RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

ARTICLE

Single and double intramolecular proton transfers in the electronically excited state of flavone derivatives

Received 00th January 20xx,
Accepted 00th January 20xx

I. E. Serdiuk[a,b] and A. D. Roshal[b]

In an attempt to create a flavone derivative able to take part in the Excited State Intramolecular Double Proton Transfer (ESIDPT), we synthesized two carbonyl derivatives of 3,7-dihydroxyflavone, both containing two different proton-transfer sites as well as related carbonyl derivatives of 3-hydroxyflavone and 7-hydroxyflavone. All the examined hydroxyflavones were found to participate in the Excited State Intramolecular Proton Transfer (ESIPT). ESIPT which involves 3-hydroxyl and 4-carbonyl groups was found to have higher barrier compared to ESIPT involving 7-hydroxyl and 6/8-carbonyl fragments. According to the data presented, 3,7-dihydroxy-2-phenyl-6-(3-phenylpropanoyl)-4*H*-chromen-4-one undergoes a two-stage ESIDPT with formation of an intermediate tautomer. This kind of ESIDPT leads to a tautomeric form with an abnormally low rate of radiative deactivation of the excited state, which conditions low fluorescence quantum yield. Behavior of 3,7-dihydroxy-4-oxo-2-phenyl-4*H*-chromene-8-carbaldehyde in the electronically excited state is similar to the one of 3-hydroxyflavone derivatives, thus we conclude occurrence of a single ESIPT in this compound.

DOI: 10.1039/x0xx00000x

www.rsc.org/

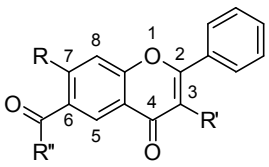
Introduction

The Excited State Intramolecular Proton Transfer (ESIPT) represents one of the fundamental reactions in photochemistry. The transformation occurs most often in compounds which contain fragments participating in keto-enol and imine-amine tautomerization reactions connected by the intramolecular hydrogen bond (IHB).[1–3] Due to its very low energetic barrier ESIPT is known to be ultrafast at various conditions, which allows it to successfully compete with other deactivation pathways of the electronically excited state, such as radiative deactivation. Followed by a reverse proton transfer in ground state, ESIPT conditions high photostability of the compounds, and specific fluorescent properties namely large red-shift of emission, which is practically insensitive to reabsorption effect and very sensitive to external hydrogen bonding. ESIPT fluorophores have various applications in optoelectronic materials[2] and as biological markers and probes.[3]

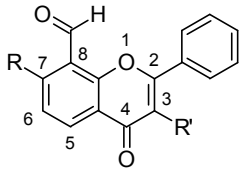
Excited State Intramolecular Double Proton Transfer (ESIDPT) is a very rare process, which involves two proton-transfer (PT) sites in one molecule. Hypothetically, ESIDPT can be as useful as ESIPT or even more, if one expects higher energy losses of the electronically excited molecule before it emits light. Various bifunctional organic compounds were designed and synthesized, including derivatives of salicylic acid,[4] oxazoles[5–7], and chromones[8–11], and subsequently investigated from the point of view of ESIDPT by steady-state and time-dependent absorption and fluorescent spectroscopies, as well as *ab initio* and semiempirical computational techniques. Generally, it was found that after excitation these compounds undergo single ESIPT, while occurrence of ESIDPT is much less favorable. It should be noticed that so far scientists' attention was mostly paid to compounds with axial symmetry and the same two PT sites.

In this article we present synthetic routine and results of spectroscopy investigations of two novel asymmetric flavone derivatives: 3,7-dihydroxy-2-phenyl-6-(3-phenylpropanoyl)-4*H*-chromen-4-one (**1a**) and 3,7-dihydroxy-4-oxo-2-phenyl-4*H*-chromene-8-carbaldehyde (**2a**) (Chart 1). Both of the investigated compounds contain two different PT sites able to

Chart 1 Canonical structures of **1a-d** and **2a-d** with numbering of atoms indicated



R, R' = OH, OH (**1a**);
R, R' = OH, H (**1b**);
R, R' = OCH_3,OH, (**1c**);
R, R' = OCH_3, H (**1d**);
R'' = $(CH_2)_2Ph$



R, R' = OH, OH (**2a**);
R, R' = OH, H (**2b**);
R, R' = OH, OCH_3 (**2c**);
R, R' = OCH_3, H (**2d**).

[a] *Department of Chemistry, University of Gdańsk, Gdańsk, 80-308 Poland. E-mail: illia.serdiuk@gmail.com*
[b] *Institute of Chemistry, V. N. Karazin Kharkiv National University, Kharkiv, 61022 Ukraine*

† Electronic Supplementary Information (ESI) available: for 1H-NMR and mass spectra of new compounds see DOI: 10.1039/x0xx00000x

participate in keto-enol tautomerization reactions. The first site is represented by a hydroxyl group in position 7 and a carbonyl fragment in *ortho* position: 3-phenylpropanoyl in position 6 (**1a**) and formyl in position 8 (**2a**). The second site includes hydroxyl and carbonyl group in positions 3 and 4, respectively. These fragments are similar to PT sites of *ortho*-hydroxybenzaldehyde and flavonol (3-hydroxy-2-phenyl-4*H*-chromen-4-one) derivatives, both known to participate in ESIPT.[12] Compounds **1a** and **2a** can possibly exist in 4 tautomeric forms (Charts 2 and 3), transforming one to another *via* intramolecular proton transfer reactions. Forms $\mathbf{T_6}$ (**1a**) and $\mathbf{T_8}$ (**2a**) can be produced *via* PT involving hydroxyl groups in position 7, $\mathbf{T_4}$ can appear in the result of PT involving hydroxyl groups in position 3, and **DT** can be formed in the result of double PT. The related compounds 7-hydroxy-2-phenyl-6-(3-phenylpropanoyl)-4*H*-chromen-4-one (**1b**), 3-hydroxy-7-methoxy-2-phenyl-6-(3-phenylpropanoyl)-4*H*-chromen-4-one (**1c**), and 7-hydroxy-4-oxo-2-phenyl-4*H*-chromene-8-carbaldehyde (**2b**), 7-hydroxy-3-methoxy-4-oxo-2-phenyl-4*H*-chromene-8-carbaldehyde (**2c**), which contain only one hydroxyl group were used as models for investigation of single PT reactions as well as properties of $\mathbf{T_6}$, $\mathbf{T_4}$, and $\mathbf{T_8}$, respectively. Compounds 7-methoxy-2-phenyl-6-(3-phenylpropanoyl)-4H-chromen-4-one (**1d**) and 7-methoxy-4-oxo-2-phenyl-4*H*-chromene-8-carbaldehyde (**2d**), which do not contain hydroxyl groups, were used for investigations of the target compounds' behavior in the absence of PT reactions. Taking into account that **1a-c** and **2a-c** can possibly exist in anionic forms besides neutral ones, spectral behavior of these compounds was investigted in the presence of DBU. This helped to define origin of absorbance and fluoresccence of **1a** and **2a**.

RESULTS AND DISSCUSSION

Synthesis

In an attempt to obtain a derivative of 3,7-dihydroxyflavone with a carbonyl fragment in position 6 we firstly made an attempt to synthesize 6-acetyl-3,7-dihydroxy-2-phenyl-4*H*-chromen-4-one starting from the commercially available 1,1'-(4,6-dihydroxy-1,3-phenylene)bisethanone. However, reaction of the latter with equimolar quantity of benzaldehyde and other aldehydes in alkalinic media led to a mixture of mono- and dichalcone derivatives,[13] which were difficult to separate. In order to eliminate formation of the undesired dichalcone product, 1,1'-(4,6-dihydroxy-1,3-phenylene)bisethanone derivatives were designed with subtituent(s) in one of the α positions (**5**, Scheme 1). Most probably, 1-(5-acetyl-2,4-dihydroxyphenyl)-2,2-dimethylpropan-1-one (**5b**) would react with only one equivalent of benzaldehyde and give a monochalcone derivative. Preparation of **5b** was, however, problematic: the pivaloyl fragment of 1-(2,4-dihydroxyphenyl)-2,2-dimethylpropan-1-one (**4b**), prepared by reaction of resorcinol with pivaloyl chloride in hot boron trifluoride etherate was unstable in the presence of Lewis acids[14] utilized in further acylation step and only 1-(3-acetyl-2,4-dihydroxyphenyl)-2,2-dimethylpropan-1-one (**6b**) was isolated in a low yield. 1-(2,4-Dihydroxyphenyl)-3-phenylpropan-1-one (**4a**, Scheme 1) on the other hand, obtained in the same conditions from resorcinol and 3-phenylpropionic acid, gave the desired 1-(5-acetyl-2,4-dihydroxyphenyl)-3-phenylpropan-1-one (**5a**) in the reaction with acetic anhydride in the presence of $ZnCl_2$ in a good yield (51%) and minor impurity of 1-(3-acetyl-2,4-dihydroxyphenyl)-3-phenylpropan-1-one (**6a**) (8%), which was separated by column chromatography. **5a** reacted with equimolar quantity of benzaldehyde in aqueous N-methylpyrrolidone (NMP) in the presence of KOH leading to the chalcone derivative **1e** in 48% yield. When **1e** was treated with H_2O_2 in MeOH in the presence of NaOH (Algar-Flynn-Oyamada reaction conditions) the desired **1a** was not identified in the reaction mixture. This phenomenon can be explained by existence of **1e** at such conditions in doubly deprotonated form, as in the case of (2*E*)-1-(2,4-dihydroxyphenyl)-3-phenylprop-2-en-1-one,[15] which does not transform to the corresponding 3-hydroxyflavone derivative. **1e** was then converted to the flavone derivative **1b** in hot DMSO in the presence of I_2 (yield 53%), which after protection of the hydroxyl group by

Chart 2 Structures of possible tautomeric forms (**N, T_4, T_6,** and **DT**) of **1a** (Chart 1)

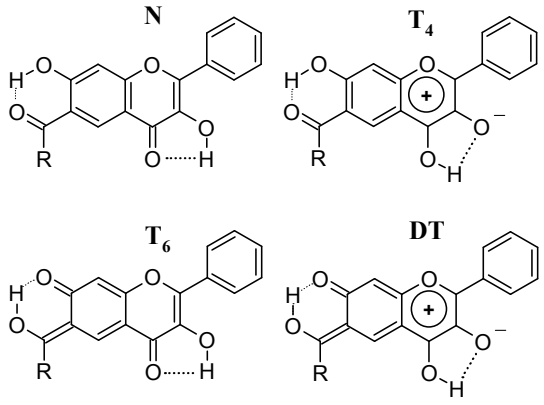
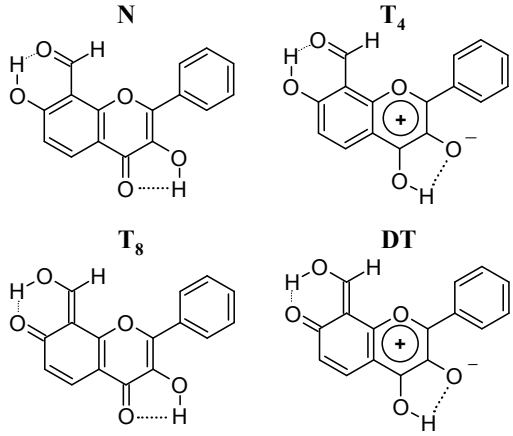


