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Synthesis and optical properties of new chalcones containing 4-[bis(2-hydroxyethyl)amino]phenyl fragment

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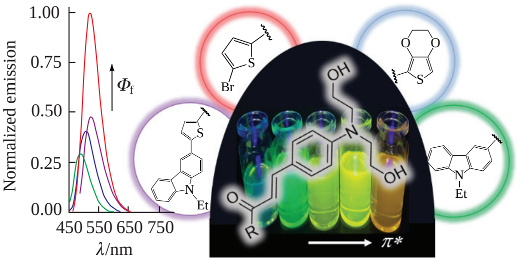
New chalcones with 4-[bis(2-hydroxyethyl)amino]phenyl fragment were obtained from 4-[bis(2-acetoxyethyl)amino]-benzaldehyde by the Claisen–Schmidt reaction. From their UV-VIS absorption and emission spectra, optical band gap values were calculated based on the Stokes shifts as well as the molar absorption coefficients and fluorescence quantum yields were estimated. The dependence of the absorption and emission maxima on solvent polarity and pH was evaluated.



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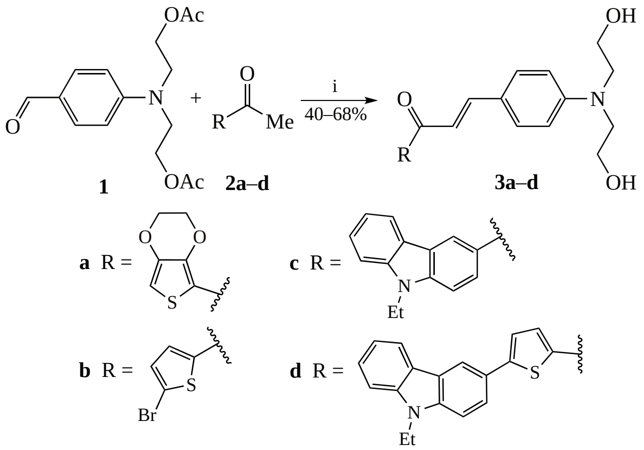
Chalcones bearing terminal electron-donating (D) and central electron-acceptor (A) groups represent a class of D–A–D′-type chromophores, in which the enone group behaves not only as an acceptor, but also provides a general extended π-conjugation, usually resulting in long-wavelength emission and large Stokes shifts.[1] Improved photophysical and nonlinear optical properties can be achieved by variation of the terminal D-fragments,[2–6] *N*,*N*-disubstituted anilines being often used as effective electron donor moieties in such structures.[7,8] It is notable that the chromophores containing terminal *N*,*N*-bis(ω-hydroxyalkyl)-aniline fragments are known to have pronounced fluorescent properties[9] and their hydroxy groups can be replaced by alkoxy ones or halogen atoms.[10]

In this work, new chalcones with terminal 4-[bis(2-hydroxyethyl)amino]phenyl moieties were designed and prepared in good yields by the Claisen–Schmidt reaction (Scheme 1). Condensation of aldehyde **1**[11] with methyl ketones **2a–d** under strong alkaline alcohol conditions was accompanied by removal of acetyl groups to provide chalcones **3a–d** containing terminal hydroxy groups. Their structures were confirmed by ^{1}H NMR spectroscopy and elemental analysis (see Online Supplementary Materials). The crystal structure of compound **3a** was additionally determined by X-ray analysis (Figure 1).[†]



Scheme 1 *Reagents and conditions*: i, KOH (10%), EtOH, room temperature, 12 h.

Chalcones **3a–d** exhibit pronounced fluorescence both in solution and in the solid state. We recorded their UV-VIS absorption and emission spectra in chloroform (Figure 2). Stokes shifts (Δλ), molar extinction coefficients (ε), band gaps (E_g^{opt}) and the fluorescence quantum yields (Φ_f) were determined from the spectral data (Table 1).[18]

[†] *Crystal data for* **3a**. $C_{19}H_{21}NO_5S$ (M = 375.43), monoclinic, space group $P2_1/c$, a = 13.394(3), b = 8.4623(19) and c = 15.555(3) Å, β = 94.12(2)°, V = 1758.6(6) Å^3, T = 295.15 K, Z = 4, d_{calc} = 1.418 g cm^{-3}, μ(MoKα) = 0.215 mm^{-1}, F(000) = 792.0. Total of 9411 reflections were collected (4179 independent reflections, R_{int} = 0.0316) and used in the refinement, which converged to wR_2 = 0.1360, GOOF = 1.037 for all the independent reflections [R_1 = 0.0514 calculated for 2929 reflections with $I > 2\sigma(I)$].

