Dyes and Pigments 92 (2012) 1257-1265

Contents lists available at ScienceDirect

Dyes and Pigments



Spectral properties of chalcone containing triphenylamino structural unit in solution and in polymer matrices

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ARTICLE INFO

Article history: Received 4 April 2011 Received in revised form 16 June 2011 Accepted 22 July 2011 Available online 30 July 2011

Keywords: Fluorescence Chalcones Triphenylamine Thiophene Solvent effect Polymer matrice

ABSTRACT

Novel chalcones (3-phenyl-1-phenylprop-2-en-1-ones) substituted on one end (position 3) with electron donating diphenylaminophenyl substituent and on the other end (position 1) with thiophenes with variable electronic effects (CH-1-CH-5) were prepared. The spectral properties of these molecules in solvents such as chloroform, cyclohexane, acetonitrile, methanol and incorporated into polymer matrices of polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC) were compared with those of 3-[4-(N,N-dimethylamino)-phenyl]-1-phenylprop-2-en-1-one (CH-1m) and 3-[4-(N,Ndimethylamino)phenyl]-1-(4-nitrophenyl)prop-2-en-1-one (CH-2m). The longest wavelength absorption band of model chalcones **CH-1m** and **CH-2m** was in the range of 400–420 nm and did not appear to be influenced by the medium. The fluorescence increased with the addition of acetonitrile, while it was effectively quenched in methanol. The strong electron-attracting nitro group quenched the fluorescence of **CH-2m** in nearly all solvents. In contrast, the fluorescence became more intense when the molecule was incorporated in a polymer matrix. The longest wavelength absorption band of novel chalcones was observed in the range of 410-450 nm in all media. The fluorescence of chalcones was red-shifted to the range of 530-575 nm and was most intense in chloroform. The quantum yield of fluorecence was the highest in chloroform for the chalcone with a methyl-thiophene (0.49) and low for the chalcone with a fluorenyl-thiophene group (0.07). The fluorescence of all chalcones (CH-1-CH-5) was effectively quenched in polar acetonitrile and methanol, and was less intense relative to chloroform when incorporated into a polymer matrix and more intense relative to other solvents. The lifetime of fluorescence was in the range of 1-4 ns. The Stokes shift was in the range of 4000-5000 cm⁻¹ in chloroform, and lower in all other media. The spectral behavior of model chalcones CH-1m and CH-2m and novel chalcones with diphenylamino substituents was similar, producing observable fluorescence in several polymer matrices. The effect of the solvent on the fluorescence is discussed in terms of negative and positive solvatokinetic effects.

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PIGMENTS

1. Introduction

The emerging science of photonics, which includes the generation, emission, transmission, modulation, signal processing, switching, amplification, detection and sensing of light, is being explored today as the basis for the new technology that exploits the capability of a photon to carry information and energy [1]. To achieve this goal, new materials containing specific chromophores with properties such as large nonlinear susceptibility, fast response, easy preparation and handling should be developed to achieve the parameters necessary for the further development of the photonic material itself and the technology based around it.

Accordingly, compounds containing both donor (D) and acceptor (A) components that exhibit interesting optical and spectral properties due to the intramolecular charge transfer (ICT) phenomenon have attracted considerable attention in the literature [2]. The electron-donating and electron-accepting substituents in these molecules are connected through a π -conjugated system of single and double bonds. Typical representatives of this class of compounds are properly substituted stilbenes or condensates of benzaldehyde and nitrile of malonic acids. These molecules exhibit various degree of flexibility in the ground and excited states that could be correlated to radiation and radiationless processes. The spectral properties of this ICT state have attracted considerable attention both in photochemistry and photobiology because they



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^{0143-7208/\$ –} see front matter \odot 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.dyepig.2011.07.011

exhibit different degrees of charge transfer, which is susceptible to some environmental parameters such as microviscosity and micropolarity [1–7].

Chalcones are another class of compounds with a strong electron donor-acceptor interactions, where in the donor and acceptor moieties are linked by a keto - vinyl bridge [8-12]. The photophysical behavior of these conjugate intermolecular charge transfer compounds has generated considerable attention due to potential applications associated with the strong emission of laser and fluorescent dyes and some theoretical problems such as the twisted intramolecular charge transfer (TICT) state [2]. It was clearly demonstrated that the luminescence properties of several chalcones with strong electron-donating and accepting substituents strongly depend on the character of the substituent, the polarity of the solvent and the temperature [8]. From the correlation of fluorescence quantum yield with solvent polarity, a clear maximum was observed indicating the presence of a negative solvatokinetic effect with moderately increasing solvent polarity and a positive solvatokinetic effect with highly polar solvents [8]. The spectral properties of enone (chalcone) derivatives also depend on the character of the bridge. The rigid structure of the enone bridge favors radiative decay even in polar solvents. In contrast, enone compounds with a free double bond have very low fluorescent quantum yields, indicating that non-radiative decay is important. In these compounds, the dissipation of electronic energy proceeds through the rotation of structural units [9]. Recently, spectral and photophysical properties of a new intramolecular charge transfer (ICT) probe, namely 4'-dimethylamino-2,5-dihydroxychalcone, were explored [11]. It was observed that while the absorption spectrum undergoes minor changes with increasing solvent polarity, the fluorescence spectrum exhibits a distinct bathochromic shift in the band position, and the fluorescence quantum yield increases, reaches a maximum and then decreases with increasing solvent polarity. The change in the dipole moment of $\Delta \mu = 6.5D$, based on Lippert–Mataga equation, is due to the redistribution of the charges in the excited state.