Chart 3 Structures of Possible Tautomeric Forms (**N, T_4, T_8,** and **DT**) of **2a** (Chart 1)

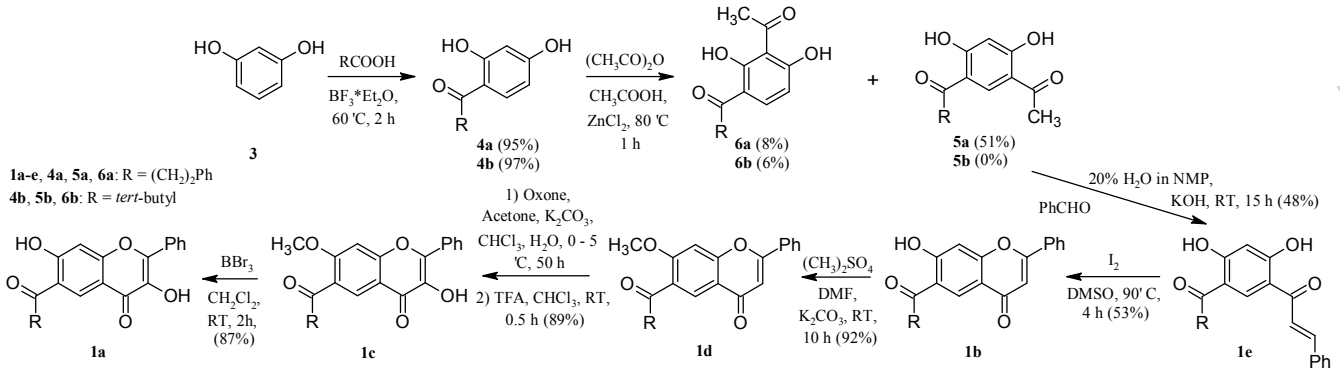


dimethylsulfate was oxidized with dimethyldioxirane, generated *in situ* by Oxone© and acetone in water-chloroform (1:1, v:v) suspension at 0 – 5 °C. The obtained epoxide of **1d** was then hydrolyzed by TFA without isolation, what produced 3-hydroxyflavone derivative **1c** in 91% yield. Finally, **1a** was obtained by reaction of **1c** with boron tribromide in CH_2Cl_2 (yield 87%). The applied synthetic route allowed for obtaining not only the target compound **1a**, but also the relative ones **1b**, **1c** and **1d**, which were used as models in the further investigations.

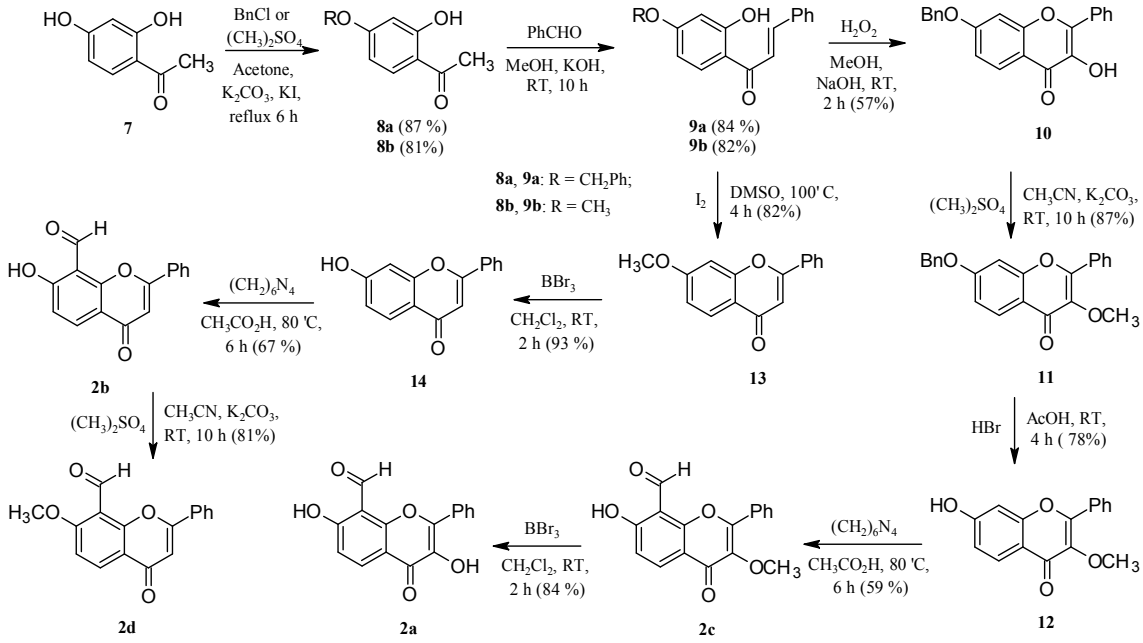
For synthesis of **2a** (Scheme 2), 3-hydroxy-7-benzyloxyflavone (**10**) was chosen as a precursor, synthesized from commercially available 1-(2,4-dihydroxyphenyl)ethanone (**7**), according to the procedure described earlier:[15] **7** was treated with benzyl chloride, leading to **8a**, then converted to chalcone derivative **9a** with benzaldehyde in basic NMP, which was then oxidatively cyclized in basic MeOH in the presence of H_2O_2 (Algar-Flynn-Oyamada reaction). **10** was subsequently alkylated with dimethylsulfate, followed by cleavage of benzyl group in HBr solution in acetic acid to yield **12**. Treatment of **12** with excess of hexamethylenetetramine in boiling glacial acetic acid (Duff reaction)[16] gave **2c** in 59% yield. Finally, **2a** was obtained by reaction of **2c** with boron tribromide. Relative compound **2b** was prepared from 7-hydroxyflavone (**14**) in the Duff reaction conditions in 67% yield. **14** was prepared starting from **7**, using methyl protection for hydroxyl group *via* stages described in [17]. **2d** was obtained from **2b** by methylation with dimethylsulfate in CH_3CN.

Steady state electronic absorption spectroscopy

The compounds investigated exhibit absorption in methylcyclohexane in the 250 – 400 nm region (Table 1, Fig. 1a and b), which supposedly corresponds to **N** form (Chart 2 and 3), usually the most stable in the ground state of flavone. Spectral properties of anionic forms of the compounds were



Scheme 1 Synthesis of **1a-d**



Scheme 2 Synthesis of **2a-d**

Table 1 Spectral parameters of the compounds investigated in methylcyclohexane at 298 and 77 K[a]

Compd	c_{DBU} (M)	T (K)	λ_{abs} (nm)	λ_{ex} (nm)	λ_{fl} (nm)	ν_{St} (cm^{-1})	Compd	c_{DBU} (M)	T (K)	λ_{abs} (nm)	λ_{ex} (nm)	λ_{fl} (nm)	ν_{St} (cm^{-1})
1a		298	352	348	562	10940	**2a**		298	339	337	551	11530
		77		378	563	8690			77		335	415	5750
											338	535	10890
	1×10^{-4}	298	430	-	-	-		1×10^{-4}	298	375[c]	-	-	-
		77		446	543	4000			77		-	-	-
	1×10^{-3}	298	392	-	-	-		1×10^{-3}	298	402	402	565	7180
		77		446	543	4000			77		404	541	6270
1b		298	324	325	546	12450	**2b**		298	336	338	505	9780
		77		325	530	11900			77		337	484	9010
	1×10^{-4}	298	412	405	526	5680		1×10^{-4}	298	392	390	518	6320
		77		404	489	4300			77		392	485	4900
1c		298	334	336	542	11320	**2c**		298	331[c]	332[c]	513	10630
		77		337	424	6090			77		332[c]	481	9330
				338	540	11070							
	1×10^{-4}	298	413	415	502	4180		1×10^{-4}	298	381	381	505	6480
		77		-	-	-			77		382	475	5130
1d		298	295	-	-	-	**2d**		298	306	-	-	-
		77			496[b]				77			538[b]	

[a] c_{DBU} – molar concentration of DBU; λ_{abs} – position of the maximum of the long-wavelength band in absorption spectra; λ_{ex} – position of the maximum of the long-wavelength band in fluorescence excitation spectra; λ_{fl} – position of the maximum in the fluorescence emission spectra (for bands with vibrational modes λ_{fl} represents center-weighted position of a band); ν_{St} – Stokes shifts, calculated as a difference between $(\lambda_{ex})^{-1}$ and $(\lambda_{fl})^{-1}$. [b] Phosphorescence maxima. [c] Maxima of the long-wavelength bands obtained by separation.

investigated in DBU solutions. Positions of the long-wavelength bands of neutral and charged species depend on the nature and position of substituents.

The long-wavelength absorption bands of **1d** and **2d** are positioned at 295 and 306 nm, respectively. The bands of **1b** and **2b**, which contain IHB, are shifted batochromically to 324 and 336 nm, respectively (Table 1, Fig. 1a and b). Compared to 7-hydroxyflavone, whose absorption band at the same conditions is positioned at 291 nm,[18] **1b** and **2b** exhibit batochromic shift, caused by polarization of the hydroxyl group at position 7 due to IHB. Compared to **1b,** the long-wavelength absorption band of **1c** is batochromically shifted to 334 nm (Table 1, Fig. 1a), which is caused by influence of the hydroxyl group in position 3. Similar spectral effect was observed previously in the case of 3-hydroxyflavone derivatives.[19] **2c** exhibits complex absorption spectra (Fig. 1b), its long-wavelength band appears in the 325–350 nm range, similarly to 2b. Methoxy group at position 3 thus has minimal effect on the S_0-S_1 transition energy, which is most probably due to high value of the torsion angle between chromone moiety and methoxy group, as was observed in the case of 3-methoxyflavone derivatives.[20]

1a (352 nm) and **2a** (339 nm) exhibit the most batochromically shifted absorption among the compounds investigated (Table 1, Fig. 1a and b). 3,7-Dihydroxyflavone in the same conditions exhibits absorption at 337 nm (unpublished data), close to that of **2a**. Thus the carbonyl substituent in position 6 affects the S_0-S_1 transition energy of 3,7-dihydroxyflavone much considerably than in position 8.

