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Photophysical properties of 2′-hydroxychalcones of 2-cinnamoyl-4-nitro-1-naphthol series

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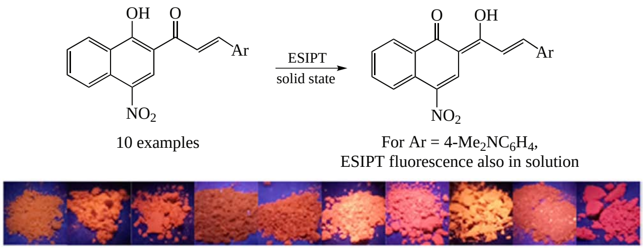
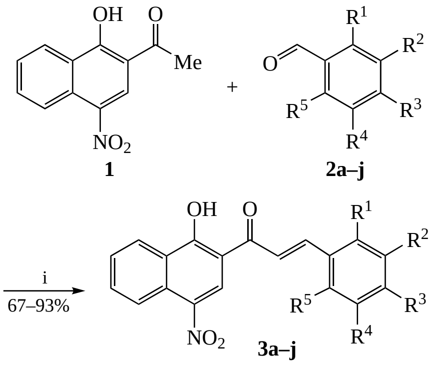
2′-Hydroxychalcones of 2-cinnamoyl-4-nitro-1-naphthol series were obtained by the condensation between 2-acetyl-4-nitro-1-naphthol and benzaldehydes. The presence of the 4-positioned nitro group in the 1-hydroxy-2-naphthyl fragment contributes to the excited state intramolecular proton transfer (ESIPT) fluorescence of these 2′-hydroxychalcones in the solid state. Compound with dimethylamino substituent, 2-(4-dimethylaminocinnamoyl)-4-nitro-1-naphthol, also demonstrates ESIPT in solution.



Keywords: 2′-hydroxychalcones, 2-cinnamoyl-4-nitro-1-naphthols, fluorescence, ESIPT, UV-Vis spectra, nitro compounds.

Chalcones are privileged scaffolds for various biologically active compounds due to their availability.[1,2] Particular attention is paid to 2′-hydroxychalcones since they serve as ligands for the synthesis of luminescent BF$_2$ complexes[3,4] and one of the examples of excited state intramolecular proton transfer (ESIPT) fluorophores.[5,6] In the course of the ESIPT photophysical process, photoexcited molecules relax their energy through tautomerism due to proton transfer. The ESIPT fluorophores are being actively studied due to their use as various sensors.[7–9] At the same time, aggregation-induced emission (AIE)[10] combines well with ESIPT, which makes it possible to combine the advantages of both processes and overcome the limitations of ESIPT dyes, which are used in the production of various solid-state emitters.[11]

In recent years, the synthesis of nitro-containing fluorophores has been developing, which is associated with the unique characteristics of this substituent.[12] This work hypothesized that the presence of a nitro group in the *para*-position relative to the hydroxy group should promote ESIPT in 2′-hydroxychalcones. Previously,[13] relative 2-(1-hydroxy-4-nitronaphtalen-2-yl)-pyridines truly demonstrated ESIPT fluorescence. Herein, with the use of condensation between 2-acetyl-4-nitro-1-naphthol **1** and a variety of benzaldehydes **2a–j** ten 2′-hydroxychalcones of 2-cinnamoyl-4-nitro-1-naphthol chemotype **3a-j** were obtained (Scheme 1), among which compounds **3b**,**d**,**f–h**,**j** are new. For this purpose, a previously described[14] method was employed using PEG-400 as a solvent.



a R^1 = R^2 = R^3 = R^4 = R^5 = H
b R^1 = MeO, R^2 = R^3 = R^4 = R^5 = H
c R^1 = R^2 = R^4 = R^5 = H, R^3 = MeO
d R^1 = R^2 = MeO, R^3 = R^4 = R^5 = H
e R^1 = R^4 = R^5 = H, R^2 = R^3 = MeO
f R^1 = R^2 = R^3 = MeO, R^4 = R^5 = H
g R^1 = R^3 = R^4 = MeO, R^2 = R^5 = H
h R^1 = R^3 = R^5 = MeO, R^2 = R^4 = H
i R^1 = R^5 = H, R^2 = R^3 = R^4 = MeO
j R^1 = R^2 = R^4 = R^5 = H, R^3 = Me$_2$N

Scheme 1 *Reagents and conditions*: i, KOH (3 equiv.), PEG-400, 100 °C, 60 min.