Recently, reports have appeared discussing the spectral and photophysical characteristics of chalcone-analogue dyes containing a butadiene bridge such as 1-(4'-R-phenyl)-5-(4'-dimethyl-aminophenyl)-2,4-pentadien-1-one where R is H, Cl and OCH₃ [10,12]. These dyes exhibit dual emission in polar solvents, which is attributed to the population of a polar locally excited (LE) state and a highly dipolar intramolecular charge transfer (ICT) state, similar to what is observed in the case of chalcones with a single double bond. The incorporation of a 2-pyridyl group in the chemical structure of the chalcone analogue dye led to the design of a potential optical sensor for probing the acidity of a medium and the presence of metal cations [12].

A dimethylaminophenyl chalcone was also used as a fluorescence probe to characterize the polarity of the inner cavity of modified montmorillonite demonstrating the importance of matching the polarity of clay's surface with that of a precursor polymer for the preparation of polymer–clay nanocomposites [13].

The chalcones with a strong donating (D) and a strong accepting (A) substituent with a π -conjugated spacer are under investigation as potential materials for non-linear optics (NLO), because they are non-symmetrical and exhibit high polarizability and hyperpolarizability.

In order to generate higher charge mobility, a dialkylamino functional group was replaced with a diarylaminophenyl substituent for chalcone dyes or in combination with a mono- or oligothiophene. A simple 1-phenyl-(3-(4-diphenylamino)phenyl)prop-2-en-1-one molecule was used as an efficient organic light color conversion material for a white LED [14]. Triphenylamine-based dyes containing thiophene units were utilized in dye-sensitized solar cells [15]. For polymer solar cells and field effect transistors, polythiophenes with an octyloxyl-triphenylamine-vinylene side chain were employed [16]. Multi-triarylamine substituted oligothiophenes were tested as potential materials for organic solar cells [17].

In this paper, we report on the spectral characteristics of five novel chalcones **CH-1–CH-5** with diphenylaminophenyl substituent linked by a propen-1-one bridge with substituted thiophene and benzene unit. The goal of this study is to perform a thorough spectral characterization of these systems and to compare spectral properties of novel chalcone derivatives with a triphenylaminosubstituent as electron donor in solution with those in a polymer matrix. A more complete understanding of photophysical and electronic processes and sufficient spectral data will increase the likelihood that these materials will find application in photonics.

2. Experimental

Silica gel 60 (230–400 mesh, Merck) was used for column chromatography. 4-(*N*,*N*-diphenylamino)benzaldehyde, 1-(5-methylthiophene-2-yl)etanone, 1-(5-bromothiophene-2-yl)ethanone, 1-(2,2'-dithiophene-5-yl)ethanone, and 1-(5-((9*H*-fluoren-9-ylidene)methyl)thiophen-2-yl)ethanone and 1-(4-bromophenyl) etanone were purchased from Georganics Ltd. (http://www.georganics.sk/) and was used as received. *N*,*N*-dimethylaniline and *N*,*N*-dimethylformamide were purchased from Sigma–Aldrich and were used as received. Anthracene was zonnally refined (Lachema n.e., Brno, CR). Methanol was in UV spectroscopy purity. Cyclohexane (Merck), chloroform, tetrahydrofuran (Slavus, SR) and acetonitrile (Merck) was spectroscopy grade purity.

Polymer films doped with chalcones were prepared by casting from solution. Films of polystyrene (PS) (Chemische Werke Huels, F.R.G.), poly(methylmethacrylate) (PMMA) (Diacon, ICI, England) were prepared by casting of 1 ml chloroform solution of polymer (5 g/100 ml) containing the respective amount of probe on a glass plate (28×35 mm). The solvent was evaporated slowly. Films of poly(vinylchloride) (PVC) (Neralit, Spolana Neratovice s.e., CR) were prepared by casting from tetrahydrofuran solution as well. The concentration of probes in polymer film was 0.002 mol kg⁻¹.

2.1. Synthesis

The structures of model chalcones **CH-1m**, **CH-2m** and **chalcones CH-1–CH-5** are given in Scheme 1. The synthesis of **CH-1m** and **CH-2m** was performed in two steps. In the first step 4-(*N*,*N*dimethylamino)benzaldehyde was prepared by reaction of dimethylaniline with dimethylformamide in the presence of phosphorousoxytrichloride. In the second step corresponding benzaldehyde reacted with the acetyl derivative to form chalcones. The details of the synthesis are given below.

2.1.1. 4-(N,N-dimethylamino)benzaldehyde

Phosphorous oxychloride (11.3 g, 45 mmol) was added dropwise to the mixture of *N*,*N*-dimethylaniline (4.54 g, 37.5 mmol) and *N*,*N*-dimethylformamide (5.48 g, 75 mmol) at 0–5 °C. The reaction mixture was stirred at room temperature for 2 h and at 65 °C for 15 h. After cooling the reaction was basified with an aqueous solution of sodium hydroxide (2 M). The formed solid residue was filtered and product was recrystallized from diluted HCl, yielding 3.5 g (63%), m.p. 72–73 °C (Ref. [18] 72–75 °C).