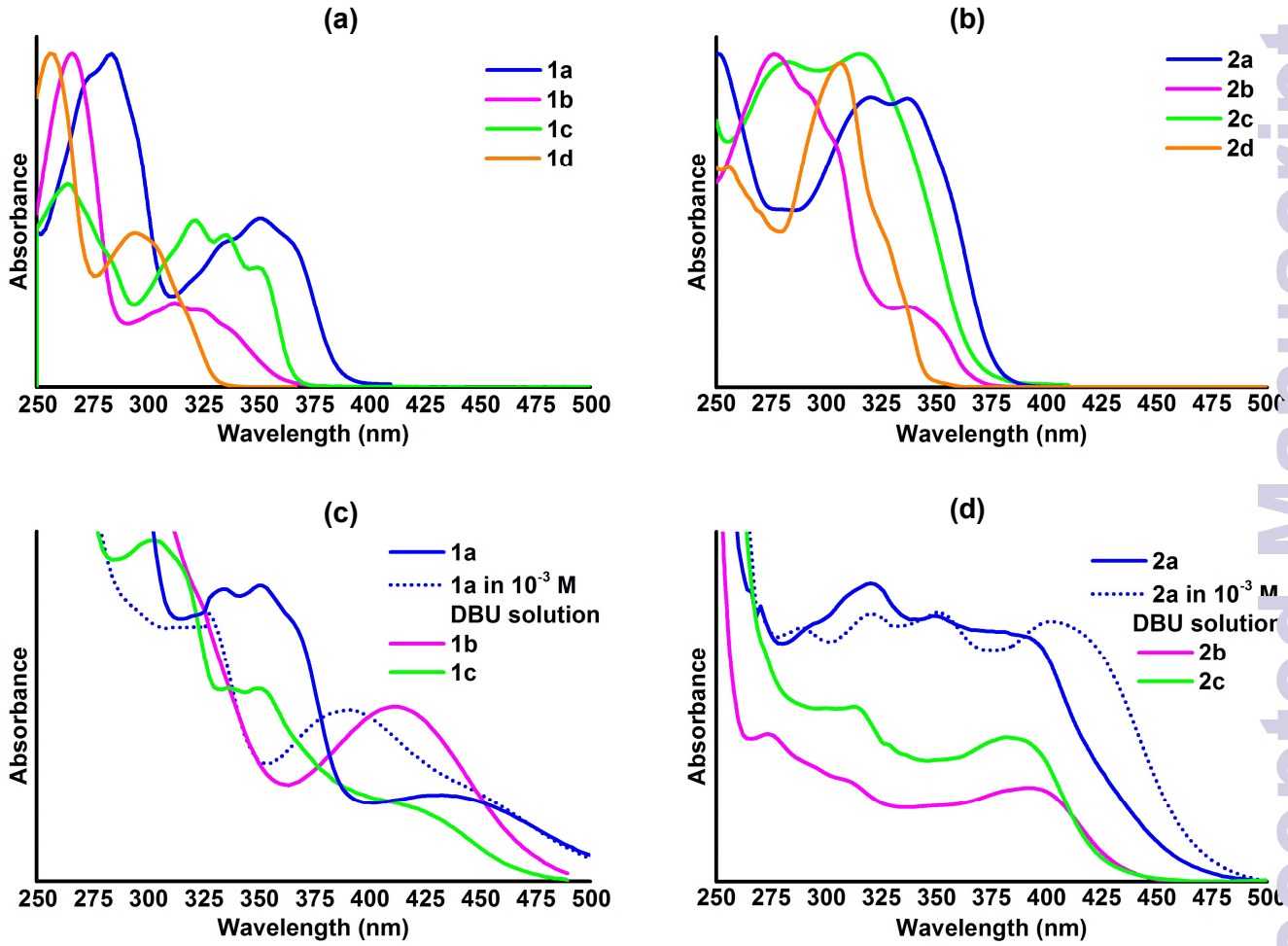


Fig. 1 Steady-state absorption spectra at 298 K: **1a-d** (**a**) and **2a-d** (**b**) in methylcyclohexane; **1a-c** (**c**) and **2a-c** (**d**) in 10^{-4} M DBU solution in methylcyclohexane

The long-wavelength absorption bands of the anionic species of the hydroxyflavones investigated, which appear in DBU solutions, are considerably shifted batochromically relative to the neutral ones. Monoanionic species $\mathbf{A_7}$ (Chart 4), formed by deprotonation of the hydroxyl group at position 7 of **1b** and **2b**, absorb light at 412 and 392 nm, respectively. Compared to anion of 7-hydroxyflavone[18] this corresponds to the batochromic shift values of 3240 and 2000 cm^{-1}, respectively, due to electron-withdrawing effect of the carbonyl substituents. More than 1.5 lower value of the shift in the case of **2b** compared to **1b** indicates less effective stabilization of $\mathbf{A_7}$ by the carbonyl substituent in position 8 compared to position 6. Absorption maximum of the similar species of **2c** is shifted hypsochromically to 381 nm relative to **2b**, which indicates that due to electron-releasing effect methoxy group at position 3 increases the S_0-S_1 transition energy in $\mathbf{A_7}$. The long-wavelength absorption band of the monoanionic species $\mathbf{A_3}$, formed by deprotonation of the hydroxyl group at position 3 of **1c**, is centered at 413 nm (Chart 4).

A monoanionic form of **1a**, which appears in 10^{-4} M DBU solution, absorbs light at 430 nm (Table 1, Fig. 1c). Deprotonation of the second hydroxyl group leads to a 2680 cm^{-1} hypsochromic shift. On the other hand, monoanionic

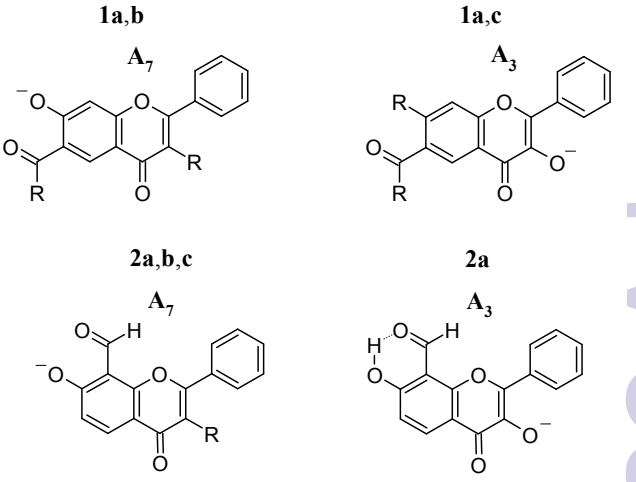


Chart 4 Possible monoanionic forms of **1a-c** and **2a-c**

species of **2a** absorb light at 375 nm, while further deprotonation leads to a 1790 cm^{-1} batochromic shift (Table 1, Fig. 1d). The described differences in the spectral behavior of anions of **1a** and **2a** may indicate different order of deprotonation of hydroxyl groups and formation of different monoanionic forms (Chart 4).

Steady state fluorescence emission and excitation spectroscopy

Since **1a** and **2a** have two different PT sites which can participate in ESIPT simultaneously, the experimental investigations of their electronically excited state behavior are complicated. In order to understand the features of each PT site, we investigated the related compounds. **1d** and **2d** enabled investigation of the **N*** forms properties in the absence of IHB and ESIPT. **1b** and **2b**,**c** provided information concerning behavior of hydroxyl group in position 7 with *ortho*-carbonyl substituents as well as spectral features of $\mathbf{T_6}$* and $\mathbf{T_8}$* forms, respectively. **1c** enabled investigation of ESIPT involving hydroxyl and carbonyl group in positions 3 and 4, respectively. Fluorescent behavior of **1b,c** and **2b,c** in DBU solutions provided information concerning features of monoanionic forms $\mathbf{A_7}$* and $\mathbf{A_3}$* as well as deprotonation order of hydroxyl groups in **1a** and **2a**. The conclusions on the excited state behavior of **1a** and **2a** were thus made based on a comparison of their spectral features with the related compounds.

Fluorescent properties of 1b,d and 2b,c,d. Fluorescence of **1d** and **2d** is observed at neither 298 K nor 77 K. Phosphorescence of the compounds is registered at 77 K (Table 1, Fig. S1), which indicates efficient intersystem crossing in their excited state. Based on previous investigations of 7-hydroxyflavone[18] the phenomenon can be due to closeness of the lowest excited states of π-π* and n-π* nature.

At 298 K all the hydroxyflavones investigated are characterized by a single-band fluorescence spectra with the abnormally large Stokes shifts (Table 1, Fig. 2 and S2) indicating occurrence of efficient ESIPT. **1b** and **2b**,**c** exhibit broad emission bands centered at 546, and 505, 513 nm, respectively (Table 1, Fig. 2c,d,f) with fluorescence quantum yields less than 1%. In contrast to **1b**, vibronic structure of the **2b** and **2c** bands is visible. When the **1b** and **2b**,**c** solutions are cooled to 77 K, their fluorescence intensity increases, maxima shift to 530 and 484, 481 nm, respectively, and bands become narrower (Table 1, Fig. 2c,d,f).

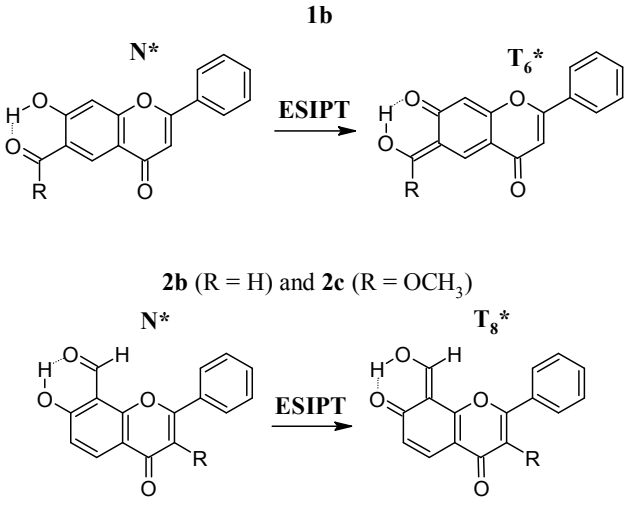
Fluorescence of anionic forms $\mathbf{A_7}$* appear in DBU solutions of **1b** and **2b**,**c** with maxima near 526 and 518, 505 nm respectively. At 77 K their intensity increases and maxima shift to 489 and 485, 475 nm, respectively. In contrast to neutral solutions, vibronic structure is not observed in the case of the **2b**,**c** fluorescence in DBU solutions.

