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Proton transfer inhibited charge transfer in a coumarinyl chalcone: Hassle free detection of chloroform vapor in alcohol medium and in neat solution

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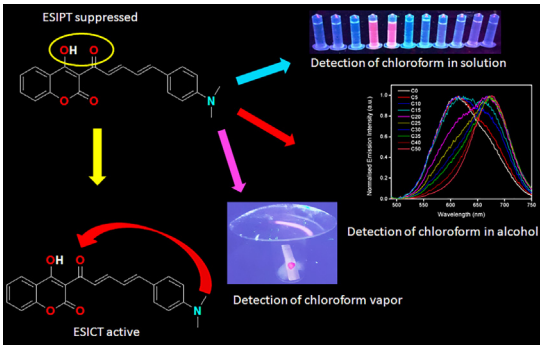
HIGHLIGHTS

- A coumarin based chalcone **DPPHC** was synthesized and characterized.
- **DPPHC** shows unique property of ESICT through suppression of ESIPT.
- **DPPHC** is able to detect chloroform in vapor phase.
- **DPPHC** can detect chloroform volume percentage in alcohol by ratiometric emission enhancement.

GRAPHICAL ABSTRACT



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ABSTRACT

The photophysical aspects of a synthesized coumarinyl chalcone derivative 3-((2E, 4E)-5-(4-(dimethylamino) phenyl) penta-2, 4-dienoyl)-4-hydroxy-2H-chromen-2-one (**DPPHC**) were explored. **DPPHC** shows excited state intramolecular proton transfer (ESIPT) suppressed excited state intramolecular charge transfer (ESICT) as evidenced from steady state and time resolved spectroscopic analysis. Interestingly, **DPPHC** behaves as a strong red emitter solely in chloroform and dichloromethane semi-polar solvents exclusively. Using this property, on-spot detection of these two solvents was achieved in paper strips coated with **DPPHC** as well as in spiked alcohol samples by emission ratiometry change.
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1. Introduction

Judiciously design of organic molecules portraying unique excited state features has posed to be an enticing problem for chemists engaged in studying and understanding excited state photophysical aspects of molecule. This interest principally stemmed after discovery of excited state intramolecular proton transfer (ESIPT) [1] and excited state intramolecular charge transfer (ESICT) [2] reaction in the molecules methyl salicylate and 4(dimethylamino) benzonitrile respectively. In case of ESIPT, a molecule undergoes tautomeric photo conversion leading to appearance of a broad emission band with unusually high Stokes shift. In ESICT, an organic molecule having the general molecular framework donor-chromophore-acceptor, exhibits a Stokes shifted band similar to ESIPT, although the band is largely affected by the polarity and hydrogen bonding ability of the solvents. The ESIPT and ESICT bands differ by their dependence on polarity of the environment. Whereas ESIPT active probes face hindrance in the excited state tautomerism in polar solvents, ESICT probes show gradual red shift

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in the emission maxima upon increment in solvent polarity [3,4]. These properties of these two classes of fluorophores have prompted to utilize them as markers in various biomimetic experiments [5,6]. However, in recent times, various groups have reported judiciously designed molecules that show a coupling of ESIPT and ESICT in a single molecule [7–10]. Our group has also been involved in designing of fluorescent probes where interplay between ESICT and ESIPT occurs (Scheme 1). In one such report, we reported ESIPT assisted ESICT in N, N'-bis (4-N, N-diethylaminosalisalidene) hydrazine (**DEASH**) [11]. We also reported 4-(diethylamino)-2-hydroxybenzaldehyde (**DEAHB**) portrays ICT suppressed ESIPT [12]. Recently, we reported a dimethylamino cinnamaldehyde based chalcone (2E, 4E)-5-(4-(dimethylamino) phenyl)-1-(2-hydroxyphenyl) penta-2, 4-dien-1-one (**DPHPD**) where the said molecule behaved as a prominent emitter in solvents like dimethylsulfoxide, dimethylformamide and dimethylacetamide [13]. Following our previous report, we designed a new chalcone platform 3-((2E, 4E)-5-(4-(dimethylamino) phenyl) penta-2, 4-dienoyl)-4-hydroxy-2H-chromen-2-one (**DPPHC**) and explored its photophysical characteristics in attempt to couple ESIPT and ESICT (Scheme 1). Since **DPPHC** contained both proton transfer (PT) and charge transfer (CT) sites, it was expected that the said probe would portray a coupling of the two. However, detailed steady state as well as time resolved spectral revealed suppression of ESIPT and portrayal of exclusive ESICT in case of **DPPHC**. Thus, after previously reporting ESIPT assisted ICT and ICT suppressed ESIPT, we currently report ESIPT suppressed ICT process in a molecule. Moreover, **DPPHC** behaves as a strong emitter exclusively in chloroform and dichloromethane observable through naked eye under UV light. Utilizing this property, the chloroform content in ethanol was determined by a ratiometric change in emission profile. Furthermore, on spot detection of chloroform and dichloromethane was achieved by the aid of paper strips. Such an application of ICT probes is by far the first of its kind. Hence, our current report holds special importance as far as design and application of ICT based probes are concerned.

