AlCl_3$ at room temperature, an exothermic reaction was observed. The reaction was generally complete in 30 min, affording (**1**) in good yield (Table 1).

The electronic absorption spectra of (**1**) display distinct long-wavelength shoulders which are absent in the spectra of the corresponding model nitrofluorene derivatives (Figure 1). We attribute these absorptions to the lowest-energy intra-



(**3**); R = alkyl



(**4**); R = alkyl

molecular CT transitions between the sulphide-donor and the nitrofluorene-acceptor moieties of (**1**). In cyclic voltammograms, (**1**) exhibits reversible one-electron reductions which are characteristic of the corresponding 9,9-disubstituted nitrofluorene acceptors. For example, the cyclic voltammetric behaviour of 9,9-bis(alkylthio)-2,4,5,7-tetranitrofluorenes (**1a,b**) is essentially identical to that of dialkyl 2,4,5,7-tetranitrofluorene-9,9-dipropionates (**3**).[8] Accordingly, one can conclude that no significant charge transfer occurs in the ground state of (**1**). As would be expected for CT complexes, the transition energies ($h\nu_{CT}$) of the long-wavelength bands of (**1**) display a linear correlation with their first electron affinities (EA).[9] Since the latter can be taken as the EA's of the acceptor moieties of (**1**), this linear relationship therefore provides a definite confirmation on the intramolecular CT character of (**1**).[10]

The transport properties of (**1**) were investigated in poly(vinylcarbazole) (PVK) matrices using a dual-layered device configuration;[5] amorphous selenium was employed as the photogenerator and the transport characteristics were studied by the xerographic space-charge-limited discharge technique and by the electroded time-of-flight method.[11] The results (Table 1) demonstrate that thioacetals (**1**) transport electrons. The electron drift mobilities of (**1**) in PVK matrices were estimated to be higher than those of the well-studied electron transport molecule, 2,4,7-trinitrofluoren-9-one[2–5] at equivalent molar loadings under similar conditions. In sharp contrast, the analogous nitrofluorene derivatives such as (**3**) and (**4**)[5] were not observed to display electron transport properties, despite their striking structural and electronic (except the CT character) resemblance to (**1**). Since (**3**) and (**4**) are also compatible with the matrix polymer (PVK), the observed electron transport capabilities of (**1**) cannot therefore be attributed to their dispersibility in the transport matrix; rather, they must arise from the involvement of their CT properties in the transport process. Unfortunately, significant trapping of electrons owing to the instability of (**1**) was encountered in these systems, and the efficiency of photoinjection of electrons into these transport media cannot be assessed. Further work is being directed towards increasing the stability of (**1**).

The present studies therefore demonstrate that CT interactions may play a definite role in the molecular charge transport process. The charge transport capability of electron acceptors, or for that matter, electron donors can be greatly enhanced by incorporation of proper intramolecular CT character.

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