As can be concluded from the 3D steady-state fluorescence spectra and similarity of the long-wavelength bands in absorption and fluorescence excitation spectra at 298 K and 77 K (Table 1, Fig. S2c,d,f and S3c,d,f), the described emission of **1b** and **2b**,**c** in neutral solutions originates from **N** species in the ground state. Generally, shape of the emission bands as well as spectral changes under cooling of neutral solutions differ from those of DBU ones, which evidences that fluorescence of anionic forms is absent at such conditions. Most probably, the $\mathbf{T_6}$* and $\mathbf{T_8}$* species (Chart 2, 3), respectively, produced *via* ESIPT in **N*** after excitation (Scheme 3), are responsible for fluorescence of these compounds in methylcyclohexane.

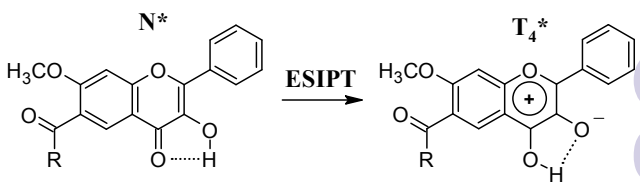
Neither **1b** nor **2b**,**c** exhibit phosphorescence at 77 K. As was discussed above, the long-wavelength absorption bands of **1b** and **2b**,**c** are considerably red-shifted compared to **1d** and **2d** due to IHB. This can emphasize decrease of the π-π* state energy, which is more sensitive to changes in electronic structure of chromofores compared to the n-π* one. Increase of the gap between π-π* and n-π* states prevents intersystem crossing and appearance of phosphorescence and should moreover enhance fluorescence of the **N*** species, as in the case of 4'-methoxyflavone.[21] Absence of the **N*** fluorescence neither at 298 K nor 77 K evidences very fast ESIPT in **1b** and **2b**,**c**.

Fluorescent properties of 1c. Compound **1c** exhibits the most intensive fluorescence among the investigated series. At room temperature, its single emission band is observed at 542 nm (Table 1, Fig. 2e and S2e), fluorescence excitation spectrum is close to the absorption one (Table 1, Fig. S3e). Under cooling to 77 K the band's vibronic structure becomes apparent, while its intensity decreases sharply (Table 1, Fig. 2e). These changes are accompanied by appearance of a fluorescence emission band at 424 nm. The excitation spectra, recordered at these bands maxima are close to absorption spectra at 298 K.

Very low intensive fluorescence of anion $\mathbf{A_3}$* appear at 502 nm in DBU solutions of **1c** at 298 K (Table 1, Fig. 2e). At 77 K



Scheme 3 ESIPT in **1b** and **2b,c**



Scheme 4 ESIPT in **1c**

no fluorescence of **1c** in DBU solutions was detected.

Most probably, the T_4* species, produced *via* ESIPT in **N*** after excitation (Scheme 4), are responsible for the long-wavelength fluorescence emission in neutral solutions of **1c** both at 298 and 77 K. The observed blue-shifted emission at 77 K most probably originates from **N*** produced by direct excitation. Appearance of the **N*** fluorescence under cooling indicates existence of energetic barrier for the ESIPT reaction **N*** $\rightarrow$ T_4*, previously observed for 3-hydroxyflavone and relative compounds.[22,23] The substituents' effect can cause stabilization of the **N*** form in the case of **1c** compared to 3-hydroxyflavone, what can explain increase of the **N*** $\rightarrow$ T_4* reaction barrier. The A_3* fluorescence, which was assumed to appear in solutions of 3-hydroxyflavone in hydrocarbons at 77

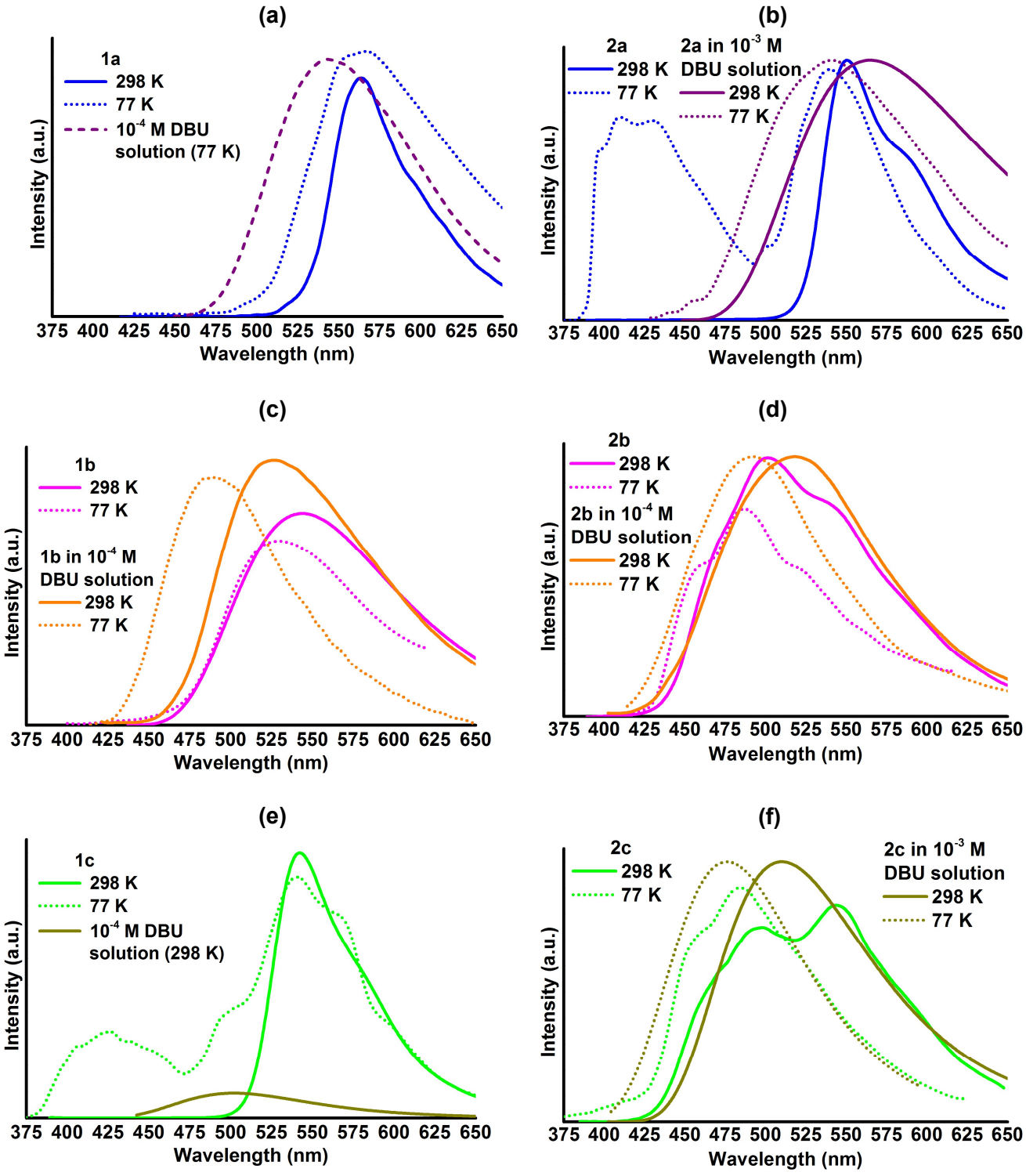
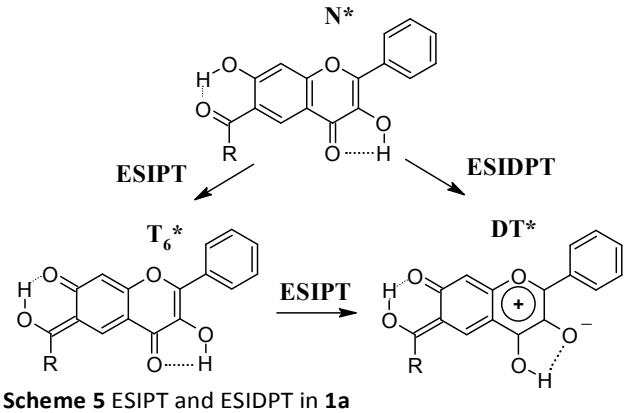
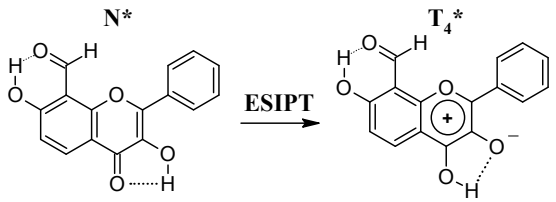


Fig. 2 Steady-state fluorescence spectra of **1a** (**a**), **2a** (**b**), **1b** (**c**), **2b** (**d**), **1c** (**e**) and **2c** (**f**) in methylcyclohexane at 298 K and 77 K.



Scheme 5 ESIPT and ESIDPT in **1a**



Scheme 6 ESIPT in **2a**

K due to the presence of impurities of protic substances,[24] can not have noticeable impact in fluorescence of **1c** due to very low emission intensity.

Fluorescent properties of 1a. The compound fluoresces at 562 nm with a very low quantum yield – 0.11% (Table 2, Fig. 2a). Based on 3D fluorescence spectra (Fig. S2a) and comparison of the absorption and fluorescence excitation spectra (Fig. S3a), the emission originates from the **N** species in the ground state. When the **1a** solution is cooled to 77 K, its fluorescence band becomes broader with no significant change of the maxima position (Table 1, Fig. 2a), while its intensity rises 1.5 times. The fluorescence excitation maxima shifts to 378 nm, demonstrating a 2280 cm^{-1} batochromic shift compared to 298 K (Table 1, Fig. S3a). No additional emission in the 400–475 nm region was observed.

1a demonstrates intensive fluorescence at 543 nm in DBU solutions under cooling to 77 K (Fig 2a). The excitation spectrum has maxima at 446 nm, which resembles absorption spectrum of monoanionic form, observed at 298 K (Table 1, Fig. S3a). The fluorescence behavior of the **1a** monoanionic species at 77 K is similar to **1b**, but not **1c**, which can indicate that $\mathbf{A_7}$* species are responsible for the **1a** fluorescence at 77 K in the presence of DBU. The excitation spectrum of **1a** in neutral solution at 77 K matches absorption/excitation of neither its $\mathbf{A_7}$* species nor $\mathbf{A_3}$* ones of **1c**. Dianionic species, which are present in the 10^{-3} M DBU solution, are either non-fluorescent or have low fluorescence intensity relative to $\mathbf{A_7}$* species at 298 and 77 K. Formation of the doubly charged dianion in neutral methylcyclohexane should be extremely unfavorable. Based on these data we conclude that deprotonation is not the reason of the batochromic shift in the excitation spectrum of **1a** at 77 K.