2. Experimental

2.1. Materials

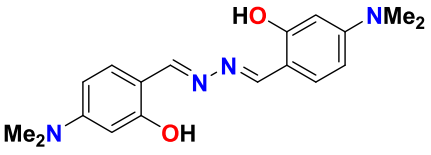
All chemicals were purchased from Sigma Aldrich and used without further purification. Spectroscopic grade solvents purchased from Spectrochem were used throughout the spectroscopic experiments.

2.2. Methods

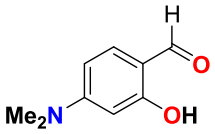
NMR spectra were recorded in Bruker Advanced Supercon 300 MHz NMR spectrophotometer using TMS as internal standard. Steady State UV–Vis absorption profiles were recorded on a Shimadzu UV-1900 spectrophotometer. Steady state emission and excited state decay profiles were recorded on HORIBA Jobin Yvon Flurolog 3 (Model 3-11) and Horiba Delta Flex-01-NL time resolved fluorimeter respectively. Mass spectrometry was carried out in Waters Xevo G2-S Q TOF mass spectrometer. During steady state absorption and emission measurements, the concentration of probe was maintained at micro molar range to avoid aggregation, re absorption or self-quenching respectively. All data were recorded at room temperature. The excited state lifetime measurements were carried out by exciting the sample using a picoseconds laser diode of 375 nm and 450 nm. The signals were obtained by setting the emission polarizer at magic angle (54.7°) to prevent anisotropy and the decays were deconvoluted using DAS6 software. The goodness of fitting was judged using χ^2 criteria. The average lifetime was calculated using standard procedures [14]. The quantum yield values were calculated using Fluorescein in 0.1 (M) NaOH as standard [15–17].

2.3. Synthesis of DPPHC

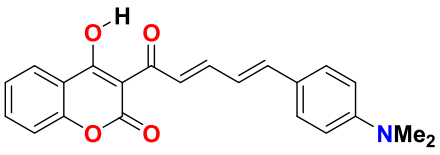
DPPHC was synthesized using Scheme 2. In short, 4-hydroxy coumarin (3 g, ~18.5 mmol) was treated with 16 mL glacial acetic acid and 5.6 mL of phosphorous oxychloride. The reaction mixture was refluxed for 30 min and then poured onto crushed ice; thereby a milky white solid was obtained. The solid was filtered and recrystallized from absolute ethanol. A golden crystalline solid was obtained in 80% yield. The 3-acetyl-4-hydroxy coumarin hence formed was characterized by ^{1}H NMR and ^{13}C NMR respectively (ESI, Fig. S1 and S2). 2 mmol of the prepared 3-acetyl-4-hydroxy coumarin was dissolved in 15 mL absolute ethanol and equimolar amount of 4-dimethylamino cinnamaldehyde, followed by addition of 0.4 mL of acetic acid. The reaction mixture was refluxed overnight to yield a violet solid in 45% yield. The solid was filtered and washed with ethanol. The purity was checked by TLC analysis and characterized by ^{1}H NMR, ^{13}C NMR and ESIMS (ESI, Fig. S3-S5).