It is known that unsubstituted 2′-hydroxychalcone exhibits almost no fluorescence in the solid state, but the introduction of a strong electron-donating substituent into the benzene ring leads to intense red fluorescence in the condensed phase with AIE.[5] It was found that all the obtained 2′-hydroxychalcones **3a–j**, regardless of the substitution pattern in the arylidene part, did fluoresce in the solid state due to ESIPT promoted by AIE (Figure 1). The nature and position of the substituents determine the position of the emission maximum and the luminescence intensity of the resulting systems. The longest wavelength emission maximum (672 nm) in the solid state, as well as the largest Stokes shift (202 nm), were recorded for dimethylamino derivative **3j** (see Online Supplementary Materials, Table S1).

Of the entire series of 2′-hydroxychalcones **3** obtained, only system **3j** with a donor dimethylamine group fluoresces in solution; therefore, the photophysical properties were studied in

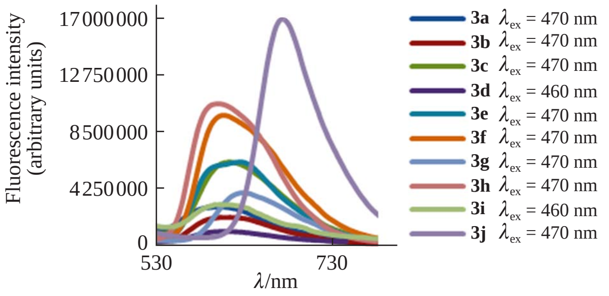


Figure 1 Emission spectra of compounds **3a–j** in the solid state.

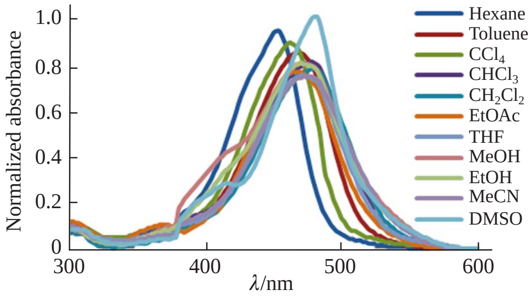
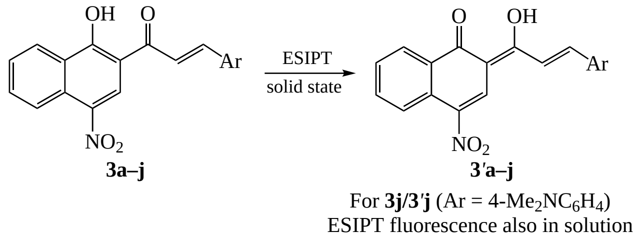


Figure 2 UV-Vis spectra in various solvents for compound **3j**.



Scheme 2

solution only using this system as an example. The UV-Vis absorption spectra for compound **3j** were measured in eleven solvents (hexane, toluene, tetrachloromethane, chloroform, dichloromethane, ethyl acetate, THF, methanol, ethanol, acetonitrile and DMSO) under neutral conditions, a sample concentration was 1×10^{-6} mol dm^{-3} (Figure 2). System **3j** is characterized by a key absorption maximum of the conjugated carbonyl group in the region from 452 nm (hexane) to 480 nm (DMSO), thus an increase in the polarity of the solvent leads to a bathochromic shift of the absorption maximum.

System **3j** fluoresces in all solvents except methanol, ethanol, acetonitrile and DMSO (Figure 3), while the nature of the solvent does not affect the position of the excitation maximum (467 nm). An increase in solvent polarity from hexane to THF leads to a bathochromic shift of the emission maximum. Photophysical properties for compound **3j** in solution are presented in Online Supplementary Materials in Table S2.

