

Absorption and Fluorescent Studies of 3-Hydroxychromones

Radhika Khanna¹ · Ramesh Kumar¹ · Aarti Dalal¹ · Ramesh C. Kamboj¹

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Abstract The synthesis and spectral studies of variously substituted 3-hydroxychromones have been carried out. A key relationship between the structural motif of synthesized 3-hydroxychromones (3-HCs) and their fluorescent properties was found. The chromones substituted with electron-donating group at 4'-position expressed the red shift of the N* and T* band and also exhibited the increased fluorescent intensity ratio while the chromones with electron-withdrawing group showed the blue shift of the N* and T* band. Therefore, these 3-HCs may behave as the possible fluorescent probes.

Keywords 3-Hydroxychromones · Fluorescence · Absorption · ESIPT

Introduction

The 3-hydroxychromones (3-HCs) derivatives have attracted the interest of researchers in the recent years as they exhibit dual emission due to the excited state intramolecular proton transfer (ESIPT) that results in two well-separated fluorescence bands belonging to excited state normal (N*) and tautomer (T*) forms [1] (Fig. 1). The spectroscopic properties of these fluorescence bands and the interplay of their intensities

are strongly governed by the structure of the 3-hydroxychromone chromophore, which assign these a wide variety of high technological utility. Many 3-HCs have been synthesized and analysed for the development of new fluorescent probes for solvent polarity [2–4], ionic binding [5] and electric fields [6, 7] with applications in the field of polymers [8], reverse micelles [9, 10], host-guest complexes [11], lipid vesicles [7, 12–15], cellular membranes [16] and proteins [17–21]. These molecules have also been found to show fascinating photochemistry furnishing the oxirane scaffold [22]. The 3-HCs have also been used as important substrates for the synthesis [23–27] of many photo-labile molecules which yielded many polycyclic exotic molecules on photoirradiation.

Keeping in view the applications and significant photochemistry elicited by these 3-HCs, in the present communication, we have made an attempt to synthesise, determine and analyse their absorption and fluorescent properties. And also the effect of different substituents located at 4'-position of 3-HCs and intensity ratio of N* and T* emission bands was assessed. Herein, we have demonstrated that, there is possibility of driving the spectroscopic properties in the desired direction by providing proper substitutions in the chromophoric system.

Methods and Materials

General

All the chemicals used in the study were procured from the market and were of highest quality available. The solvents required were purified by the standard procedures.

Melting points were determined in open capillaries and are thus uncorrected. IR spectra were recorded on a Perkin-Elmer

✉ Ramesh C. Kamboj
rckamboj@hotmail.com

¹ Department of Chemistry, Kurukshetra University,
Kurukshetra 136119, Haryana, India

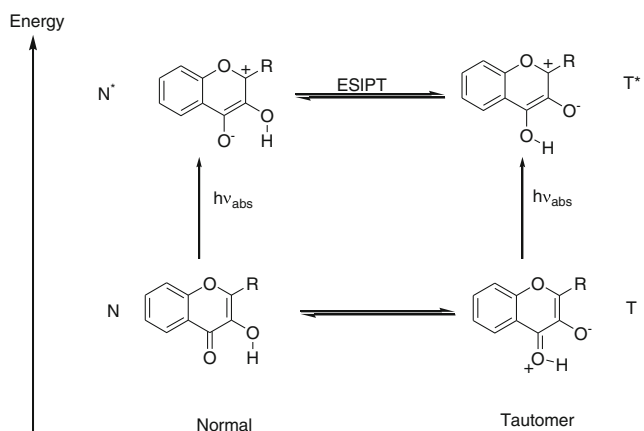


Fig. 1 The dual fluorescent behavior of 3-hydroxychromones is represented in an energy diagram. Upon excitation, the normal excited species (N^*) undergoes an excited intramolecular proton transfer (ESIPT) to give the excited tautomer (T^*)

IR spectrophotometer. ^1H and ^{13}C spectra were recorded in $\text{CDCl}_3/\text{DMSO}$ on a 300 MHz/400 MHz and 75.4 MHz/100.6 MHz Bruker spectrometer using TMS as an internal standard.

Synthesis of 3-HCs (Scheme 1)

A General Procedure for the Synthesis of Chalcone A

A solution of substituted 2-hydroxyacetophenone (0.05 mol) and substituted benzaldehyde (0.055 mol) in absolute ethanol and sodium hydroxide (0.1 mol) was stirred for 8–9 h. The dark red mixture was poured on ice-HCl to obtain **A** as yellow solid which was crystallized from EtOH.