2.1.2. General procedure for synthesis of chalcones

To 4-(*N*,*N*-dimethylamino)benzaldehyde or 4-(*N*,*N*-diphenylamino)benzaldehyde (1 equivalent) and corresponding acetyl derivative (1 equivalent) in ethanol was added aqueous solution of sodium hydroxide (13 M). Reaction mixture was stirred at room temperature for 4 h in the case of **CH-1m** and **CH-2m** and 3 days in



Scheme 1. Chemical structures and names of the investigated chalcones.

the case of **CH-1–CH-5**. The precipitated product was filtered. The crude product was purified by crystallization or column chromatography.

2.1.3. 3-(4-(N,N-Dimethylamino)phenyl)-1-phenylprop-2-en-1-one (CH-1m)

For reaction 4-(*N*,*N*-dimethylamino)benzaldehyd (1.77 g, 10.7 mmol) and acetophenone (1.3 g, 10.8 mmol) in ethanol (15 mL) was used. The crude product was recrystallized from ethanol, yielding 0.63 g of yellow crystals (24%), m.p. 111–113 °C (Ref. [13] 110.5–111.5 °C).

¹H NMR (400 MHz, CDCl₃, ppm) δ: 3.05 (s, 6H, $2 \times CH_3$), 6.68–6.71 (d, 2H, J = 8.8 Hz, <u>Ph</u>–N<), 7.31–7.36 (d, 1H, J = 15.4 Hz, -CH = <u>CH</u>–CO), 7.45–7.60 (m, 3H <u>Ph</u>–CO + 2H <u>Ph</u>–CH=, J = 8.8 Hz), 7.77–7.82 (d, 1H, J = 15.4 Hz, <u>Ph</u>–<u>CH</u>=), 7.99–8.02 (d, 2H, J = 8.8 Hz, <u>Ph</u>–CO). ¹H NMR was the same as for chalcone reported in [13].

2.1.4. 3-(4-(N,N-Dimethylamino)phenyl)-1-(4-nitrophenyl)prop-2en-1-one (**CH-2m**)

For reaction 4-(*N*,*N*-dimethylamino)benzaldehyde (1.77 g, 10.7 mmol) in ethanol (25 mL) and 4-nitroacetophenone (1.78 g,

10.8 mmol) in diethylether (25 mL) was used. The crude product was purified by recrystallization from ethanol, yielding 0.25 g (8%) of red crystals, m.p. 219–220 $^{\circ}$ C.

UV (CHCl₃, 25 °C, nm) λ_{max}: 267, 350, 447.

¹H NMR (400 MHz, CDCl₃, ppm) δ : 3.07 (s, 6H, 2 × C<u>H</u>₃), 6.69–6.72 (d, 2H, *J* = 9.3 Hz, <u>Ph</u>–N<), 7.24–7.29 (d, 1H, *J* = 15.4 Hz, –CH=), 7.55–7.58 (d, 2H, *J* = 9.3 Hz, <u>Ph</u>–CH=), 7.80–7.85 (d, 1H, *J* = 15.4 Hz, –CH–), 8.10–8.13 (d, 2H, *J* = 9.3 Hz, <u>Ph</u>–CO), 8.32–8.35 (d, 2H, *J* = 9.3 Hz, Ph–NO₂).

¹³C NMR (100 MHz, DMSO, ppm) δ: 40.3, 112.3, 116.0, 122.0, 124.0, 129.7, 131.8, 143.9, 145.0, 147.3, 149.9, 188.0 (C=O).

FT-IR (KBr) v: 1647 (CO) cm⁻¹.

Elem. Anal.: For $C_{17}H_{16}N_2O_3$ required C68.90; H5.44; N9.45% Found: C69.31; H5.53; N9.49%.

2.1.5. 1-(5-Methylthiophene-2-yl)-3-(4-(N,N-diphenylamino) phenyl)-prop-2-en-1-one (**CH-1**)

For reaction 4-(*N*,*N*-diphenylamino)benzaldehyde (0.5 g, 3.5 mmol) and 1-(5-methylthiophene-2-yl)etanone (0.97 g, 3.5 mmol) in ethanol (50 mL) was used. Crude product was crystallized from methanol with yielding 0.79 g (57%), m.p. 126–132 °C.

UV (CH₂Cl₂, 25 °C, nm) λ_{max}: 246, 295; 361, 421.

¹H NMR (300 MHz, CDCl₃, ppm) δ: 2.59 (s, 3H, CH₃), 7.06–7.04 (m, 2H), 7.13 (t, J = 3.9 Hz, 2H), 7.19–7.17 (m, 2H), 7.21–7.20 (m, 2H), 7.21–7.20 (m, 4H), 7.33 (t, J = 3.9 Hz, 2H), 7.37 (t, J = 3.9 Hz, 2H), 7.51 (d, J = 4.2 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃, ppm) δ : 16.1 (q, CH₃), 121.6 (d), 121.9 (s), 124.0, 125.1, 125.4, 126.3, 129.1, 129.6 (15 × d), 131.3, 143.2 (2 × d), 146.1, 146.8, 153.3 (5 × s), 181.6 (s, CO).

FT-IR (KBr) v: 1653 (CO) cm^{-1} .

Elem. Anal.: For C₂₆H₂₁NOS required C78.95; H5.35; N3.54% Found: C80.64; H5.49; N3.59%.

2.1.6. 1-(5-Bromothiophene-2-yl)-3-(4-(N,N-diphenylamino) phenyl)prop-2-en-1-one (**CH-2**)

For reaction 4-(*N*,*N*-diphenylamino)benzaldehyde (266 mg, 0.975 mmol) and 1-(5-bromothiophene-2-yl)ethanone (200 mg, 0.975 mmol) in ethanol (20 mL) was used. Crude product was purified by column chromatography on silikagel with mixture hexane:ethylacetate, 99:1 as eluent, yielding 130 mg of yellow crystals (29%), m.p. 187–188 °C (methanol).