X-ray diffraction intensities were measured on an Xcalibur Ruby diffractometer (Agilent) with MoKα radiation (λ = 0.71073 Å). The empirical absorption correction was introduced by multi-scan method using the SCALE3 ABSPACK algorithm.[12] Employing the OLEX2,[13] the structure was solved with the SHELXS program[14] and refined by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms with the SHELXL software.[15] Hydrogen atoms were located from the Fourier synthesis of electron density and refined using the riding model. For some of the disordered atoms the SADI, SIMU and DELU restraints were applied.

CCDC 2094902 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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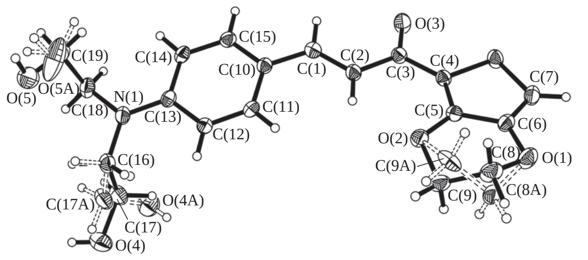

Figure 1 Molecular structure of compound **3a** with 30% probability displacement ellipsoids.

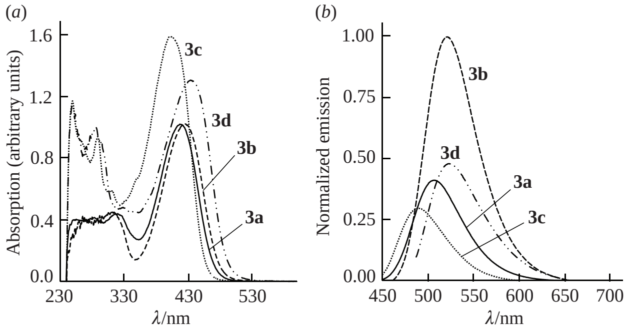

Figure 2 UV spectra of chalcones **3a**–**d** in $CHCl_3$ at 5×10^{-5} mol dm^{-3}: (*a*) absorption and (*b*) emission.

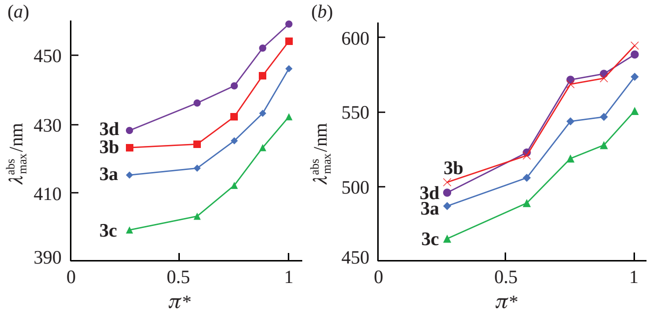

Figure 3 Plots of the Kamlet–Taft constants[19] for chalcones **3a**–**d** based on (*a*) absorption and (*b*) emission.

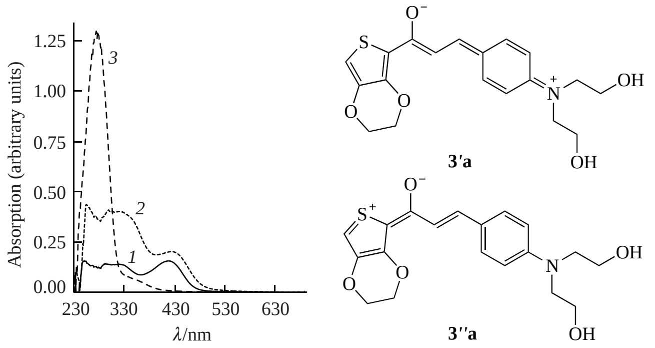

Figure 4 (*a*) Absorption spectra of chalcone **3a** in $CHCl_3$ at 2×10^{-5} mol dm^{-3} in neutral (*1*), basic (piperidine, *2*) and acidic (HCl, *3*) media. (*b*) Possible intramolecular charge transfer structures for compound **3a**.