DEASH; ESIPT assisted ICT

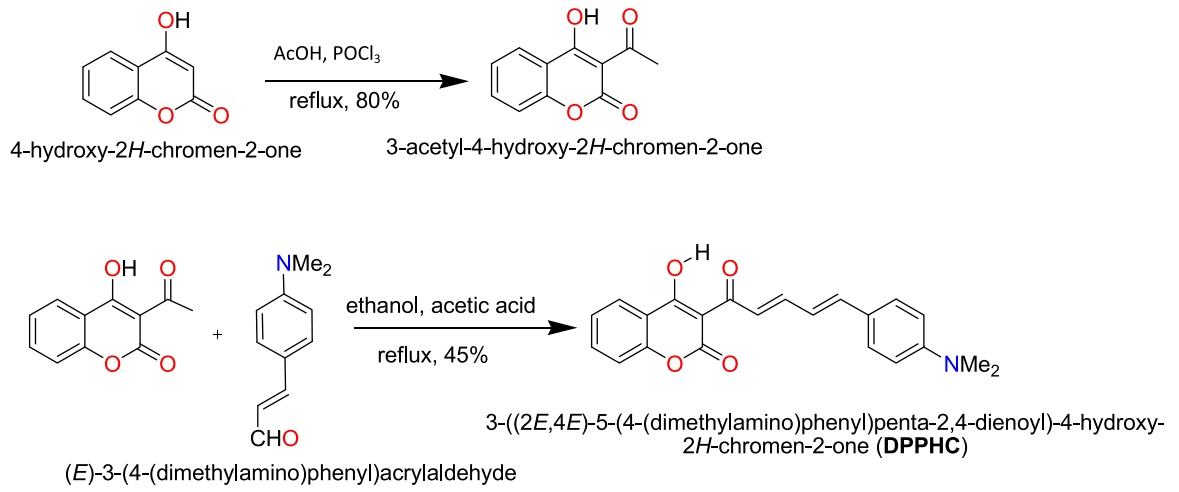


DEAHB; ICT suppressed ESIPT



DPPHC; ESIPT suppressed ICT

Scheme 1. Previously reported probes showing interplay between ICT and ESIPT and our current probe **DPPHC.**



Scheme 2. Synthetic outline of **DPPHC**.

^{1}H NMR ($CDCl_3$, 300 MHz, TMS): 8.07 (d, 2H), 7.91 (d, 1H), 7.64–7.74 (m, 2H), 7.44 (d, 1H), 7.28–7.36 (m, 5H), 7.03 (d, 1H), 6.77 (s, 1H).^{13}C NMR ($CDCl_3$, 75 MHz, TMS): 205.6, 178.3, 159.6, 154.4, 135.7, 129.4, 125.4, 125.2, 124.0, 123.7, 116.6, 114.9, 101.0, 29.6. ESI-MS: calculated for $[M-H]^+$: 362.1392, Obtained: 362.1385.

3. Results and discussions

3.1. Steady state spectral studies

The photophysical properties of **DPPHC** were investigated by recording the absorption profiles of the compound in various solvents (Fig. 1a, Table 1). The absorption profile consisted of a high energy band at ~300 nm and a low energy band which ranged from ~485 nm to ~523 nm depending on the polarity of the solvents. In polar solvent DMSO the absorption maxima shifted to ~400 nm, whereas in polar protic solvent methanol the band at ~400 nm was present along with the bands at ~300 and ~500 nm. In order to assign the nature of these bands, effect of addition of base and acid was observed in acetonitrile medium. Upon adding base to **DPPHC** in acetonitrile (Fig. 1b), the band at ~516 nm shows decrement in absorbance followed by generation of a high energy band at ~400 nm with clear isosbestic points, indicating equilibrium among different absorbing species in solution. Since **DPPHC** contains a hydroxyl unit, addition of base results in deprotonation of the hydroxyl unit, thereby furnishing the higher energy band. Hence, the high energy band at 400 nm was assigned to be the anion of **DPPHC**. Addition of acid to **DPPHC** resulted in slight increment of the band at ~516 nm (Fig. 1c).