UV (CH₂Cl₂, 25 °C, nm) λ_{max}: 297, 436.

¹H NMR (300 MHz, CDCl₃, ppm) δ: 7.02 (d, J = 8.7 Hz, 2H), 7.19–7.09 (m, 8H), 7.34–7.28 (m, 4H), 7.47 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 4.2 Hz, 1H), 7.79 (d, J = 15.6 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃, ppm) δ : 117.5, 121.3 (2 × d), 122.2 (s), 124.2, 125.5, 127.2, 129.5, 129.8 (14 × d), 131.2, 144.4 (2 × d), 146.7 (2 × s), 147.49 (2 × s), 150.4 (s), 180.8 (s, CO).

FT-IR (KBr) v: 1652 (CO) cm⁻¹.

Elem. Anal.: For C₂₅H₁₈BrNOS required C65.22; H3.94; N3.04%. Found: C67.21; H4.01; N3.14%.

2.1.7. 1-(2,2'-Dithiophene-5-yl)-3-(4-(N,N-diphenylamino)phenyl) prop-2-en-1-one (**CH-3**)

For reaction 4-(*N*,*N*-diphenylamino)benzaldehyde (150 mg, 0.55 mmol) and 1-(2,2'-dithiophene-5-yl)ethanone (114 mg, 0.55 mmol) in ethanol (15 mL) was used. Crude product was crystallized from mixture methanol–water, yielding 120 mg of yellow crystals (47%), m.p. 186–189 °C.

UV (CH₂Cl₂, 25 °C, nm) λ_{max}: 234, 300, 441.

¹H NMR (300 MHz, CDCl₃, ppm) δ: 7.03 (d, J = 8.7 Hz, 2H), 7.11–7.08 (m, 2H), 7.16–7.14 (m, 5H), 7.24–7.21 (m, 1H), 7.34–7.28 (m, 7H), 7.49 (d, J = 8.7 Hz, 2H), 7.73 (d, J = 3.9 Hz, 1H), 7.80 (d, J = 15.6 Hz, 1H). 13 C NMR (75 MHz, CDCl₃, ppm) δ : 118.4, 121.5, 124.1, 124.2, 125.5, 126.3 (12 \times d), 127.6 (s), 128.2, 129.5, 129.7, 132.1 (8 \times d), 136.5 (s), 143.6 (d), 144.1, 145.4, 146.7, 150.2 (5 \times s), 181.5 (s, CO).

FT-IR (KBr) v: 1653 (CO) cm⁻¹.

Elem. Anal.: For $C_{29}H_{21}NOS_2$ required C75.13; H4.57; N3.02% Found: C76.28; H4.62; N3.11%.

2.1.8. 1-(5-((9H-Fluoren-9-ylidene)methyl)thiophene-2-yl)-3-(4-(N,N-diphenylamino)phenyl)prop-2-en-1-one (**CH-4**)

For reaction 4-(*N*,*N*-difenylamino)benzaldehyd (90.4 mg, 0.331 mmol) and 1-(5-((9*H*-fluoren-9-ylidene)methyl)thiophen-2-yl)ethanone (100 mg, 0.331 mmol) in ethanol (30 mL) was used. Crude product was purified by column chromatography (hexane:ethylacetate, 95:5), yielding 70 mg of red crystals (38%), m.p. 201–206 °C.

UV (CH₂Cl₂, 25 °C, nm) λ_{max}: 232, 264, 299, 451.

¹H NMR (300 MHz, CDCl₃, ppm) δ : 7.04 (d, *J* = 8.7 Hz, 2H), 7.22–7.09 (m, 7H), 7.40–7.29 (m, 7H), 7.56–7.50 (m, 5H), 7.75–7.67 (m, 5H), 7.87–7.83 (m, 1H).

¹³C NMR (75 MHz, CDCl₃, ppm) δ: 118.4, 121.5, 124.1, 124.2, 125.5, 126.3 (22 × d), 127.6 (s), 128.2, 129.5, 129.7, 132.1 (8 × d), 136.5 (s), 143.6 (d), 144.1, 145.4, 146.7, 150.2 (5 × s), 181.5 (s, CO).

FT-IR (KBr) v: 1653 (CO) cm⁻¹.

Elem. Anal.: For $C_{39}H_{27}NOS$ required C83.99; H4.88; N2.51% Found: C86.50; H4.99; N2.58%.

2.1.9. 1-(4-Bromophenyl)-3-(4-(N,N-diphenylamino)phenyl)prop-2-en-1-one (**CH-5**)

For reaction 4-(*N*,*N*-diphenylamino)benzaldehyde (273 mg, 1 mmol) and 1-(4-bromophenyl)etanone (200 mg, 1 mmol) in ethanol (50 mL) was used. Product was re-crystallized from methanol, yielding 250 mg of white crystals (55%), m.p. 131–134 °C. UV (CH₂Cl₂, 25 °C, nm) λ_{max} : 262, 294, 425.