Similarly to 3,7-dihydroxyflavone,[19,25] in the ground state of **1a** hydroxyl groups and carbonyl group at position 4 should be of low acidity and basicity, respectively, thus formation of tautomeric species $\mathbf{T_3}$ is unfavorable. As follows from acid-base properties of acetophenones,[26] basicity of the carbonyl group at position 6 of **1a** should be also very low, thus formation of $\mathbf{T_6}$ as well as **DT** in the ground state is unfavorable too. Taking into account that concentrations of the investigated solutions of **1a** were below 5×10^{-5} M, formation of aggregates is of low probability. These considerations support the mentioned above conclusion on origination of **1a** fluorescence from **N** species in the ground state. Hypothetically, the mentioned above batochromic shift of the excitation spectra of **1a** under cooling can be explained by strengthening of both of its hydrogen bonds, which can decrease relative energy of the excited Franck-Condon state and thus decrease the S_0-S_1 transition energy of **N** species.

Based on the data presented, one can notice the basic difference in the spectral behavior of **1a** and **1c** such as much lower fluorescence quantum yield (Table 2), absence of the **N*** emission at 77 K in the case of **1a** and different behavior of monoanionic forms (Fig 2a,e). This can indicate that **1a** does not exist in $\mathbf{T_4}$* form. Compared to **1b**, **1a** has a tenfold lower fluorescence quantum yield, however, behavior of both compounds at 77 K is generally similar in both neutral and DBU methylcyclohexane solutions (Fig 2a,c). These observations can indicate that hydroxyl group at position 7 has prior influence on the **1a** properties due to its higher acidity compared to hydroxyl group at position 3. The fluorescence of **1a** in the neutral solutions can be, thus, generated by either $\mathbf{T_6}$*, **DT*** or both, but not the $\mathbf{T_4}$* form (Scheme 5).

Fluorescent properties of 2a. At 298 K **2a** fluoresces at 551 nm with 1.6% quantum yield (Table 2). Based on 3D fluorescence spectra (Fig. S2b) and comparison of the absorption and fluorescence excitation spectra (Fig. S3b), the emission originates from the **N** species in the ground state. At 77 K the fluorescence band undergoes a hypsochromic shift to 535 nm, accompanied by rise of a band at 415 nm (Table 1, Fig. 2b), most probably emitted by **N*** species. The excitation spectra measured at these bands are similar to that at 298 K (Table 1, Fig S3b).

Monoanionic forms of **2a**, which according to the described above absorption spectra appear in the 10^{-4} M DBU solution, are fluorescent neither at 298 K nor 77 K. This phenomenon, in contrast to intensive fluorescence of the $\mathbf{A_7}$* forms of **2b** and **2c**, can indicate that hydroxyl group of position 3 of **2a** is deprotonated first, producing $\mathbf{A_3}$* form. Different from **1a** deprotonation order of hydroxyl groups in **2a** can indicate that acidity of the hydroxyl group at position 7 is for less extent affected by the carbonyl substituent at position 8 than at position 6. This conclusion correlates with the discussed above influence of the substituents on the $\mathbf{A_7}$ spectral properties of **1b** and **2b**.

Broad fluorescence band appear in spectrum of **2a** in the 10^{-3} M DBU solution at 565 nm at 298 K and shifts to 541 nm at 77 K. According to the excitation spectrum the emission originates from dianionic form.

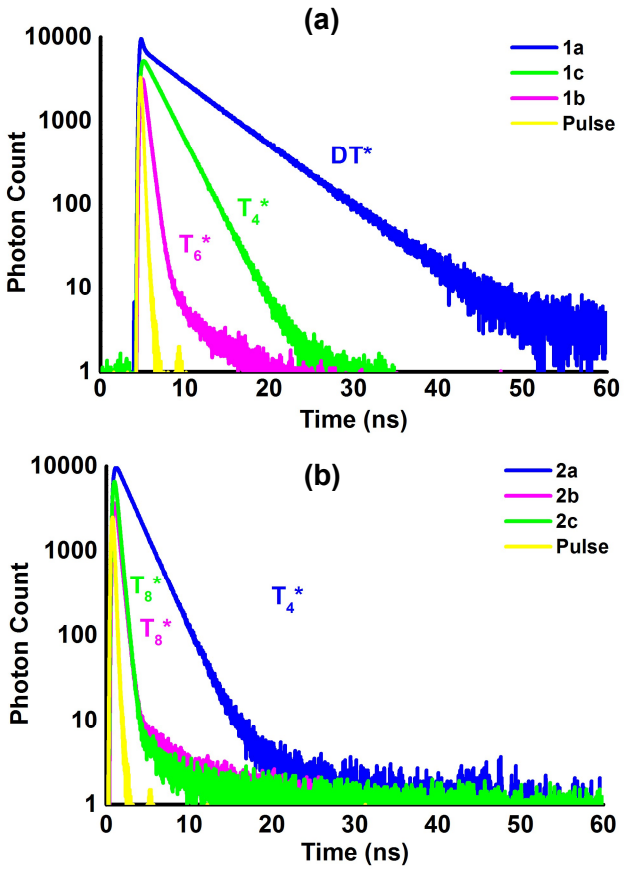


Fig. 3 Fluorescence decays of **1a-c** (**a**) and **2a-c** (**b**) in hexane at 298 K recorded at the fluorescence maxima

Compared to **2b** and **2c**, in neutral solutions **2a** has a few times higher fluorescence quantum yield and exhibits **N*** fluorescence emission at 77 K, which indicates absence of $\mathbf{T_8}$* form in the excited state of **2a**. Even though a model compound for $\mathbf{T_4}$* form of **2a** was not available in this study, spectral properties including positions of the fluorescence emission and excitation maxima together with behavior at 77 K of **2a** and **1c** are very similar. The fluorescence of **2a** can be, thus, generated by either $\mathbf{T_4}$* (Scheme 6), **DT*** forms or both, but not the $\mathbf{T_8}$*, as hydroxyl group at position 3 has prior influence on the **2a** properties.

Time-Resolved Fluorescence Spectroscopy

Fluorescence decays of **1b** and **2b**,**c** in hexane are biexponential without rise components in the investigated time domain. The major components have lifetimes of less than 0.5 ns (Table 2, Fig. 3a and b), while the minor ones have very low intensity and lifetimes near 1.5 – 3.0 ns. Precise determination of the latter components' lifetimes is complicated. The major components most probably characterize decay of $\mathbf{T_6}$* and $\mathbf{T_8}$* species, respectively. Appearance of the minor components may indicate co-existence of $\mathbf{T_6}$* and $\mathbf{T_8}$* species in two isomers, different as regards the PT sites conformations. Based on the assumption that the main deactivation pathway of the **N*** forms of **1b** and **2b**,**c** is ESIPT, we calculated rates of radiative (k_f) and non-radiative deactivation (k_d) for their $\mathbf{T_6}$* and $\mathbf{T_8}$* forms (Table 2) using the major components' lifetimes. According to the obtained values, non-radiative processes with a summary rate of $2.1 - 2.7\times10^9$ s^{-1} are the main deactivation pathway for both types of forms. $\mathbf{T_6}$* form of **1b** is characterized by higher k_f value compared to $\mathbf{T_8}$* of **2b**,**c** which conditions higher quantum fluorescence yield of the former (Table 2).

In hexane at 550 nm, **1c** exhibits a monoexponential decay of fluorescence with 2.19 ns lifetime (Table 2, Fig. 3a) and no rise component in the investigated time domain, corresponding to deactivation of the $\mathbf{T_4}$* species. The k_f value of $\mathbf{T_4}$*, calculated based on the assumption that the main deactivation pathway of the **N*** form is ESIPT, is the highest among the compounds investigated, what together with low k_d value conditions the highest quantum yield of fluorescence (Table 2).

Fluorescence decay of **1a** at 560 nm differs from the other compounds investigated: it contains two decay components with lifetimes of ~ 25 ps and 5.3 ns (Table 2, Fig. 3a). Due to a drastic difference in the lifetimes, the long-living species have the overwhelming impact in **1a** fluorescence quantum yield (94%), which enables estimation of their k_f and k_d values (Table 2). The obtained k_f value is extremely low and unique among the ones of **1b** and **1c**, which implies that the long-living species are neither $\mathbf{T_4}$* nor $\mathbf{T_6}$*. As formation of $\mathbf{T_4}$* species in the excited state of **1a** was suggested to be unlikely according to the steady-state fluorescence investigations, we consider that the long decay corresponds to **DT*** and the fast decay corresponds to $\mathbf{T_6}$*. The observed broadening of the **1a** fluorescence emission spectra at 77 K (Fig. 2a) can thus be explained by co-existence of $\mathbf{T_6}$* and **DT*** forms. Most probably, that the $\mathbf{T_6}$* species are produced by ultrafast ESIPT with no or very small energetic barrier, similarly to **1b**, since **N*** emission is observed even at 77 K. Considering similar structure and close spectral properties of $\mathbf{T_6}$* forms of **1a** and **1b**, their rates of radiative and non-radiative deactivation should be of the same ranges. Much faster decay of the $\mathbf{T_6}$* species of **1a** can indicate existence of an additional efficient dark deactivation pathway, which we suppose is ESIPT resulting in **DT***. If one suggests that the main excited state deactivation route of $\mathbf{T_6}$* is ESIPT, the rate constant of the second stage should be near 4×10^{10} s^{-1}. The ESIDPT tautomer is, thus, most probably formed *via* two single ESIPT reactions: **N*** $\rightarrow$ $\mathbf{T_6}$* $\rightarrow$ **DT*** (Scheme 5). The second stage should have an energetic barrier, as it is detectable in the sub-nanosecond time domain. Under cooling the $\mathbf{T_6}$* $\rightarrow$ **DT*** transformation should be suppressed, thus $\mathbf{T_6}$* should have higher impact to fluorescence of **1a**.

Simultaneous ESIDPT (**N*** $\rightarrow$ **DT***), if it occurs, should not be accompanied by formation of intermediate species (Scheme 5), which contradicts the observed experimental evidences of $\mathbf{T_6}$* formation at both 298 and 77 K. Simultaneous ESIDPT can hardly be a barrierless process, because the observed ESIPT involving hydroxyl group at position 3 proceed with an energetic barrier. Therefore, at low temperatures, **N*** fluorescence of **1a** would be registered, which is not the case.

We thus conclude, that possibility of **DT*** formation *via* concerted mechanism, is less likely.