A General Procedure for the Synthesis of 3-HCs from Chalcone A

To a well stirred suspension of **A** (0.01 mol) in MeOH was added aq. KOH (20 %). This mixture was cooled to 0 °C. To this dark red solution was added H_2O_2 (30 %) drop-wise under Algar-Flynn-Oyamada (AFO) reaction conditions [28] till the colour changed to yellow and the stirring was continued for 3 h. The reaction mixture was neutralized with ice-HCl to give light yellow precipitates, crystallized (chloroform-ethanol) to

Scheme 1 Synthesis of 3-hydroxychromones. Reagents and conditions: (a) NaOH/EtOH, stirring overnight; (b) KOH, H_2O_2 (30 %), 0 °C, Stiring (2 h)

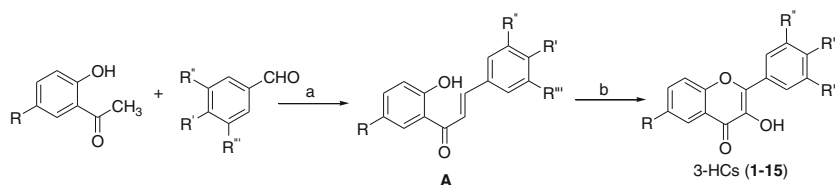


Table 1 Melting point data of 3-HCs

3-HC No.	R	R'	R''	R'''	M. pt.
1	H	H	H	H	170 °C
2	H	Cl	H	H	192 °C
3	H	CH ₃	H	H	206 °C
4	H	OCH ₃	H	H	228 °C
5	H	OCH ₃	OCH ₃	OCH ₃	182 °C
6	CH ₃	H	H	H	175 °C
7	CH ₃	Cl	H	H	221 °C
8	CH ₃	CH ₃	H	H	184 °C
9	CH ₃	OCH ₃	H	H	140 °C
10	CH ₃	OCH ₃	OCH ₃	OCH ₃	182 °C
11	Cl	H	H	H	169 °C
12	Cl	Cl	H	H	232 °C
13	Cl	CH ₃	H	H	192 °C
14	Cl	OCH ₃	H	H	219 °C
15	Cl	OCH ₃	OCH ₃	OCH ₃	210 °C

yield 3-HCs as light yellow solid. The melting points (Table 1), IR and ^1H -NMR spectral data of these 3-HCs overlapped with the data reported in the literature [29].

Absorption and Fluorescence Spectra of 3-HCs

The 3-HCs synthesized above were purified to the highest level of purity and then crystallized. Absorption and fluorescence spectra (Figs. 2, 3 and 4) of these purified and crystallized chromones were recorded on T90+ UV/VIS Spectrophotometer and Shimadzu RF-5301Pc Spectrofluorophotometer. The solutions of 3-HCs were made in methanol of spectroscopic grade. In all cases the concentrations of the solutions were made such that absorption was close to 0.1 and these concentrations were between 3 and 5 μM . The solutions of these 3-HCs were also prepared in acetonitrile, the polar aprotic solvent and ethanol separately to observe solvatochromism.

Results and Discussion

The fluorescent spectra of these 3-HCs in methanol, a polar protic solvent exhibited two bands: one situated between 400

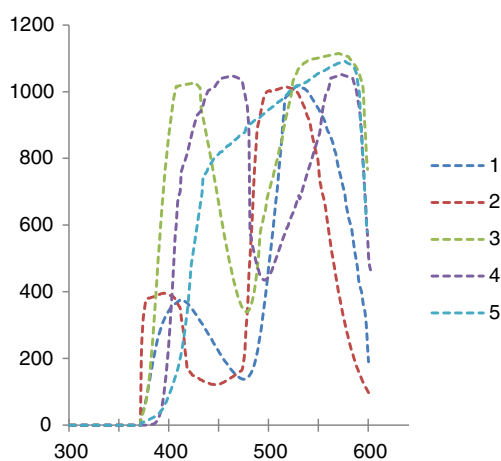


Fig. 2 Fluorescence spectra of 3-hydroxychromones **1**, **2**, **3**, **4** and **5** (in methanol)

and 473 nm and another between 476 and 576 nm. A look of these fluorescent spectra revealed that there is definitely a close relationship between the 3-hydroxychromone structural motifs and their spectral behaviors (Table 2). These results of the fluorescence spectra indicate that the tethering of electron-donating group at 4'-position of 3-hydroxychromone results in the red-shifts of the N^* and T^* bands. Simultaneously, this also increases the intensity ratio of N^* and T^* bands (Fig. 5). While the electron withdrawing group reflected the blue-shifts of the N^* and T^* bands simultaneously decreasing their intensity ratio. Such a strong effect of the donor group on the fluorescence profile of 3-HCs may provide a prospect to design new sensitive fluorescent sensors of ions. No appreciable change in these absorption and fluorescent properties were observed by replacing methanol with ethanol as another polar protic solvent. The absorption and fluorescent spectra of all these chromones were also determined in acetonitrile (polar aprotic solvent). It was found that the fluorescent intensity ratio of