The low energy absorption band (i.e. ~485 nm to ~523 nm) has significantly lower molar extinction coefficient and higher solvent dependence compared to the high energy band at ~300 nm. The diminishing of the low energy band with addition of base is due to the formation of anion with high energy absorption band at 400 nm. Lower stabilization of the anion compared to the neutral species could be due to the presence of charge donor dimethylamino moiety. When acid was added, probably protonation occurs on the coumarin carbonyl oxygen, thereby facilitating stabilization of positive ion by the charge donation from dimethylamino moiety to the coumarin moiety (Scheme 3). The appearance of anion at 400 nm in DMSO could be rationalized by considering the basic nature of the solvent itself. Similarly, the relative low basicity of methanol as well as its protic nature leads to partial anion formation of **DPPHC**, thereby furnishing three bands in its absorption spectrum. Following the absorption spectral studies, the emission spectra were recorded in various solvents by exciting **DPPHC** at 490 nm (Fig. 2a, b Table 1). In solvents of very low polarity, dual emission was observed with one strong band at ~550 nm, whereas a weak shoulder was observed at ~590 nm. The dual nature of emission band of **DPPHC** changed into a single band when observed in polar solvents. Starting from chloroform to acetonitrile, the emission band underwent steady red shift from ~643 nm to ~675 nm. In case of DMSO, the emission intensity was too poor to be recorded. In case of methanol, the emission maxima of **DPPHC** went a noticeable blue shift to ~617 nm. In all other protic solvents, the emission maxima was blue shifted compared to acetonitrile. The apparently anomalous observation can be rationalized by considering the hydrogen bonding interaction prevalent between **DPPHC** and protic solvents [18]. Solvent dependency and the large Stokes Shift (3459 cm^{-1} (~97 nm) in heptane to 5593 cm^{-1} (~159 nm) in acetonitrile) of the low energy emission band indicated that there could be much higher the excited state dipole moment through higher charge separation leading to the above observations. Excited state dipole moment, a gauge for charge separation in the excited state, was calculated by utilizing the Lippert-Mataga equation [16]:

$$\bar{\nu}_A - \bar{\nu}_E = \frac{2}{hc}\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right)\frac{(\mu_G-\mu_E)^2}{a^3} + const$$

where $\bar{\nu}_A$ and $\bar{\nu}_E$ represents wave numbers of absorption and emission maxima respectively,ε denotes dielectric constant of the medium, *n* denotes refractive index of the medium and μ_G and μ_E denote dipole moments in ground and excited state respectively. The term *a* (5.87A) is the Onsager Cavity radius obtained from theoretical calculations. The ground state dipole moment was calculated to be 4.57 Debye using Gaussian 09 Software [19]. From the slope of the Lippert-Mataga plot, the excited state dipole moment was calculated to be 9.87 Debye (Fig. 2c). Since the excited state dipole moment was almost doubled, it was strong evidence that considerable charge separation occurred in the excited state with the generation of higher dipolar species compared to the ground state. The solvent polarity dependence of **DPPHC** emission was verified by obtaining excellent linear correlation of the inverse of emission wavelength (in cm^{-1}) against the E_T (30) parameter of aprotic solvents (Fig. 2d) [20]. The effect of addition of base and acid were also observed in acetonitrile medium (ESI, Figure S6). Addition of base resulted in quenching of the band at ~675 nm. On the other hand, acid addition resulted in intensity increment of the emission band.