2a in hexane exhibits a monoexponential decay of fluorescence with lifetime of 1.98 ns with no rise component (Fig. 3b). Compared to **2b**,**c**, deactivation rates of **2a** differ a few times (Table 2), which supports the suggestion of absence of $\mathbf{T_8}$* form in its excited state, based on the steady-state fluorescence investigation. Generally, spectral and kinetic properties of **2a** resemble the $\mathbf{T_4}$* form of **1c**, a difference between k_f values may be caused by substitution effect. The **DT*** species if they appear, should be formed *via* ESIPT in $\mathbf{T_4}$*. Taking into account the observed evidence of much lower energetic barrier of ESIPT taking place in PT site including hydroxyl group in position 7, transformation $\mathbf{T_4}^* \rightarrow \mathbf{DT}^*$ should be too fast to be detected by the techniques used. Formation of **DT*** *via* concerted ESIDPT seems to us unlikely due to differences of ESIPT barriers of two sites. The discussed above different deprotonation order in **1a** and **2a** can be the main reason of different behavior of these compounds. The following experimental and theoretical investigations may probably allow for verification of these suggestions.

Table 2 Fluorescence quantum yields and deactivation kinetic parameters of the excited state of the compounds investigated in hexane[a]

Compd	Form	τ (ns) / f (%)	$k_f \times 10^{-7}$ (s^{-1})	$k_d \times 10^{-9}$ (s^{-1})	φ (%)
1a	**DT***	5.89 ± 0.02 / 94	0.02	0.17	0.11
	$\mathbf{T_6}$*	0.025 ± 0.005 / 6			
1b	$\mathbf{T_6}$*	0.473 ± 0.007	2.11	2.09	1.0
1c	$\mathbf{T_4}$*	2.19 ± 0.03	5.30	0.40	11.6
2a	$\mathbf{T_4}$*	1.98 ± 0.04	0.81	0.50	1.6
2b	$\mathbf{T_8}$*	0.377 ± 0.008	0.58	2.65	0.22
2c	$\mathbf{T_8}$*	0.415 ± 0.004	0.65	2.40	0.27

[a] τ – lifetime of the electronically excited form; f – fractional contribution, calculated as $f_i = A_i \cdot \tau_i / \sum A_i \cdot \tau_i$, where A_i are the pre-exponential factors; k_f – rate constant of radiative deactivation; k_d – rate constant of non-radiative deactivation; φ – quantum yield of fluorescence.

EXPERIMENTAL

Reagents of relevant grade for syntheses and spectroscopic investigations were purchased from Sigma-Aldrich. Identity of the investigated compounds was confirmed with H^1-NMR, C^{13}-NMR and MALDI TOF MS, their purity was controlled with TLC and elemental analysis. NMR spectra were recorded on 500 MHz ^{1}H (125 MHz ^{13}C) or 200 MHz ^{1}H spectrometers with trimethylsilane as reference. Mass spectra were obtained on MALDI-TOF MS Bruker Daltonics mass spectrometer. Chromatography was performed on silica gel (230 – 400 mesh) or Waters HPLC chromatograph, TLC was conducted on Merck 60 F254 silicagel plates in appropriate eluents. Elemental analysis was performed on an Elementar Vario El Cube CHNS analyzer.

Absorption and fluorescence, phosphorescence spectra were recorded on a Perkin-Elmer Lambda UV/VIS 40 spectrophotometer and Varian Cary Eclipse Fluorescence Spectrophotometer, respectively. Fluorescence and phosphorescence emission and excitation spectra were corrected on the instrumental sensitivity. Fluorescence decay curves were measured on a FluoTime 300 fluorescence lifetime spectrometer equipped with a compact emission monochromator, a TimeHarp 300E TCSPC device (minimal time resolution 4 ps), a PLS 340 LED-head for sub-nanosecond pulse driven by a PDL 820 device and a MCP-PMT photomultiplier (type R3809U-50) (PicoQuant GmbH, Germany) controlled by EasyTau system software.

Investigations of spectral properties were carried out in methylcyclohexane solutions with concentrations $1–5\times10^{-5}$ M. Investigations of anionic forms were carried out in the methylcyclohexane solutions of DBU (1,8-diazabicyclo[5.4.0] undec-7-ene). Measurements at 77K were held in FL-1013 liquid nitrogen dewar assembly using quartz 10×10 mm cuvettes with a stopper. Time-resolved fluorescence investigations were held in hexane. The solvents were treated with $LiAlH_4$ and distilled prior use in order to eliminate trace amounts of water. The compounds were additionally dried before measurements at 373 K under reduced pressure.

Fluorescence quantum yields were determined relative to quinine sulphate solution in 1 M H_2SO_4.[27] Rates of the excited state deactivation were calculated according to equations:[28]

$$\varphi = \tau \cdot k_f,$$

$$\tau = \frac{1}{k_f + k_d},$$

where φ – quantum yield of fluorescence, τ – lifetime of the electronically excited form; k_f – rate constant of radiative deactivation; k_d – rate constant of non-radiative deactivation.

Synthesis. 7-Hydroxy-2-phenyl-4*H*-chromen-4-one (**14**) was prepared according to [17], its chemical physical properties correspond to the ones described in literature. Synthetic procedure and results of analysis for 7-(benzyloxy)-3-hydroxy-2-phenyl-4*H*-chromen-4-one (**10**) were described previously.[15]

General procedure for 1-(2,4-dihydroxyphenyl)-3-phenylpropan-1-one (4a) and 1-(2,4-dihydroxyphenyl)-2,2-dimethylpropan-1-one (4b). Resorcinol (1.10 g, 10 mmol) and 3-phenylpropanoic acid (1.50 g, 10 mmol) or pyvaloyl chloride (1.48 ml, 12 mmol) in boron trifluoride etherate (5.5 ml) were stirred at 60°C for 2 h, then diluted with sodium acetate aqueous solution, stirred for 0.5 h at RT and extracted with ethyl acetate. Crude product after evaporation was purified with use of flash chromatography (SiO_2, 5 % i-PrOH in $CHCl_3$).

4a: White moist solid (2.19 g, 95%), ^{1}H NMR (500 MHz, DMSO-d_6, δ): 2.91 (t, 2H, J = 7.6 Hz), 3.23 (t, 2H, J = 7.6 Hz), 6.23 (d, 1H, J = 2.2 Hz), 6.34 (dd, 1H, J = 2.2 Hz, J = 8.9 Hz), 7.17 (m, 1H, J = 4.3 Hz), 7.26 (d, 4H, J = 4.3 Hz), 7.80 (d, 1H, J = 8.9 Hz), 10.60 (broad s, 1H), 12.57 (s, 1H). Mass spectrum, m/z: 243.3 $[M+H]^+$, 265.1 $[M+Na]^+$, 281.0 $[M+K]^+$.

4b: White moist solid (1.88 g, 97%), ^{1}H NMR (200 MHz, DMSO-d_6, δ): 1.30 (s, 9H), 6.25 (d, 1H, J = 2.4 Hz), 6.32 (dd, 1H, J = 2.4 Hz, J = 8.9 Hz), 7.80 (d, 1H, J = 8.9 Hz), 10.42 (s, 1H), 12.57 (s, 1H). Mass spectrum, m/z: 195.2 $[M+H]^+$, 217.2 $[M+Na]^+$.

1-(5-Acetyl-2,4-dihydroxyphenyl)-3-phenylpropan-1-one (5a) and 1-(3-acetyl-2,4-dihydroxyphenyl)-3-phenylpropan-1-one (6a). 1-(2,4-Dihydroxyphenyl)-3-phenylpropan-1-one **4a** (1.97 mg, 8.1 mmol), zinc chloride (1.66 mg, 12.2 mmol), acetic anhydride (1.54 ml, 16.2 mmol) and glacial acetic acid (10 ml) were stirred at 80°C for 1 h under N_2, then poured on ice and extracted with $CHCl_3$, washed with 0.1 M HCl and then water, and dried over $MgSO_4$. The obtained mixture of isomers **5a** and **6a** was separated using column chromatography (SiO_2, $CHCl_3$).

5a: White moist solid (1.17 g, 51%), ^{1}H NMR (200 MHz, DMSO-d_6, δ): 2.61 (s, 3H), 2.92 (t, 2H, J = 7.6 Hz), 3.43 (t, 2H, J = 7.6 Hz), 6.36 (s, 1H), 7.18 (m, 1H, J = 4.4 Hz), 7.25 (d, 4H, J = 4.4 Hz), 8.39 (s, 1H), 12.70 (broad s, 2H). Mass spectrum, m/z: 285.2 $[M+H]^+$, 307.1 $[M+Na]^+$.

6a: White moist solid (0.18 g, 8%), ^{1}H NMR (200 MHz, DMSO-d_6, δ): 2.58 (s, 3H), 2.92 (t, 2H, J = 7.5 Hz), 3.30 (t, 2H, J = 7.5 Hz), 6.47 (d, 1H, J = 9.0 Hz), 7.18 (m, 1H, J = 4.4 Hz), 7.27 (d, 4H, J = 4.4 Hz), 8.04 (d, 1H, J = 9.0 Hz), 12.89 (broad s, 1H), 14.24 (broad s, 1H). Mass spectrum, m/z: 284.9 $[M+H]^+$, 306.8 $[M+Na]^+$, 322.8 $[M+K]^+$.

1-(3-Acetyl-2,4-dihydroxyphenyl)-2,2-dimethylpropan-1-one (6b). The compound was prepared from 1-(2,4-dihydroxyphenyl)-2,2-dimethylpropan-1-one (**4b**) according to the procedure described for **5a** and **6b**. White moist solid (6%). ^{1}H NMR (200 MHz, DMSO-d_6, δ): 1.27 (s, 9H), 2.58 (s, 3H), 6.46 (d, 1H, J = 9.0 Hz), 7.81 (d, 1H, J = 9.0 Hz), 12.16 (broad s, 1H), 14.12 (broad s, 1H). Mass spectrum, m/z: 237.2 $[M+H]^+$.

