



ORIGINAL ARTICLE

Spectroscopic investigation of novel donor–acceptor chromophores as specific application agents for opto-electronics and photonics



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Received 25 May 2011; accepted 2 August 2011

Available online 16 August 2011

KEYWORDS

Chromophores;
Knoevenagel condensation;
Photostability;
Photobleaching

Abstract Donor–acceptor chromophores were synthesized by Knoevenagel condensation and characterized by using spectroscopic measurements (FT-IR, ¹H NMR, ¹³C NMR, and mass) and elemental analyses. UV–Vis and fluorescence spectroscopic studies provided that these dyes are good absorbent and fluorescent. The results of photostability study showed that photobleaching of Dyes 2 and 4 was more significant than that of Dyes 1 and 3, providing that Dyes 1 and 3 are more photostable than Dyes 2 and 4. In addition, all dyes included in this study are found to be sensitive to the polarity of the microenvironment provided by different solvents based on the results of fluorescence polarity studies.

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1. Introduction

Donor–acceptor chromophores have been recognized for several decades as a promising field with important applications in the domain of opto-electronics and photonics (Schafer

et al., 2011; Bhuiyan et al., 2011) and high performance electrooptic switching elements for telecommunications and optical (Avci, 2010). The first step in designing nonlinear optical information processing is based on materials with high optical (NLO) properties. Hence, various materials have been investigated by using their nonlinear optical properties, e.g. inorganic materials (Peng et al., 2011), organometallic compounds (Liu et al., 2011a,b), liquid crystals (Raposo et al., 2011), and organic molecules and polymers (Karaoglan et al., 2011). Organic molecules are one of the best organic compounds, it can be easily synthesized. Knoevenagel condensation is one of the most important reactions for the formation of donor–acceptor chromophores by the nucleophilic addition of an active hydrogen compound to a carbonyl group followed by a dehydration reaction. Several synthetic methods have been

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Peer review under responsibility of King Saud University.



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reported so far, such as refluxing in an organic solvent (Asiri et al., 2009), the solvent-free solid-phase reaction (Shang et al., 2011), ultrasonication (Liu et al., 2011a,b), photosensitization (Leon and Ganem, 1997), and microwave radiation (Benito et al., 2008). Therefore, this study aimed to explore the optical and spectroscopic properties of newly prepared donor–acceptor chromophores derived from carbazole. In addition, the effect of photobleaching on the photostability of these dyes was investigated by using time-based fluorescence steady-state measurements. The sensitivity of new synthesized dyes toward the polarity of the microenvironment provided by different solvents was also examined by fluorescence polarity studies.

2. Experimental

2.1. Chemicals and reagents

Carbazole aldehyde was purchased from Acros organic and used without further purification. Other solvents (A.R.) and reagents were obtained commercially and used without further purification except chloroform, ethanol, and methanol.

2.2. Instrumental methods

Melting points were recorded on a Thomas Hoover capillary melting apparatus without correction. FT-IR measurements were performed on KBr disks on a Nicolet Magna 520 FTIR spectrometer. ^1H and ^{13}C NMR spectroscopic experiments were recorded in CDCl_3 on a Bruker DPX 600 MHz spectrometer using tetramethyl silane (TMS) as an internal standard. Microanalyses were carried out using a Perkin Elmer 240B analyzer. UV–Vis absorption and fluorescence measurements were acquired by use of a Perkin–Elmer UV–Vis scanning spectrophotometer and luminescence spectrofluorometer, respectively. Absorption and emission spectra were collected using a 10 mm quartz spectrophotometer and spectrofluorometer cells, respectively. The emission spectra of all dyes were excited at 310 nm excitation wavelength with slit widths set for entrance and exit bandwidths of 4 and 2 nm on both excitation and emission monochromators, respectively. For the photostability study of dyes, time-based fluorescence steady-state measurements were acquired with excitation and emission bandpass set at 15 and 5 nm, respectively. The fluence level of the excitation source was open for a period of 30 min. The excitation wavelength for all dyes was set at 310 nm, while the emission wavelength was set at 420 nm for Dye 1 (D1), 512 nm for Dye 2 (D2), 524 nm for Dye 3 (D3), and 500 nm for Dye 4 (D4).