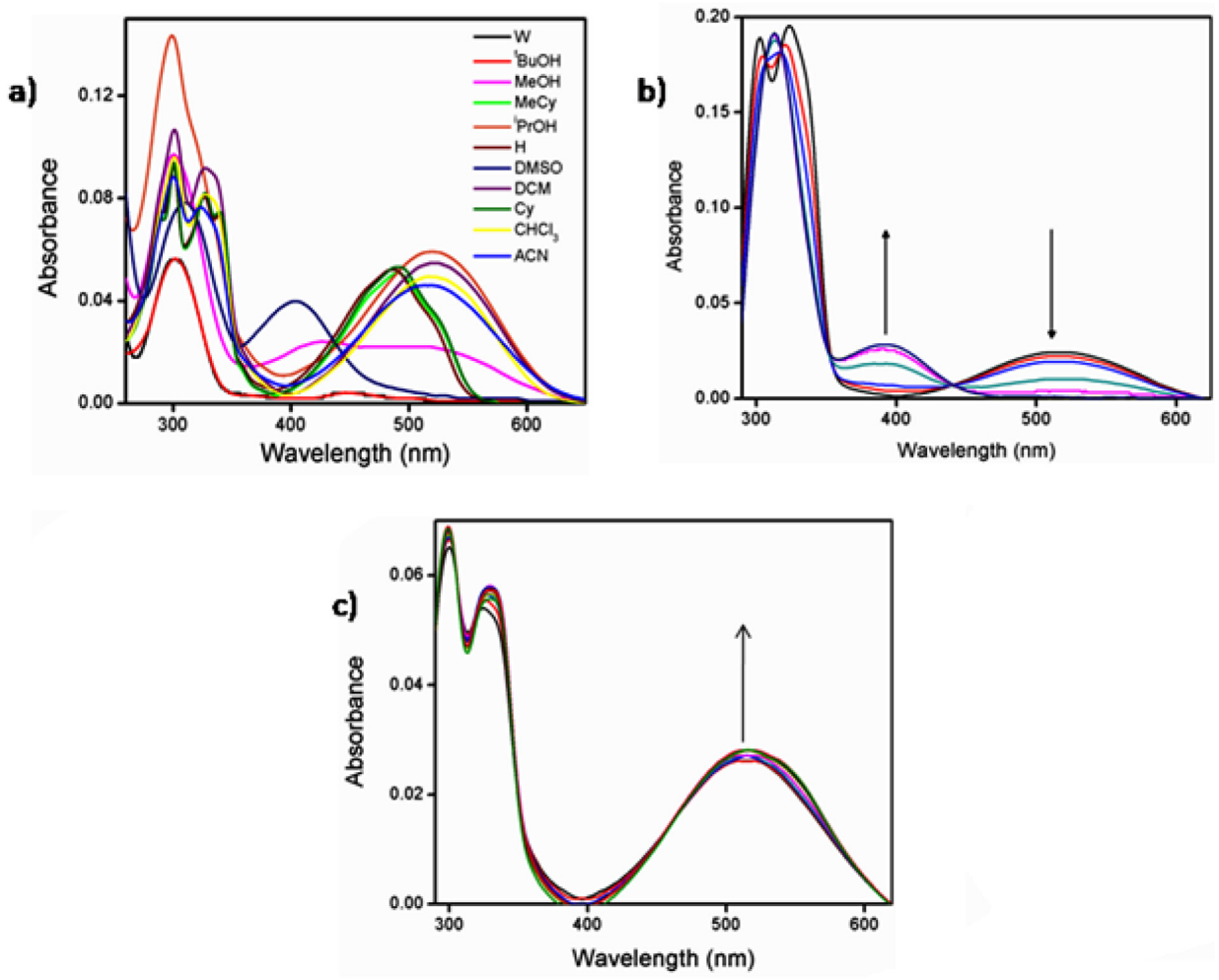
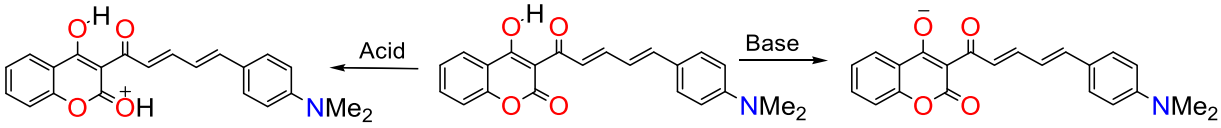


Fig. 1. (a) Absorption profile of 2 μM **DPPHC** in various solvents. (b) UV–Vis titration of **DPPHC** (2 μM) with triethylamine (0–4 μM) as base in acetonitrile medium. (c) UV–Vis titration of **DPPHC** (2 μM) with Trifluoroacetic acid (0–8 μM) in acetonitrile medium.