(2*E*)-1-[2,4-dihydroxy-5-(3-phenylpropanoyl)phenyl]-3-phenylprop-2-en-1-one. (1e): 1-(5-Acetyl-2,4-dihydroxyphenyl)-3-phenylpropan-1-one **5a** (0.284 mg, 1 mmol), benzaldehyde (117 mg, 1.1 mmol), KOH (448 mg, 8 mmol) and 80% aqueous NMP (2 ml) were stirred for 15 h at RT, neutralized by 0.1 M HCl, extracted with $CHCl_3$ and washed 3 times with water. The crude product was purified with use of flash chromatography (SiO_2, $CHCl_3$). Yellow powder (180 mg, 48 %), ^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.15 (t, 2H, J = 7.7 Hz), 3.36 (t, 2H, J = 7.7 Hz), 6.51 (s, 1H), 7.25 (t, 1H, J = 7.0 Hz), 7.30 (d, 2H, J = 7.6 Hz), 7.34 (t, 2H, J = 7.0 Hz), 7.45 (d, 1H, J = 15.5 Hz), 7.47 – 7.51 (m, 3H), 7.76 – 7.70 (m, 2H), 7.96 (d, 1H, J = 15.5 Hz), 8.31 (s, 1H), 13.08 (s, 1H), 13.61 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 203.7, 191.9, 170.0, 169.0, 146.1, 140.5, 134.4, 134.3, 131.2, 129.1, 128.8, 128.7, 128.5, 126.6, 119.1, 113.8, 113.2, 105.3, 39.7, 30.7. Mass spectrum, m/z: 373.0 $[M+H]^+$, 394.9 $[M+Na]^+$, 410.9 $[M+K]^+$. Anal. Calcd. for $C_{24}H_{20}O_4$, %: C 77.40; H 5.41. Found, %: C 77.03; H 5.49.

7-Hydroxy-2-phenyl-6-(3-phenylpropanoyl)-4*H*-chromen-4-one. (1b): (2*E*)-1-[2,4-dihydroxy-5-(3-phenylpropanoyl)phenyl]-3-phenylprop-2-en-1-one **1e** (372 mg, 1 mmol), iodine (13 mg, 0.1 mmol) and DMSO (2 ml) were heated at 90°C for 4 h, diluted with thiosulfate aqueous solution, extracted by $CHCl_3$ and purified by flash chromatography (SiO_2, 2% i-PrOH in $CHCl_3$). White solid (195 mg, 53%), ^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.04 (t, 2H, J = 7.6 Hz), 3.42 (t, 2H, J = 7.6 Hz), 6.68 (s, 1H), 6.97 (s, 1H), 7.16 (t, 1H, J = 7.3 Hz), 7.20 (d, 2H, J = 7.6 Hz), 7.25 (t, 2H, J = 7.3 Hz), 7.44 – 7.49 (m, 3H), 7.83 (dd, 2H, J = 8.0 Hz, J = 1.8 Hz), 8.64 (s, 1H), 12.62 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 205.4, 177.3, 166.2, 163.6, 160.5, 140.2, 131.9, 131.3, 130.0, 129.1, 128.7, 128.4, 126.5, 126.3, 118.2, 116.6, 107.2, 105.4, 40.2, 29.7. Mass spectrum, m/z: 371.2 $[M+H]^+$, 393.2 $[M+Na]^+$, 409.2 $[M+K]^+$. Anal. Calcd. for $C_{24}H_{18}O_4$, %: C 77.91; H 4.90. Found, %: C 77.83; H 4.95.

7-Methoxy-2-phenyl-6-(3-phenylpropanoyl)-4*H*-chromen-4-one. (1d): 7-hydroxy-2-phenyl-6-(3-phenylpropanoyl)-4*H*-chromen-4-one **1b** (185 mg, 0.5 mmol), dimethylsulfate (69 mg, 0.55 mmol), K_2CO_3 (76 mg, 0.55 mmol) and DMF (1 ml) were stirred at RT for 10 h, and then diluted with water. The collected precipitate was purified with use of flash chromatography (SiO_2, 2% i-PrOH in $CHCl_3$). White solid (1 mg, 92%), ^{1}H NMR (500 MHz, $CDCl_3$, δ): 2.97 (t, 2H, J = 7 Hz), 3.22 (t, 2H, J = 7.6 Hz), 3.92 (s, 3H), 6.71 (s, 1H), 6.94 (s, 1H), 7.13 (t, 1H, J = 7.3 Hz), 7.16 (d, 2H, J = 7.6 Hz), 7.22 (t, 2H, J = 7.3 Hz), 7.44 – 7.50 (m, 3H), 7.83 (dd, 2H, J = 7.9 Hz, J = 1.7 Hz), 8.42 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 199.8, 177.3, 163.3, 162.3, 159.4, 141.3, 131.7, 131.5, 129.1, 128.8, 128.4, 127.5, 126.2, 117.4, 107.8, 99.8, 56.4, 45.1, 30.2. Mass spectrum, m/z: 385.0 $[M+H]^+$, 407.0 $[M+Na]^+$, 422.9 $[M+K]^+$. Anal. Calcd. for $C_{25}H_{20}O_4$, %: C 78.11; H 5.24. Found, %: C 78.02; H 5.29.

3-Hydroxy-7-methoxy-2-phenyl-6-(3-phenylpropanoyl)-4*H*-chromen-4-one. (1c): 7-Methoxy-2-phenyl-6-(3-phenylpropanoyl)-4*H*-chromen-4-one (**1d**) (0.096 g, 0.25 mmol), acetone (0.25 ml), $CHCl_3$ (2.5 ml) and water (2.5 ml) were cooled to 0 - 5°C. Oxone© (0.3 g) and K_2CO_3 (0.2 g, 3.6 mmol) were added in four portions to the vigorously stirred suspension within 5 h, the mixture temperature was maintained at ≤ 5°C. The organic layer was separated, TFA (0.05 ml) was added, and the mixture was stirred for 0.5 h at RT. The residue after evaporation was reprecipitated from DMSO solution by dropwise addition of MeOH. Pale yellow powder (89 mg, 89%), ^{1}H NMR (500 MHz, $CDCl_3$, δ): 2.98 (t, 2H, J = 7.6 Hz), 3.23 (t, 2H, J = 7.6 Hz), 3.93 (s, 3H), 6.93 (s, 1H), 7.13 (t, 1H, J = 7.3 Hz), 7.17 (d, 2H, J = 7.5 Hz), 7.22 (t, 2H, J = 7.4 Hz), 7.40 (t, 1H, J = 7.4 Hz), 7.46 (t, 2H, J = 7.6 Hz), 8.15 (d, 2H, J = 7.9 Hz), 8.45 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 198.7, 171.7, 161.2, 157.5, 143.5, 140.2, 137.3, 129.8, 129.2, 127.8, 127.6, 127.5, 127.4, 126.5, 126.4, 125.1, 113.2, 98.6, 55.4, 44.1, 29.3. Mass spectrum, m/z: 401.2 $[M+H]^+$, 423.2 $[M+Na]^+$, 439.1 $[M+K]^+$. Anal. Calcd. for $C_{25}H_{20}O_5$, %: C 74.98; H 5.03. Found, %: C 75.05; H 5.10.

3,7-Dihydroxy-2-phenyl-6-(3-phenylpropanoyl)-4*H*-chromen-4-one. (1a): To a solution of 3-hydroxy-7-methoxy-2-phenyl-6-(3-phenylpropanoyl)-4*H*-chromen-4-one **1c** (40 mg, 0.1 mmol) in CH_2Cl_2 (1 ml) under N_2, BBr_3 (125 mg, 0.5 mmol) was added and the mixture was stirred for 2 h. A few drops of methanol were added, the solution was diluted with CH_2Cl_2 and washed with water. Residue after evaporation was purified using HPLC with gradient elution (C_{18}, 50 – 80 % acetonitrile in water). Pale yellow solid (34 mg, 87%), ^{1}H NMR

(500 MHz, $CDCl_3$, δ): 3.05 (t, 2H, J = 7.6 Hz), 3.43 (t, 2H, J = 7.6 Hz), 6.82 (broad s, 1H), 6.98 (s, 1H), 7.16 (t, 1H, J = 7.3 Hz), 7.20 (d, 2H, J = 7.3 Hz), 7.26 (t, 2H, J = 7.3 Hz), 7.41 (t, 1H, J = 7.5 Hz), 7.47 (t, 2H, J = 7.9 Hz), 8.14 (d, 2H, J = 7.9 Hz), 8.67 (s, 1H), 12.55 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 203.3, 169.1, 164.9, 158.2, 143.9, 140.1, 136.7, 129.4, 129.0, 127.7, 127.4, 127.3, 127.2, 126.6, 126.4, 125.4, 112.5, 104.1, 39.1, 28.7. Mass spectrum, *m*/*z*: 386.9 $[M+H]^+$, 408.8 $[M+Na]^+$, 424.7 $[M+K]^+$. Anal. Calcd. for $C_{24}H_{18}O_5$, %: C 74.60; H 4.70. Found, %: C 74.65; H 4.76.

General procedure for 7-methoxy-4-oxo-2-phenyl-4*H*-chromene-8-carbaldehyde (2d) and 7-(benzyloxy)-3-methoxy-2-phenyl-4*H*-chromen-4-one (11). 7-hydroxy-4-oxo-2-phenyl-4*H*-chromene-8-carbaldehyde **2b** or 7-(benzyloxy)-3-hydroxy-2-phenyl-4*H*-chromen-4-one **10** (1 mmol), K_2CO_3 (276 mg, 2.2 mmol), dimethylsulphate (252 mg, 2.1 mmol) and acetonitrile (10 ml) were stirred at RT for 10 hours, then diluted with water. The precipitate was filtered off and recrystallized from methanol.

2d: White solid (227 mg, 81%), ^{1}H NMR (200 MHz, DMSO-d_6, δ): 4.05 (s, 3H), 7.10 (s, 1H), 7.38 (d, 1H), 7.55 – 7.64 (m, 3H), 8.20 – 8.32 (m, 3H), 10.54 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 187.8, 176.5, 166.8, 163.2, 155.6, 133.3, 132.6, 131.5, 129.8, 127.1, 117.9, 113.3, 111.5, 107.4, 57.9. Mass spectrum, *m*/*z*: 281.3 $[M+H]^+$. Anal. Calcd. for $C_{17}H_{12}O_4$, %: C 72.85; H 4.32. Found, %: C 72.77; H 4.35.

11: White solid (308 mg, 86%), ^{1}H NMR (500 MHz, DMSO-d_6, δ): 3.82 (s, 3H), 5.27 (s, 2H), 7.14 (dd, 1H, J = 8.8 Hz, J = 1.9 Hz), 7.34 – 7.38 (m, 2H), 7.42 (t, 2H, J = 7.0 Hz), 7.49 (d, 2H, J = 7.6 Hz), 7.56 – 7.61 (m, 3H), 8.00 (d, 1H, J = 8.8 Hz), 8.01 – 8.05 (m, 2H). Mass spectrum, *m*/*z*: 359.1 $[M+H]^+$, 381.2 $[M+Na]^+$, 397.2 $[M+K]^+$. Anal. Calcd. for $C_{23}H_{18}O_4$, %: C 77.08; H 5.06. Found, %: C 76.95; H 5.12.