It is known that the fluorescence of dimethylamino-substituted chalcones contributes to the photophysical process of intramolecular charge transfer (ICT), and a change in the polarity of the solvent makes it possible to shift the excitation and emission maxima.[15–20] This is typical of a carbonyl group conjugated with a dimethylaminophenyl substituent. ESIPT is advantageous in low-polarity solvents due to strong hydrogen bonding compared to polar solvents, and the maximum excitation wavelength is practically independent of the polarity of the medium.[21–26] Despite the fact that the nitro group is a luminescence quencher, nitro-substituted fluorophores would exhibit luminescence predominantly in nonpolar media,[12] and ICT promotes the fluorescence of push–pull nitro aromatic systems.[27] In this case, the nitro group has high positive values of the Hammett constant and Swain–Lupton parameters.[28]

In the 2′-hyrdoxychalcones **3**, the nitro group would increase the acidity of the hydroxy group in the ground state; in the excited state, the acidity increases even greater, due to which the ESIPT process occurs in the solid state for all compounds **3**. As a result, the photophysical process ICT is implemented, which promotes the push–pull fluorescence of the nitro-substituted phototautomers **3′a**–**j** (Scheme 2). The absence of substituents in the aromatic ring in system **3a** or the presence of weak donor methoxy groups in compounds **3b**–**i** does not contribute to luminescence in solution; thus, in the solid state the nitro group contributes to luminescence in ESIPT while related systems without a nitro group do not fluoresce in the solid state.[6] Pictures of compounds **3** under sunlight and under UV irradiation are presented in Figures S23,S24.

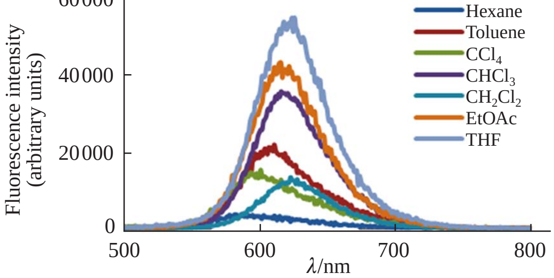


Figure 3 Emission spectra in various solvents for compound **3j** at λ_{ex} = 467 nm.

System **3j** fluoresces only as a push–pull phototautomer in solution due to cross-conjugation of the strong electron-donating dimethylamino group (which has high negative values of the Hammett constant and Swain–Lupton parameters) with the nitro and carbonyl groups. Large values of the Stokes shift in solution (123–159 nm) confirm the fluorescence of ESIPT 2′-hydroxychalcone **3j** in non-polar media under neutral conditions. Compound **3j** does not fluoresce in THF when a solution of NaOH or trifluoroacetic acid is added, which leads to blocking of the ESIPT process due to the destruction of the push–pull chromophore by the formation of a sodium salt or an acceptor of protonated dimethylamino groups. In polar solvents, the **3j** system does not luminesce due to the quenching of the fluorescence of nitro fluorophores by polar media. In the case of the **3j** system, the harmonious combination of a strong electron acceptor nitro group and a strong electron donor dimethylamino group favors fluorescence in solution, in contrast to dimethylamino-substituted 2′-hydroxychalcones without nitro group, which luminesce only in the solid state.[6]

In summary, 2′-hydroxychalcone ESIPT fluorophores of 2-cinnamoyl-4-nitro-1-naphthol series have been obtained. The presence of a nitro group in the *para*-position relative to the hydroxy group in the 1-naphthol core promotes this photophysical process in the solid state, regardless of the nature of the substituents at the aromatic ring in the target systems. Dimethylamino-substituted derivative **3j** has the largest Stokes shift in the solid state (202 nm), and is also the only representative that fluoresces in non-polar media due to the ESIPT process, as evidenced by a constant maximum excitation wavelength (467 nm) and high Stokes shift values (123–159 nm).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.09.014.

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