



Electronic properties of indan-1,3-dione-carbazole-based compounds revealed by time resolved spectroscopy



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ABSTRACT

Two new indan-1,3-dione and carbazole-based (IDC) compounds with single and four covalently connected chromophores were synthesized and their optical properties were investigated in solutions and in solid films with the emphasis on the interchromophore interactions. Because of molecule twisting, opening transitions to $n\pi^*$ states, IDC chromophores experience ultrafast excited state relaxation with the time constant of about 2 ps in solutions and several times slower solid films. Chromophore connection into quadruplicate molecules only weakly influence their spectroscopic properties in solutions, however prevents H-type aggregate formation and concomitant spectral changes in solid films.

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1. Introduction

Small molecules, forming glasses in solid state, are very perspective for electronic applications, since formation of molecular layers may be often performed by vacuum evaporation and by processing from solutions, which not only gives technological flexibility, but also allows better manipulation of the layer morphology. Materials for organic electronics shall meet many requirements for mechanical, optical and electronic properties, which are often difficult to combine. Therefore, current state of the art molecular compounds are often composed of several building blocks responsible for one or another material functionality.

Carbazole, which is a strong electron-donating chromophore [1–13] is one of the most common building blocks, particularly in design of molecular compounds where intramolecular or intermolecular charge transfer is desirable. Indan-1,3-dione moiety is a very strong electron acceptor [10,14–19] and is also quite common in materials for molecular electronics, in particular as an electron-accepting moiety of so-called push–pull molecules where intramolecular charge transfer takes place under the molecule excitation. Electrooptically active materials containing such push–pull

molecules are currently being investigated for their application in light manipulation devices for optoelectronics and optical information processing [9,20]. Such donor-acceptor compounds enable creation of materials possessing high bipolar, electron and hole mobilities [21]. Because of the presence of absorption bands in the visible spectral range, optical properties of indan-1,3-dione/carbazole materials may be controlled by light of the visible spectral range, convenient for laser sources, eg. these molecules may be subject to all–optical orientation [22,23].

In this paper we report synthesis of new indan-1,3-dione and carbazole-based (IDC) compounds with one and four covalently connected chromophore units. We denominate the latter ones as quadruplicate compounds. Such connection of relatively small molecules into large compounds, prevents material crystallization in solid films, but may also influence their optoelectronic properties, and definitely should change their translational and rotational diffusion. The investigated compounds form well-defined molecular glasses. The existence of several diastereoisomers, the possibility of intermolecular hydrogen bonding and flexibility of aliphatic linking chains ensure high morphological stability of these glasses. Another feature of these compounds is the presence of two hydroxyl groups in the molecule. This improves adhesion and compatibility with various binders and they can be chemically crosslinked in the layer by reaction of the hydroxyl groups with

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polyisocyanates [24]. Very fast excited state relaxation, as will be discussed in the current paper, suggests application of the investigated compounds in high speed electronic devices, or in nonlinear optics, for example, as fast saturable absorbers. We characterize optical properties and excited state dynamics of IDC compounds and show that chromophore units weakly interact in the quadruplicate compound, and branched structure of this compound prevents formation of crystallites and excitonically coupled aggregate species in solid films.

2. Materials and methods

2.1. Synthesis of materials

9-ethyl-3-carbazolecarboxaldehyde, indan-1,3-dione were purchased from Aldrich Chemical Co. and were used without purification. Bis[4-[6-(3-formylcarbazol-9-methyl)-7-(3-formylcarbazol-9-yl)-3-hydroxy-5-oxa-1-thiaheptyl]phenyl]sulphide was synthesized earlier according to the method described in [25].

2.1.1. 9-ethyl-3-(1,3-dioxindan-2-ylmethylene)carbazole (IDC1, $C_{24}H_{17}NO_2$)