High fluorescence quantum yields (9.8–44.3%) are inherent to all the synthesized compounds, with the largest value belonging to compound **3b** with 5-bromothiophene moiety. The thiophene unit insertion into the structure of chalcone **3c** leading to chalcone **3d** significantly increases the quantum yield and shifts the absorption edge value (λ_{onset}) towards the longwave region. The narrowest band gap (2.32 eV) was determined for chalcone **3d**, possibly due to its long conjugation chain.

The effect of solvent polarity on the optical properties was also explored. UV-VIS absorption and fluorescence spectra of chalcones **3a**–**d** were recorded in solvents of different polarity, namely, Et_2O, $CHCl_3$, MeCN, DMF and DMSO. The compounds are characterized by positive solvatochromism confirmed by the red shift with an increase in solvent polarity: on going from Et_2O to DMSO the color of the chalcone solution changes from yellow to orange, while glow under UV light alters from blue to orange. The diagrams of $\lambda_{\max}^{\text{abs}}$ *vs.* π^* and $\lambda_{\max}^{\text{em}}$ *vs.* π^* are presented in Figure 3, where π^* is the the Kamlet–Taft constant as the function of the solvent polarity. The positive solvatochromism confirms the π–π^* electronic transitions in the molecules of chalcones **3a**–**d**.

To gain a more complete understanding of the alkylamino group role in intramolecular charge transfer (ICT), the UV-VIS absorption spectra of compound **3a** were recorded in neutral chloroform as well as in the presence of HCl or piperidine (Figure 4). The addition of acid resulted in visible discoloration and disappearance of the absorption band at ~417 nm, while an increase in the intensity of the band at ~320 nm was observed. On the other hand, the addition of a base practically does not change the positions of the absorption maxima with just slight increase in their intensity.

According to the structure of the synthesized compounds, two possible processes of ICT can be distinguished giving different betaines. The first one [see Figure 4(*b*), structure **3′a**] corresponds to the ICT from alkylamino group onto the enone fragment, while in the second process the 3,4-ethylenedioxythiophen-2-yl moiety acts as a donor (structure **3″a**). Moreover, in both cases, the propenone group acts as an acceptor. According to the work,[20] protonation of the chalcone *N*,*N*-dialkylamino group disables an ICT process leading here to structure **3′a**.

In summary, the optical properties of new readily available chalcones with 4-[bis(2-hydroxyethyl)amino]phenyl moiety and other electron donor units have been investigated. The obtained compounds appeared to have high values of the molar absorption coefficient and quantum yield as well as exhibit positive solvatochromism, which makes them promising as components of materials for organic electronics.

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Table 1 Optical characteristics of chalcones **3a**–**d** in $CHCl_3$ at 5×10^{-5} mol dm^{-3}.

Compound	$\lambda_{\max}^{\text{abs}}$/nm ($\varepsilon$/ dm^3 mol^{-1} cm^{-1})	λ_{onset}/nm	$\lambda_{\max}^{\text{em}}$/nm (at λ_{ex} = 405 nm)	$\Delta\lambda$/nm	E_g^{opt}/eV^a	Φ_f (%)^b
3a	320 (8735), 417 (20250)	505	504	87	2.46	17.4
3b	312 (9817), 424 (21000)	509	521	97	2.44	44.3
3c	284 (22843), 289 (17738), 403 (31100)	491	489	86	2.53	9.8
3d	247 (26165), 248 (26165), 436 (27860)	535	522	86	2.32	24.9

[a] E_g^{opt} was calculated on the basis of the absorption red edge (λ_{onset}),[16] $E_g^{\text{opt}} = 1241/\lambda_{\text{onset}}$. [b] Fluorescence quantum yields were determined relative to 3-aminophthalimide in EtOH (Φ_f = 60%)[17] as a standard.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.03.039.

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