Table 1
Steady state spectral parameters of **DPPHC.**

Solvent*	λ^{abs}_{max} **(nm)**	λ^{em}_{max} **(nm)**	**E (mol^{-1} cm^{-1}) × 10^4**	Φ (quantum yield)
Heptane	300,487	548, 584	2.00	0.03
Cyclohexane	300,490	548, 587	2.00	0.05
Methylcyclohexane	300, 490	550, 593	2.00	0.05
Chloroform	300,520	643	2.28	0.88
Dichloromethane	300,523	659	2.50	0.79
Acetonitrile	300,516	675	1.80	0.07
DimethylSulfoxide	310,400	–	1.75	–
Methanol	300,420,523	617	0.88	0.06
Isopropanol	300,519	667	2.35	0.04
Tertiary Butanol	300,517	665	0.35	0.31
Water	300,485	668	0.24	0.01

* Solvent abbreviation provided in solvent abbreviation index of Supplementary Section.



Scheme 3. Schematic representation of addition of acid and base to **DPPHC** in solution.

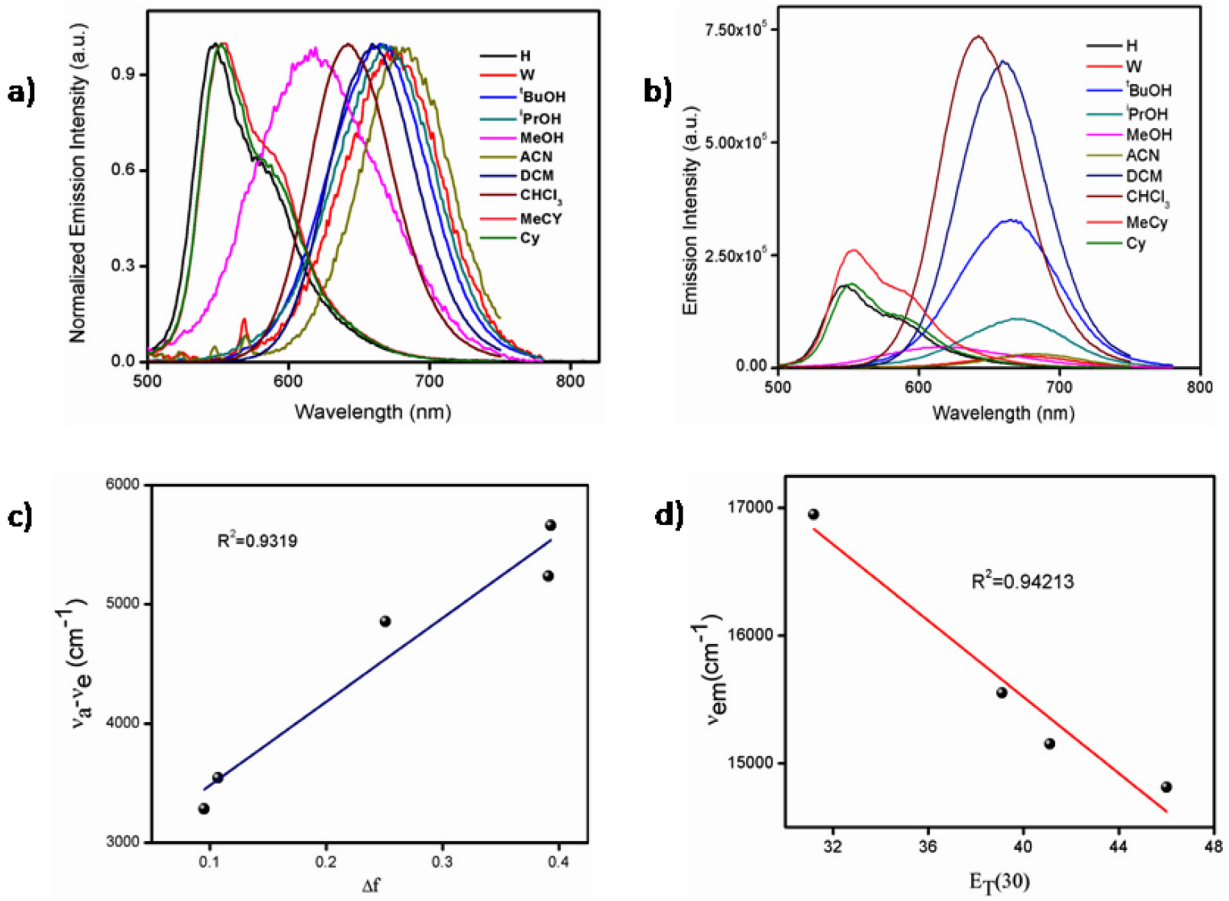


Fig. 2. (a) Normalized Emission profile of 2 μM **DPPHC** in various solvents (λ_{ex} = 490 nm), (b) Emission profile of 2 μM **DPPHC** in various solvents (λ_{ex} = 490 nm), (c) Lippert-Mataga plot of **DPPHC**, (d) Plot of inverse of emission wavelength (in cm^{-1}) against $E_T(30)$ parameter of aprotic solvents.

The results of acid and base addition further supported the exited state charge transfer occurring in **DPPHC**. Since the emission band is essentially controlled by intramolecular charge transfer (ICT) from dimethylamino moiety to the chalcone carbonyl, addition of base results in inhibition of charge transfer due to donation of charge from phenoxide to the chalcone carbonyl. Similarly, addition of acid results in the possible protonation of the coumarin carbonyl, thereby facilitating ICT. The existence of dual emission bands in non-polar solvents could be a consequence of poor charge separation in solvents of low dielectric constant, thereby the ICT band appears as a shoulder near the local