¹H NMR (300 MHz, CDCl₃, ppm) δ : 7.03 (d, *J* = 4.2 Hz, 2H), 7.12 (t, *J* = 3.9 Hz, 2H), 7.15 (d, *J* = 4.2 Hz, 4H), 7.34–7.30 (m, 5H, H-1, phenyl), 7.48 (d, *J* = 4.5 Hz, 2H), 7.63 (d, *J* = 4.2 Hz, 2H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 4.2 Hz, 2H).

¹³C NMR (75 MHz, CDCl₃, ppm) δ : 118.7, 121.4, 124.2, 125.5 (9 × d), 127.5, 129.3 (4 × s), 129.5, 129.8, 129.9, 131.8 (10 × d), 137.4, 145.2 (2 × s), 146.7 (s), 189.3 (s, CO).

FT-IR (KBr) v: 1652 (CO) cm⁻¹.

Elem. Anal.: For C₂₇H₂₀BrNO required C71.37; H4.44; N3.08% Found: C73.51; H4.57; N3.18%.

2.2. Spectral measurements

NMR spectra (¹H at 300 and/or 400 MHz, ¹³C at 75 and/or 100 MHz) were obtained in CDCl₃ and DMSO using a VARIAN spectrometer with tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in parts per million (ppm). Coupling constants are reported in Hertz (Hz). Splitting patterns are designated as s: singlet, d: doublet, t: triplet m: multiplet. Reactions and the collected fraction samples were monitored by TLC (Merck 60 F254 silica gel). Visualization was afforded using a UV hand lamp with 254 nm wavelength light. Melting points were recorded on a Kofler block and are uncorrected. Infrared spectra (KBr) were determined on a Perkin–Elmer 1600 FT-IR and Nicolet 8700 (Thermo, USA) systems. Elemental analyses were measured by means of Carlo Erba Elemental Analyzer 1108.

UV—VIS absorption spectra were obtained on a UV 1650PC spectrometer (Shimadzu, Japan). Emission spectra were recorded on a RF-5301PC spectrofluorophotometer (Shimadzu, Japan). Solution fluorescence was measured in a 1 cm cuvette using the right angle arrangement. Polymer film fluorescence was measured using the front face arrangement in a solid sample holder.

The quantum yield of fluorescence of the chalcones was determined in solution and in polymer films using anthracene as the standard in the respective medium, using the quantum yield of 0.25 for anthracene in cyclohexane [19]. The quantum yield of anthracene fluorescence in different media was determined by comparing the fluorescence of anthracene in cyclohexane and various other media. It was found to be 0.22 in acetonitrile, 0.20 in methanol, and 0.11 in chloroform. In polymer matrices, the quantum yield was assumed to be 0.20 in PMMA, 0.16 in PS and 0.11 in PVC. The quantum yield in solution and film was corrected to different absorptions at the excitation wavelength [20]. The fluorescence spectra were obtained by exciting at the maximum of the longest wavelength absorption band.

The fluorescence lifetime measurements were performed on a LIF 200 (Lasertechnik Ltd., Berlin, F.R.G.), which operates as a stroboscope. The excitation source is a nitrogen laser emitting at 337 nm and the emission is selected by a cut-off filter. The output signal of the Box Car Integrator was digitized and transferred to a PC using a home-made program. The fluorescence decay curves were evaluated by a simple phase plane method [21], using program designed by J. Snyder discussed in reference [22]. The standard deviation, derived from equation: $G^{1/2} = \Sigma((I_{exp} - I_{calc})^2/n)^{1/2}$, where I_{exp} and I_{calc} are intensity of emission experimental and calculated respectively, is used to determine whether the decay is monoexponential. It is assumed that the decay curve satisfies the monoexponential condition when $G^{1/2}$ is lower than 5%. Alternatively, the fitting of the fluorescence decay curves to a model of biexponential decay was performed using an adapted FluoFit MatLab package [23].

3. Results and discussion

As shown in Fig. 1, the absorption spectra of the model chalcone **CH-1m** containing an electron-donating group exhibits the longest wavelength band at approximately 410 nm being at 417 nm in polar methanol and at 403 nm in non-polar PS. This band is relatively strong in all media, with log $\varepsilon > 4$ (Table 1). The fluorescence of the **CH-1m** is red-shifted up to 540 nm in methanol. In non-polar PS, the fluorescence maximum is only at 480 nm. Clearly, the fluorescence maximum of **CH-1** is more sensitive to the medium than the



Fig. 1. Absorption and fluorescence spectra of model chalcones **CH-1m** and **CH-2m** in chloroform, methanol at $10^{-5} \text{ mol L}^{-1}$ and PS at 0.002 mol kg⁻¹. Excitation wavelengths for **CH-1m** were 415 nm in MeOH and CHCl₃ and 403 nm in PS. Excitation wavelengths for **CH-2m** were 445 nm in all media.

Table 1

Spectral properties of model chalcones **CH-1m** and **CH-2m** in solution and polymer matrices.

Medium ^a	λ _A b	log ε ^c	λ_F^d	$\Delta \nu^{e}$	Φ^{f}	τ^{g}	G ^{1/2,h}	
	(nm)	-	(nm)	(cm^{-1})		(ns)	(%)	
(2E)-3-[4-(N,N-dimethylamino)phenyl]-1-phenylprop-2-en-1-one (CH-1m)								
MeOH	417	4.23	542	5502	0.040			
CHCl ₃	415	4.43	510	4489	0.165			
PS	403	4.28	477	3850	0.080	0.9	4.4	
PMMA	407	4.24	483	3866	0.200	1.5	2.8	
PVC	422	4.17	512	4177	0.407	1.8	2.9	
(2E)-3-[4-(N,N-dimethylamino)phenyl]-1-(4-nitrophenyl)prop-2-en-1-one								
(CH-2m)								
MeOH	444	3.92	526	3511	0.020			
CHCl ₃	447	4.81	520	3141	0.008			
PS	441	4.55	551	4527	0.528	2.6	3.3	
PMMA	443	4.31	554	4497	0.240	2.0	3.7	

^a Medium: MeOH – methanol, CHCl₃ – chloroform, PS – polystyrene, PMMA – poly(methylmethacrylate), PVC – poly(vinylchloride).