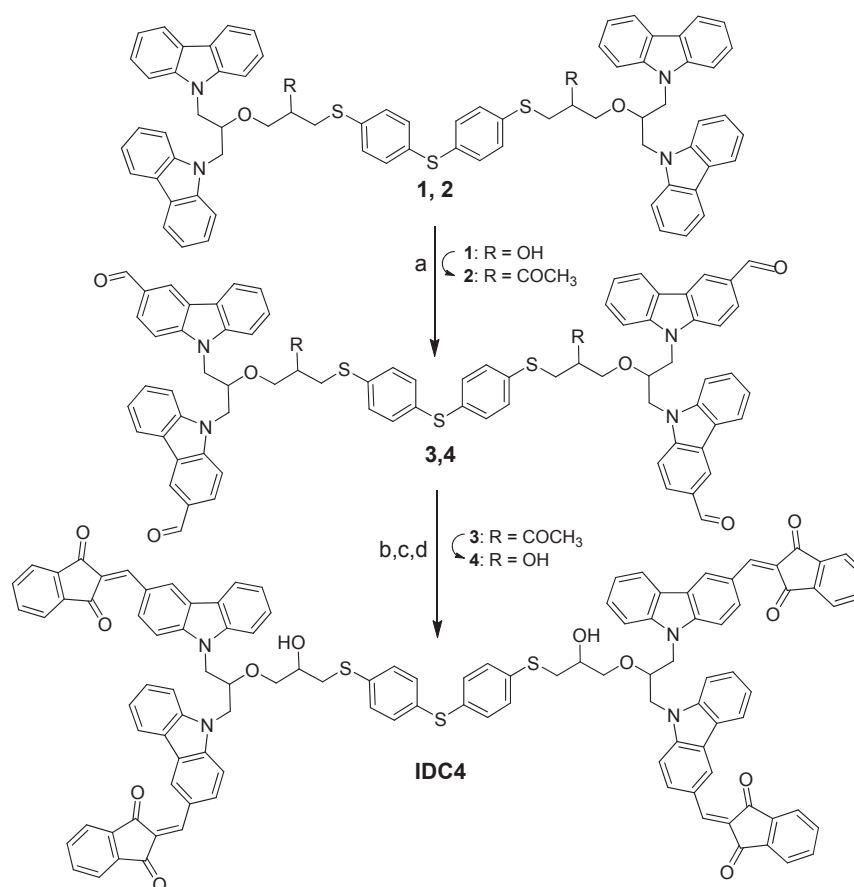
5.58 g (0.025 mol) of 9-ethyl-3-carbazolecarboxaldehyde and 3.65 g (0.025 mol) of indan-1,3-dione were stirred in 70 ml of ethanol at room temperature overnight. The crystalline product that had been formed was filtered off, washed with ethanol and recrystallized from toluene. Yield 6.0 g (68.3%); IR (KBr): $\bar{\nu}$ = 3069, 3049, 3000 (CH_{arom}), 2958, 2917, 2861 (CH_{aliph}), 1715, 1675 ($C=O$) cm^{-1} ; 1H NMR ($CDCl_3$, 300 MHz): δ = 9.34 (1H, s, CH of methylene), 8.59 (1H,

d, J = 8.7 Hz, H-2 of carbazole), 8.18 (1H, d, J = 7.7 Hz, H-5 of carbazole), 8.00–7.22 (9H, m, Ar), 4.31 (2H, q, J = 7.2 Hz, CH_2CH_3), 1.43 (3H, t, J = 7.2 Hz, CH_2CH_3) ppm. Anal. Calcd for $C_{24}H_{17}NO_2$: C, 82.03; H, 4.88; N, 3.99. Found, %: C, 81.85; H, 4.60; N, 3.64.

2.1.2. Bis[4-[6-(3-(1,3-dioxindan-2-ylmethylene)carbazol-9-methyl)-7-(3-(1,3-dioxindan-2-yl-methylene)carbazol-9-yl)-3-hydroxy-5-oxa-1-thiaheptyl]phenyl]sulphide (IDC4, $C_{112}H_{78}N_4S_3O_{12}$)

1.26 g (0.001 mol) of bis[4-[6-(3-formylcarbazol-9-methyl)-7-(3-formylcarbazol-9-yl)-3-hydroxy-5-oxa-1-thiaheptyl]phenyl] sulphide and 0.73 g (0.005 mol) of indan-1,3-dione were stirred in the mixture of 30 ml of ethanol and 15 ml of chloroform at room temperature overnight. After termination of the reaction solvents were removed and the residue was purified by column chromatography (eluent: acetone:n-hexane = 1:4). The obtained compound was isolated as solid product. Yield 0.87 g (49.2%); IR (KBr): $\bar{\nu}$ = 3436 (OH), 3051 (CH_{arom}), 2927, 2917 (CH_{aliph}), 1715, 1679 ($C=O$) cm^{-1} . 1H NMR ($CDCl_3$, 300 MHz): δ = 9.45–9.14 (4H, m, CH of methylene), 8.67–6.67 (52 H, m, Ar), 4.64–3.83 (12H, m, $N-CH_2CHCH_2-N, CHOH$), 3.35–2.68 (4H, m, OCH_2), 2.60–2.21 (4H, m, $S-CH_2$), 1.85–1.60 (2H, m, OH) ppm. Anal. Calcd for $C_{112}H_{78}N_4S_3O_{12}$: C, 76.08; H, 4.45; N, 3.17. Found, %: C, 75.75; H, 4.12; N, 2.79.

To synthesize the desired structure IDC4, possessing four indan-1,3-dione chromophores, we have selected a strategy in which the main step included the preparation of an intermediate **4** starting from readily available bis[4-[6-(3-formylcarbazol-9-methyl)-7-(3-formylcarbazol-9-yl)-3-hydroxy-5-oxa-1-thiaheptyl]phenyl]sulphide (**1**) [26] (Scheme 1).



Scheme 1. Synthesis of IDC4 possessing four indan-1,3-dione moieties. (a) acetic anhydride, pyridine, 50 °C; (b) $POCl_3/DMF$, 90–95 °C; (c) 85% KOH, acetone/ H_2O , b.t.; (d) indan-1,3-dione, EtOH, r.t.

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