emission band at 550 nm. The high energy band could be due to the local emission arising from normal deexcitation from the S_1 state, whereas the low energy hump was due to the charge separated state [21]. Since efficient charge transfer occurs in polar solvents, the local emission is suppressed and the emission could be originating exclusively from the CT state [6]. Hence, it was concluded that the excited state photophysics of **DPPHC** was controlled by ICT. Although ICT in **DPPHC** was established, the possibility of ESIPT was to be considered since **DPPHC** contains a hydroxyl unit which could act as a proton donor in order to undergo ESIPT. However, the steady state spectral characteristics indicated ESIPT not operative in **DPPHC**. In general, the ESIPT active compounds are reported to show pronounced keto emission in non-polar solvents which is characterized by the unusually high Stokes Shifted emission band [22,23]. However, in **DPPHC**, the low energy band appeared as a mere band. Furthermore, since ESIPT is disfavored in polar solvents due to formation of H-bonds, ESIPT active compounds show dual emission in polar solvents [24], thereby furnishing the dual emission bands. On the other hand, only the polarity dependant band exists in **DPPHC**. Most importantly, in a typical example of an ESIPT coupled ICT probe *N*, *N*-diethylamino substituted 3-hydroxy flavones [10], dual emission was observed in all solvents irrespective of the polarity. The low energy band in *N*, *N*-diethylamino substituted 3-hydroxy flavone which showed solvent dependant maxima was assigned to be originating from the coupling of ESIPT and ICT states. All these features were absent in case of **DPPHC**. Hence, it could be concluded that ESIPT suppressed ICT is operative in **DPPHC**.