4183

0 3 4 7

2.0

43

565

^b Maximum of the longest wave absorption.

4.29

^c Molar decadic extinction coefficient calculated from ε in Lmol⁻¹ cm⁻¹ or kg mol⁻¹ cm⁻¹.

^d Maximum of fluorescence band.

457

Stokes shift.

PVC

^f Quantum yield based on anthracene.

^g Life time of fluorescence.

^h Error of lifetime determination.

absorption band. The Stokes shift is larger in methanol (5500 cm^{-1}) than it is in PS and PMMA (3800 cm^{-1}). The quantum yield of fluorescence of **CH-1m** is comparable with that of anthracene in chloroform. In addition, when incorporated into the PVC polymer



Fig. 2. Changes in fluorescence spectra of **CH-1m** (3-[4-(*N*,*N*-dimethylamino)phenyl]-1-phenylprop-2-en-1-one) measured at $10^{-5} \text{ mol } L^{-1}$ in different solvent mixtures chloroform/methanol expressed in emission maxima shift and Stern–Volmer equation.



Fig. 3. Changes in fluorescence spectra of **CH-1m** (3-[4-(*N*,*N*-dimethylamino)phenyl]-1-phenylprop-2-en-1-one) measured at $10^{-5} \text{ mol L}^{-1}$ in different solvent mixtures chloroform/acetonitrile expressed in emission maxima shift and Stern–Volmer equation.

matrix, the greatest increase in quantum yield is observed (\sim 0.4). The addition of polar methanol quenches the fluorescence of **CH-1m** in a Stern–Volmer like manner (Fig. 2) and red-shifts the fluorescence maximum. In contrast, the addition of polar aprotic



Fig. 4. Absorption and fluorescence spectra of **CH-1** (3-(4-(*N*,*N*-diphenylamino) phenyl)-1-(5-methylthiophene-2-yl)prop-2-en-1-one, **CH-2** (1-(5-Bromothiophene-2-yl)-3-(4-(*N*,*N*-diphenylamino)phenyl)prop-2-en-1-one) and **CH-3** (1-(2,2'-Dithiophene-5-yl)-3-(4-(*N*,*N*-diphenylamino)phenyl)prop-2-en-1-one) in chloroform at 10^{-5} mol L⁻¹. Excitation wavelengths for chalcones were the same as its absorption maxima listed in Table 2.



Fig. 5. Absorption and fluorescence spectra of **CH-4** (1-(5-((9*H*-Fluoren-9-ylidene) methyl)thiophene-2-yl)-3-(4-(*N*,*N*-diphenylamino)-phenyl)prop-2-en-1-one) and **CH-5** (1-(4-Bromophenyl)-3-(4-(*N*,*N*-diphenylamino)phenyl)prop-2-en-1-one) in chloroform at 10^{-5} mol L⁻¹. Excitation wavelengths for chalcones were the same as its absorption maxima listed in Table 2.

acetonitrile results in the enhancement of fluorescence (Fig. 3). The acetonitrile solvent does not contain groups capable of hydrogen bounding, so a negative solvatochromic effect is observed for **CH-1m** [8]. The lifetime of fluorescence was determined in polymer matrices only and is approximately 1 ns in PS and slightly longer in PMMA and PVC.



Fig. 6. Absorption and fluorescence spectra of **CH-1** (3-(4-(*N*,*N*-diphenylamino) phenyl)-1-(5-methylthiophene-2-yl)prop-2-en-1-one) in chloroform, cyclohexane and acetonitrile at concentration 10^{-5} mol L⁻¹ with excitation wavelengths 423, 413 and 409 nm, respectively.

For **CH-2m**, with an electron-donating dimethylamino group on one end and electron-accepting nitro on the other end, the maximum of the longest wavelength absorption band is redshifted to 445 nm in all media (Fig. 1, Table 1). The fluorescence of CH-2m in polymer matrices is red-shifted even more to 550 nm compared to the solution value of 520 nm. The Stokes shift lies in the range of 3000–4500 cm⁻¹, with a larger increase observed for polymer matrices. The quantum vield of fluorescence for CH-2m is low in solution even in moderately polar chloroform, as was observed previously [8]. In contrast, the fluorescence of CH-2m is fairly intense when incorporated into polymer matrices. The lifetime of **CH-2m** is about 2 ns in polymer matrices. The intense fluorescence of **CH-2m** might be due either to the suitable degree of charge transfer, which still supports the radiation deactivation or because of the stabilization of the structure in the polymer (hindering some vibrations), which again supports radiation deactivation.

Comparison of spectral data of model chalcones **CH-1m** and **CH-2m** shows that the range of spectral shifts is larger for **CH-1m** than is observed for **CH-2m**. For both probes, the quantum yield is larger in the solid matrices than in solution. Clearly, the additional substitution of **CH-1m** with a strong electron-withdrawing nitro group resulting in **CH-2m** does not generate more intense fluorescence in solution [7], but it does yield a more intense fluorescence when doped in a polymer matrix.