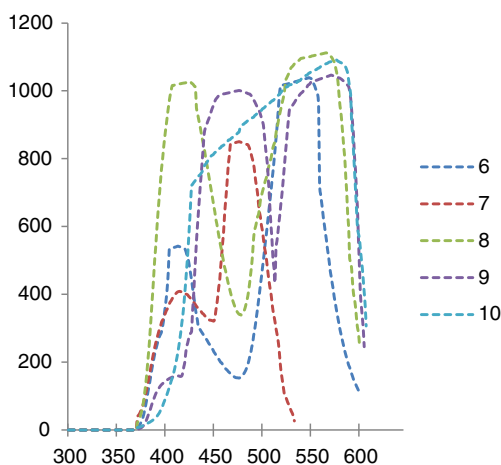


Fig. 3 Fluorescence spectra of 3-hydroxychromones **6**, **7**, **8**, **9** and **10** (in methanol)

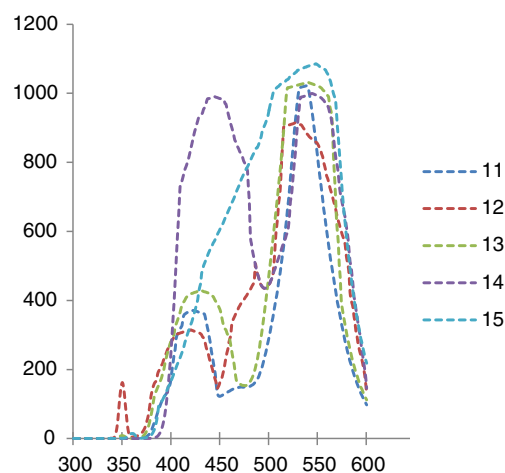


Fig. 4 Fluorescence spectra of 3-hydroxychromones **11**, **12**, **13**, **14** and **15** (in methanol)

these 3-HCs was significantly larger in acetonitrile, polar aprotic solvent than that in methanol (polar protic solvent). This is because of the H-bonding interaction of the protic solvents with the carbonyl and $-OH$ functionalities of the chromones which inhibit the ESIPT reactions of 3-HCs. This kind of interaction is absent in aprotic solvents.

These results on fluorescent behavior of the chromones can find an application as highly promising candidates in environment-sensitive probes vis-a-vis possible labels for biological applications in body fluids, cells and tissues.

Table 2 Spectrophotometric data of the studied 3-hydroxychromones

3HCs	$\lambda_{\text{abs max}}/\text{nm}$	$\lambda_{\text{max}}^{N^*}/\text{nm}$	$\lambda_{\text{max}}^{T^*}/\text{nm}$	I_{N^*}/I_{T^*}
1	340	403	528	0.442
2	326	395	517	0.389
3	346	426	570	0.945
4	330	463	573	0.962
5	354	—	576	—
6	346	413	548	0.522
7	316	415	476	0.474
8	348	417	566	0.913
9	354	473	572	0.953
10	358	—	580	—
11	348	423	538	0.369
12	348	420	527	0.341
13	352	427	540	0.417
14	360	444	544	0.982
15	360	—	548	—

where “ $\lambda_{\text{abs max}}$ ” is the position of the absorption maximum; “ $\lambda_{\text{max}}^{N^*}$ ” and “ $\lambda_{\text{max}}^{T^*}$ ” are the positions of the fluorescence maxima of the N^* and T^* forms respectively

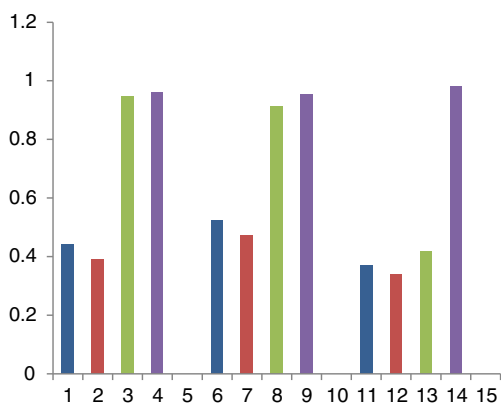


Fig. 5 Fluorescence intensity ratio of 3-HCs

Conclusion

It is concluded that in the absorption and fluorescent spectra of 3-hydroxychromones the N^* and T^* band shifts depend on the nature of substituents. The electron-donating groups in 3-HCs result in sequential red shift of the emission band and also increase the fluorescence intensity ratio, I_{N^*}/I_{T^*} . And the electron withdrawing groups have the reverse effect on these parameters.

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