2.3. General procedure for the synthesis of carbazole derivatives

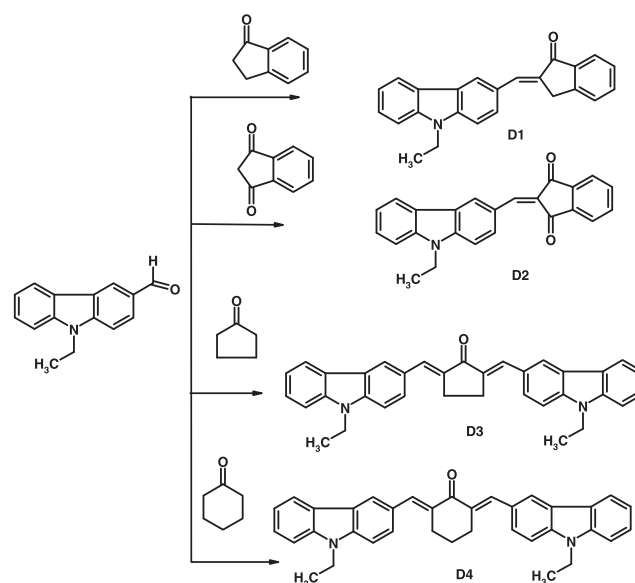
A mixture of carbazole aldehyde (0.0058 mol) and corresponding active methylene (0.0058 mol) in anhydrous ethanol (15 ml) and in the presence of few drops of pyridine was refluxed at 80 °C for 3 h with continuous stirring. Progress of reaction was monitored by TLC. After completion of the reaction, the solution was cooled. Thus, the heavy precipitate obtained was collected by filtration and purified by recrystallization from a mixture of methanol and chloroform (Scheme 1).

2.3.1. 2-(9-Ethyl-9H-carbazole-3-ylmethylene)-indan-1-one (D1)

Yield: 87.00%; m.p. 155 °C; Anal. Calcd for $\text{C}_{24}\text{H}_{19}\text{ON}_2$: C, 85.43; H, 5.68; N, 4.15. Found: C, 85.35; H, 5.62; N, 4.11; IR (KBr) ν_{max} cm^{-1} : 1687 (C=O), 1590 (C=C), 1177(C–N), 2974 (C–H, aliphatic), 3057 (C–H, aromatic); ^1H NMR (CDCl_3) δ : 7.02 (H1, d, $J = 1.8$ Hz), 8.19 (H2, d, $J = 7.2$ Hz), 8.17 (H3, s), 7.45 (H4, d, $J = 4.2$ Hz), 7.82 (H5, dd, $J = 8.4$ Hz), 7.62 (H6, dd, 1.2 Hz), 7.44 (H7, d, $J = 4.2$ Hz), 8.73 (H8, s), 7.45(H9, d, $J = 4.2$ Hz), 7.32 (H10, dd, $J = 7.2$ Hz), 7.62 (H11, dd, $J = 4.2$ Hz), 7.45 (H12, d, $J = 4.2$ Hz), 4.15 (H13, s), 4.41 ($\text{CH}_3\text{—CH}_2\text{—N}$, t, $J = 7.2$ Hz), 1.46 ($\text{CH}_3\text{—CH}_2\text{—N}$, q, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3) δ : 194.49, 192.05, 149.57, 148.67, 141.42, 140.67, 138.47, 135.67, 134.18, 133.76, 131.60, 129.95, 127.53, 126.29, 124.54, 119.80, 108.91, 107.89, 107.89, 77.02, 37.77, 35.77, 32.78, 13.88; GC–MS m/z (rel. int.%): 338 (52) $[\text{M} + 1]^+$.

2.3.2. 2-(9-Ethyl-9H-carbazole-3-ylmethylene)-indan-1,3-dione (D2)

Yield: 21.01%; m.p. 142 °C; Anal. Calcd for $\text{C}_{24}\text{H}_{17}\text{ON}_2$: C, 82.03; H, 4.88; N, 3.94. Found: C, 81.97; H, 4.82; N, 3.92; IR (KBr) ν_{max} cm^{-1} : 1673 (C=O), 1554 (C=C), 1220 (C–N), 2968 (C–H, aliphatic), 3042 (C–H, aromatic); ^1H NMR (CDCl_3) δ : 8.02 (H1, d, $J = 1.8$ Hz), 8.08 (H2, d, $J = 7.2$ Hz), 7.81 (H3, s), 7.58 (H4, d, $J = 7.8$ Hz), 7.49 (H5, dd, $J = 6.6$ Hz), 7.51 (H6, dd, $J = 7.2$ Hz), 7.44 (H7, d, $J = 7.2$ Hz), 8.65 (H8, s), 7.58 (H9, d, $J = 7.8$ Hz), 7.49 (H10, dd, $J = 6.6$ Hz), 7.51 (H11, dd, $J = 6.6$ Hz), 4.05 ($\text{CH}_3\text{—CH}_2\text{—N}$, t, $J = 3.6$ Hz), 1.47 ($\text{CH}_3\text{—CH}_2\text{—N}$, q, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3) δ : 209.12, 204.40, 202.55, 191.25, 189.75, 148.81, 143.15, 140.54, 139.04, 134.97, 133.38, 128.79, 126.66, 125.79, 124.85, 120.80, 109.12, 77.23, 63.22, 49.22, 44.54, 37.93, 18.44, 13.89; GC–MS m/z (rel. int.%): 552 (58) $[\text{M} + 1]^+$.



Scheme 1 Synthetic route of dyes (D1, D2, D3, and D4).

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