The absorption spectra of novel chalcones **CH-1–CH-5** exhibit the longest wavelength band in the range of 410–450 nm in solutions (Figs. 4–6, Table 2) as well as in polymer matrices (Fig. 7, Table 3). In the absorption spectra of **CH-1** in non-polar cyclohexane and in polar methanol and acetonitrile, the longest

Table 2	
Spectral properties of substituted chalcones CH-1–CH-5 in various solve	nts.

Sample	λ_A^a	log ε ^b	λ _F c	$\Delta \nu^{d}$	Φ^{e}	τ ^f
	(nm)		(nm)	(cm^{-1})		(ns)
Chloroforn	1					
CH-1	423	4.19	538	5053	0.49	3.6
CH-2	439	4.57	551	4630	0.36	3.1
CH-3	444	4.59	550	4341	0.47	2.0
CH-4	452	4.64	574	4702	0.07	1.5
CH-5	429	4.57	545	4961	0.37	3.4
Cyclohexai	пе					
CH-1	413	3.89	440s, 463	1486	0.016	1.8
	352	4.39	405s, 419		0.020	
CH-2	430	4.49	454, 476s	1229	0.084	0.8
CH-3	433	4.53	454, 480s	1068	0.086	0.6
CH-4	433	4.61	487, 512s	2501	0.002	1.4
CH-5	410	4.47	419s, 446, 472s	1968	0.069	1.3
Acetonitril	е					
CH-1	409	4.05	448, 553	2128	0.0200	0.6
	352	4.30	530		0.0160	
CH-2	426	4.36	461, 583	1782	0.0060	0.6
CH-3	433	4.56	589s	6117	0.0080	0.4
CH-4	441	4.58	502, 536	2755	0.0002	2.0
CH-5	416	4.43	468, 558	2671	0.0030	2.0
Methanol						
CH-1	435s		523		0.0058	3.6
	356	4.34	440		0.0020	
CH-2	433	4.28	504	3253	0.0068	2.2
CH-3	441	4.50	502	2755	0.0020	1.5
CH-4	453	4.49	502	2155	0.0004	6.0
CH-5	424	4.34	477	2621	0.0016	5.6

^a Maximum of the longest wave absorption (**s** means shoulder).

^b Molar decadic extinction coefficient calculated from ε in L mol⁻¹ cm⁻¹.

^c Maximum of fluorescence band (**s** means shoulder).

^d Stokes shift.

e Quantun yield of fluorescence based on anthracene.

^f Life time of fluorescence.



Fig. 7. Absorption and fluorescence spectra of **CH-1** (3-(4-(*N*,*N*-diphenylamino)phenyl)-1-(5-methylthiophene-2-yl)prop-2-en-1-one) in chloroform (at $c = 10^{-5}$ mol L⁻¹, poly-styrene (PS) and poly(vinylchloride) at c = 0.002 mol kg⁻¹. Excitation wavelengths were 423 nm in CHCl₃, 415 nm in PS and 427 nm in PVC.

wavelength is observed as a shoulder on the more intense absorption band around 350 nm. For **CH-1–CH-5**, the longest wavelength band has a high intensity in all media, and exhibits log ε of more than 4.0 (see Tables 2 and 3).

Table 3

Spectral properties of substituted chalcones CH-1-CH-5 in polymer matrices.

Sample	$\lambda_{A}^{a}(nm)$	$\log \varepsilon^{b}$	$\lambda_{F}^{c}(nm)$	$\Delta \nu^{\rm d}~({\rm cm}^{-1})$	Φ^{e}	$\tau^{f}(ns)$		
Polystyre	Polystyrene							
CH-1	359, 415s	4.26	428s, 483	732	0.024	2.2		
CH-2	437	4.71	519	3615	0.077	2.1		
CH-3	443	4.44	491s, 517	2206	0.028	1.2		
CH-4	449	4.43	548	4024	0.029	1.2		
CH-5	427	4.42	510	3811	0.093	2.4		
Poly(metl	Poly(methylmethacrylate)							
CH-1	299, 412s	4.34	499	4232	0.041	3.9		
CH-2	433	4.39	526	4083	0.064	2.7		
CH-3	437	4.41	532	4086	0.058	1.3		
CH-4	444	4.41	558	4601	0.028	1.6		
CH-5	416	4.65	517	4696	0.102	2.7		
Poly(vinylchloride)								
CH-1	362, 427s	4.13	436s, 513	4834	0.088	3.8		
CH-2	445	4.23	548	4224	0.297	2.9		
CH-3	452	4.27	556	4138	0.036	1.5		
CH-4	464	4.58	544s, 598	3169	0.020	1.7		
CH-5	436	4.30	542	4486	0.248	3.5		

^a Maximum of the longest wave absorption (**s** means shoulder).

^b Molar decadic extinction coefficient calculated from ε in kg mol⁻¹ cm⁻¹.

Maximum of fluorescence band (s means shoulder).

Stokes shift.

d

^e Quantum yield of fluorescence based on anthracene.

^f Life time of fluorescence.