7-Hydroxy-3-methoxy-2-phenyl-4*H*-chromen-4-one. (12): 7-(Benzyloxy)-3-methoxy-2-phenyl-4*H*-chromen-4-one **11** (358 mg, 1 mmol) was dissolved in 33% HBr solution in acetic acid (3 ml) and the mixture was stirred at room temperature for 4 hours, then diluted with water. The precipitate was filtered off and recrystallized from methanol. White solid (209 mg, 78%), ^{1}H-NMR (200 MHz, DMSO-d_6, δ): 3.78 (s, 3H), 6.87 – 6.97 (m, 2H), 7.51 – 7.58 (m, 3H), 7.92 (d, 1H, J = 9.3 Hz), 7.95 – 8.02 (m, 2H), 10.85 (broad s, 1H). Mass spectrum, *m*/*z*: 269.2 $[M+H]^+$, 291.1 $[M+Na]^+$, 307.0 $[M+K]^+$. Anal. Calcd. for $C_{16}H_{12}O_4$, %: C 71.64; H 4.51. Found, %: C 71.87; H 4.62.

General procedure for 7-hydroxy-4-oxo-2-phenyl-4*H*-chromene-8-carbaldehyde (2b) and 7-hydroxy-3-methoxy-4-oxo-2-phenyl-4*H*-chromene-8-carbaldehyde (2c) (Duff reaction). 7-Hydroxy-2-phenyl-4*H*-chromen-4-one **14** or 7-hydroxy-3-methoxy-2-phenyl-4*H*-chromen-4-one **12** (1 mmol), hexamethylenetetramine (421 mg, 3 mmol) and acetic acid (4 ml) were refluxed for 2 h, then 1 M HCl was added (2 ml) and the mixture was stirred for 1 h at 60°C. Precipitate collected after cooling was recrystallized from MeOH.

2b: White powder (67%), ^{1}H NMR (500 MHz, DMSO-d_6, δ): 7.05 (s, 1H), 7.09 (d, 1H, J = 8.9 Hz), 7.55 – 7.60 (m, 3H), 8.14 (d, 1H, J = 8.9 Hz), 8.16 – 8.21 (m, 2H); 10.60 (s, 1H), 12.16 (broad s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 190.5, 176.3, 167.0, 162.8, 157.1, 133.4, 132.5, 131.5, 129.8, 127.1, 116.8, 116.4, 111.0, 107.8. Mass spectrum, *m*/*z*: 267.3 $[M+H]^+$. Anal. Calcd. for $C_{16}H_{10}O_4$, %: C 72.18; H 3.79. Found, %: C 72.28; H 3.77.

2c: Pale yellow powder (59%), ^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.95 (s, 3H), 7.03 (d, 1H, J = 9.0 Hz), 7.54 – 7.60 (m, 3H), 8.02 – 8.07 (m, 2H); 8.40 (d, 1H, J = 9.0 Hz), 10.69 (s, 1H), 12.49 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 192.0, 173.5, 167.6, 157.0, 154.8, 142.0, 135.0, 131.0, 130.4, 128.8, 128.1, 116.8, 116.2, 108.8, 60.3. Mass spectrum, *m*/*z*: 297.2 $[M+H]^+$, 319.1 $[M+Na]^+$, 335.0 $[M+K]^+$. Anal. Calcd. for $C_{17}H_{12}O_5$, %: C 68.92; H 4.08. Found, %: C 68.79; H 4.15.

3,7-Dihydroxy-4-oxo-2-phenyl-4*H*-chromene-8-carbaldehyde. (2a): the compound was prepared from 7-hydroxy-3-methoxy-2-phenyl-4*H*-chromen-4-one **12** following the procedure described for **1a**. Crude product was purified by recrystallization from hot MeOH – $CHCl_3$ solution. Pale yellow powder (84%), ^{1}H NMR (500 MHz, DMSO-d_6, δ): 7.09 (d, 1H, J = 8.9 Hz), 7.50 (t, 1H, J = 6.9 Hz), 7.58 (t, 2H, J = 7.5 Hz), 8.24 (d, 1H, J = 8.9 Hz), 8.37 (d, 2H, J = 7.5 Hz), 9.77 (s, 1H), 10.60 (s, 1H), 12.23 (broad s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6, δ): 190.0, 172.3, 166.9, 155.6, 145.0, 139.8, 133.5, 131.7, 130.2, 129.0, 128.0, 115.9, 114.8, 110.5. Mass spectrum, *m*/*z*: 283.2 $[M+H]^+$. Anal. Calcd. for $C_{16}H_{10}O_5$, %: C 68.09; H 3.57. Found, %: C 68.01; H 3.61.

Conclusions

Two novel types of carbonyl derivatives of flavones with two different proton-transfer sites, able to undergo different types of ESIPT were synthesized. All the hydroxyflavones investigated undergo ESIPT in their electronically excited states. ESIPT involving 3-hydroxyl and 4-carbonyl groups was found to have higher barrier compared to ESIPT involving 7-hydroxyl and 6/8-carbonyl fragments. 3,7-Dihydroxy-2-phenyl-6-(3-phenylpropanoyl)-4*H*-chromen-4-one (**1a**) probably undergoes ESIDPT *via* formation of a transition tautomer $\mathbf{T_6^*}$. This kind of ESIDPT leads to a tautomeric form with a very low rate constant of radiative deactivation of the excited state, what results in low fluorescence quantum yields. 3,7-Dihydroxy-4-oxo-2-phenyl-4*H*-chromene-8-carbaldehyde most probably undergoes single ESIPT, however, we hope further investigations will reveal more details on the behavior of this compound.

Acknowledgements

The research was financed by the Polish National Science Center (NCN) under Grant No. 2014/13/N/ST4/04105. PhD studies of I. E. Serdiuk were supported by scholarship of the Polish Bureau for Academic Recognition and International Exchange (BUWiWM). The authors gratefully acknowledge Prof. dr hab. Wiesław Wiczk for valuable consultations and technical support on the low-temperature and time-resolved fluorescence investigations. A special acknowledgment is

addressed to Prof. dr hab. inż. Jerzy Błażejowski for technical support.

Notes and references

1 J. Zhao, S. Ji, Y. Chen, H. Guo and P. Yang, *Phys. Chem. Chem. Phys*., 2012, **14**, 8803.
2 J. E. Kwon and S. Y. Park, *Adv. Mater*., 2011, **23**, 3615.
3 S. Protti and A. Mezzetti, *Photochemistry*, 2012, **40**, 295.
4 C. Randino, M. Ziołek, R. Gelabert, J. A. Organero, M. Gil, M. Moreno, J. M. Lluch and A. Douhal, *Phys. Chem. Chem. Phys.*, 2011, **13**, 14960.
5 A. Mordziński, A. Grabowska, W. Kühnle and A.Krówczyński, *Chem. Phys. Lett.,* 1983, **101**, 291.
6 R. Wortmann, S. Lebus, H. Reis, A. Grabowska, K. Kownacki and S. Jarosz, *Chem. Phys. Lett.*, 1999, **243**, 295.
7 V. Enchev, N. Markova, M. Stoyanova, P. Petrov, M. Rogozherov, N. Kuchukova, I. Timtcheva, V. Monev, S. Angelova and M. Spassova, *Chem. Phys. Lett.*, 2013, **563**, 43.
8 E. Falkovskaia, V. G. Pivovarenko and J. C. Valle, *J. Phys. Chem. A,* 2003, **107**, 3316.
9 A. D. Roshal, V. I. Moroz, V. G. Pivovarenko, A. Wróblewska and J. Błażejowski, *J. Org. Chem.*, 2003, **68**, 5860.
10 V. V. Moroz, A. G. Chalyi, I. E. Serdiuk, A. D. Roshal, B. Zadykowicz, V. G. Pivovarenko, A. Wróblewska and J. Błażejowski, *J. Phys. Chem. A*, 2013, **117**, 9156.
11 D. A. Svechkarev, A. O. Doroshenko and D. Yu. Kolodezny, *Cent. Eur. J. Chem.*, 2012, **10**, 205.
12 S. Formosinho and L. G. Arnaut, *J. Photochem. Photobiol. A: Chem.,* 1993, **75**, 21.
13 M. Wera, A. G. Chalyi, A. D. Roshal, B. Zadykowicz and J. Błażejowski, *Struct. Chem.*, 2014, **25**, 969.
14 G. Geetha, K. Viswanathan and S. N. D. Pradeep, *Org. Lett.*, 2002, **4**, 781.
15 I. E. Serdiuk, A. D. Roshal and J. Błażejowski, *Chem. Heterocycl. Compd*., 2014, **50**, 396.
16 J. C. Duff and E. J. J. Bills, *J. Chem. Soc.*, 1934, 1305.
17 Y. S. Chi, T. Th. Dao, H. P. Kim, J. Kim, H. Park and S. Kim, *Bioorg. Med. Chem. Lett.,* 2004, **14**, 1165.
18 I. E. Serdiuk, A. S. Varenikov and A. D. Roshal, *J. Phys. Chem. A*, 2014, **118**, 3068.
19 A. S. Varenikov, I. E. Serdiuk and A. D. Roshal, *French-Ukrainian Journal of Chemistry*, 2013, **1**, 153-157.
20 I. E. Serdiuk, M. Wera, A. D. Roshal and J. Błażejowski, *Acta Cryst. E,* 2013, **69**, 895.
21 O. S. Wolfbeis and R. Schipfer, *Ber. Bunsenges. Phys. Chem.,* 1982, **86**, 237.
22 G. A. Brucker, T. C. Swinney and D. F. Kelley, *J. Phys. Chem.,* 1991, **95**, 3190.
23 A.D. Roshal, J.A. Organero and A. Douhal, *Chem. Phys. Lett.*, 2003, **379**, 53.
24 P. K. Sengupta and M. Kasha, *Chem. Phys. Lett.*, 1979, **68**, 382.
25 N. A. Tyukavkina and N. N. Pogodaeva, *Chem. Nat. Compd.*, 1971, **7**, 8.
26 E. Otyepkova, T. Nevěčná, J. Kulhánek and O. Exner, *J. Phys. Org. Chem.*, 2003, **16**, 721.
27 R. D. B. Fraser and E. Suzuki, in *Spectral Analysis,* ed. J. A. Blackburn, Marcel Dekker, New York. 1970, p. 171.
28 J. B. Birks, in *Photophysics of Aromatic Molecules*, ed. J. B. Birks, Wiley, London, 1970, p. 718.

Graphical and textual abstract for the Table of contents entry

3,7-Dihydroxyflavone derivatives containing carbonyl fragments were synthesized. Results of the fluorescent spectroscopy investigations indicate that one of them undergoes Excited State Intramolecular Double Proton Transfer (ESIDPT).