The fluorescence of the **CH-1–CH-5** is red-shifted up to 575 nm in chloroform and the Stokes shift is large - up to 5000 cm⁻¹ for CH-1 (Table 2). The fluorescence quantum yield for all chalcones except CH-4 is comparable or even higher than that of anthracene in chloroform. In non-polar cyclohexane, the maximum of fluorescence is less red-shifted than in chloroform and exhibits some vibrational structure. The Stokes shift lies in the range of 1500–2500 cm⁻¹. The fluorescence of **CH-1–CH-5** in cvclohexane is less intense up to 30 times. A similar but more pronounced effect is observed with polar solvents such as acetonitrile and methanol (decrease in intensity of approximately 250 times). One would expect that the maxima of fluorescence bands in polar solvents are more red-shifted than in chloroform. However, we observed that the fluorescence maximum in methanol lies in the range of 440 up 520 nm. Further, the fluorescence spectra of CH-1-CH-5 in acetonitrile show some structure – one band at approximately 460 nm and second one at 550 nm. A red-shifted fluorescence band, larger than that observed in chloroform (589 nm), is observed for CH-3 in acetonitrile. In this case, the Stokes shift is a rather large 6117 cm^{-1} .

Clearly, the fluorescence of chalcones **CH-1–CH-5** is influenced by solvents in a similar pattern as was reported in paper [8]. In nonpolar solvents such as cyclohexane, the fluorescence is rather weak. In moderately polar solvents such as chloroform, the intensity of fluorescence increases, indicating that a negative solvatokinetic effect is taking place. In strong polar solvents, the fluorescence is strongly quenched due to large degree of intramolecular charge transfer (ICT), which causes an increase in the rate of radiationless relaxation of an excited state, indicating that the positive solvatokinetic effect is taking place.



In some media the less intense fluorescence is observed for **CH-4** having the complex substituent 5-((9*H*-fluoren-9-ylidene) methyl)thiophene. It might exhibit an increased rate of radiation-less process in some media probably because it has got more flexible structure. Ratio of quantum yields of **CH-5** and **CH-4** is about 5 in chloroform. It is lower for PS, PMMA (about 3), but larger for PVC (about 12). The comparison of quantum yields of novel chalcones **CH-1–CH-5** in solution and in the polymer matrices indicates some fixation of structure in polymer matrices leading to lower rate of radiationless deactivation. The quantum yields data for complex **CH-4** confirms this conclusion in some extent.

The comparison of the solvent effects on the properties of **CH-1m** and **CH-1** demonstrates that there is a difference in behavior. Both chalcones are quenched by polar methanol (Figs. 2



Fig. 8. Changes in fluorescence spectra of **CH-1** (3-(4-(*N*,*N*-diphenylamino)phenyl)-1- (5-methylthiophene-2-yl)prop-2-en-1-one) measured at 10^{-5} mol L⁻¹ in different solvent mixtures chloroform/methanol expressed in emission maxima shift and Stern–Volmer equation.



Fig. 9. Changes in fluorescence spectra of **CH-1** (3-(4-(*N*,*N*-diphenylamino)phenyl)-1-(5-methylthiophene-2-yl)prop-2-en-1-one) measured at 10^{-5} mol L⁻¹ in different solvent mixtures chloroform/acetonitrile expressed in emission maxima shift and Stern–Volmer equation.

and 8) with a large red-shift in the fluorescence maximum. The quenching of **CH-1** ($K_{SV} = 6.1 \text{ Lmol}^{-1}$) is about ten times more efficient than that of **CH-1m** ($K_{SV} = 0.49 \text{ Lmol}^{-1}$). The efficiency of quenching of **CH-1** in acetonitrile ($K_{SV} = 0.61 \text{ Lmol}^{-1}$) is substantially lower than that of methanol ($K_{SV} = 6.1 \text{ Lmol}^{-1}$) and comparable with that of **CH-1m** quenched with methanol ($K_{SV} = 0.49 \text{ Lmol}^{-1}$). Methanol is an efficient quencher of **CH-1** due to the effect of polarity and hydrogen bond formation. In contrast, acetonitrile quenches the fluorescence of **CH-1** (Figs. 3 and 9), while it enhances fluorescence of **CH-1m**. It follows that for the system **CH-1m**/chloroform/acetonitrile, a negative solvatokinetic effect is observed, while for the system **CH-1**/chloroform/acetonitrile, apact.

The lifetime of fluorescence in all media used in this study lies in the range of 0.5–6 ns. There is no obvious influence of the solvent or the polymer matrix on the lifetime of fluorescence. Therefore, fluorescence lifetime cannot be used to monitor the effect of the medium.

In comparing the spectral properties of model chalcones **CH-1m** and **CH-2m** with those of the novel series of chalcones **CH-1**–**CH-5**, it is shown that the spectral behavior exhibits a similar pattern. Surprisingly, both types of chalcones yield reasonably intense fluorescence in polymer matrices, with the greatest intensity observed in PVC.

Chalcones with a strong donating D and a strong accepting A substituents with a π -conjugated spacer have potential to be used as the material for non-linear optics (NLO), because they are non-symmetrical and exhibit polarizability and as well as hyperpolarizability.

In conclusion, the **CH-1–CH-5** series of substituted chalcones exhibits interesting spectral properties, namely intense fluorescence in chlorinated media and a specific solvent effect. The spectral properties of these molecules are preserved when doped in polymer matrices, yielding an increase in the fluorescence intensity. This property favors their potential use in sensor applications.

Acknowledgement

Authors thank grant agency VEGA for support of projects 2/ 0097/09 and 1/0660/11. This publication is the result of the project implementation: Centre for materials, layers and systems for applications and chemical processes under extreme conditions Stage II supported by the Research & Development Operational Programme funded by the ERDF.

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