3.2. Excited state lifetime measurements

To gain further insight into the excited state lifetime of **DPPHC**, fluorescence decay experiments were carried out using a pulsed LASER diode of 450 nm (Fig. 3, Table 2). **DPPHC** showed fast decay beyond the instrumental resolution in non-polar solvents and thus could not be deconvoluted. In chloroform and DCM, monoexponential decays having lifetime values ~1.70 and ~2.0 ns were observed, respectively. The fluorescence lifetime in protic solvents were fitted into biexponential curves. The faster component was assigned to be due to some hydrogen bonded cluster formation which undergoes fast decay [16]. The slower component was assigned to be due to the decay from charge separated form of **DPPHC**. In case of tertiary butanol, a reversal of the population of the species is observed. This could be due to the lower propensity of Hydrogen bonding of the bulky alcohol in question as also its viscosity. Although the charge separated form is expected to have greater excited state population in polar protic solvents, the hydrogen bonding interactions largely account for the deactivation of the

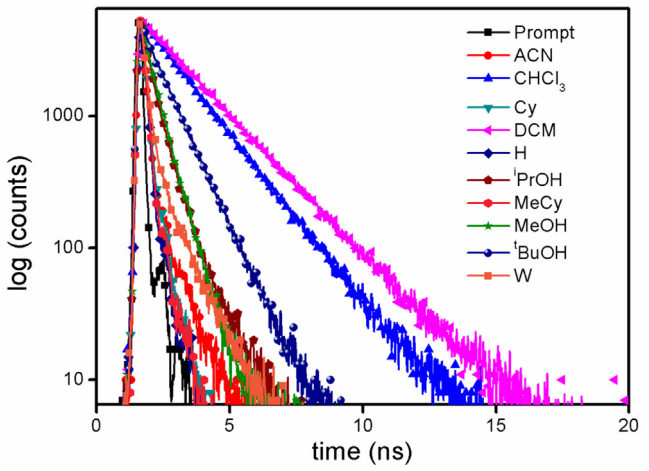


Fig. 3. Excited State decay profiles of **DPPHC** in solvents of varying polarity (λ_{ex} = 450 nm).

Table 2
Excited state lifetime parameters of **DPPHC.**

Solvent	τ_1 (ns)/α_1 (%)	τ_2 (ns)/α_2 (%)	χ^2
Chloroform	1.65/100	–	1.10
Dichloromethane	1.99/100	–	1.06
Methanol	0.48/91	1.12/9	1.02
Isopropnaol	0.38/71	0.95/29	0.98
Tertiary Butanol	0.23/5	0.96/95	1.03
Water	0.19/71	0.95/29	1.02

χ^2 denotes standard deviation.

charge separated form, leading to less excited state population in these solvents.

3.3. Application of DPPHC as a chloroform sensor

The quantum yield values of **DPPHC** in chloroform and dichloromethane were very high compared to other organic solvents (Table 1). This was reflected from the color of **DPPHC** observed under UV light (Fig. 4a), where **DPPHC** behaved as an excellent red emitter in the aforementioned two solvents. Thus, **DPPHC** can be used to identify neat chloroform in solution by simple observation of the color under UV light. Inspired by this result, a practical application for **DPPHC** to detect chloroform was devised. Due to its anesthetic nature [25], chloroform detection is important in its vapor phase as well as in solution. Initially, detection of chloroform in alcohol was attempted (Fig. 4b, 4c) as chloroform can be used to poison alcohol due to the appreciable miscibility of the two solvents. Upon gradual addition of chloroform to an ethanolic solution of **DPPHC**, the emission intensity increased with gradual red shift from ~600 to ~670 nm (Fig. 4b). However, upon normalization a more useful pattern was obtained (Fig. 4c). A ratiometric shift in emission maxima was obtained upon gradual addition of chloroform. The ratio of the intensity of two bands was plotted against the chloroform concentration (volume percentage, ESI, Figure S7). Excellent linear fit was obtained (R^2 = 0.9655). The limit of detection, calculated using IUPAC mentioned guidelines [26] was 3.0% in volume. Hence, **DPPHC** could act as a ratiometric probe to determine chloroform percentage in an alcohol sample. It should be mentioned in this context that the emission profiles of **DPPHC** in ethanol was recorded to assure its similarity with methanol (ESI, Figure S8). It is noteworthy that although the emission maximum of DPPHC was ~643 nm, the maxima for ethanol

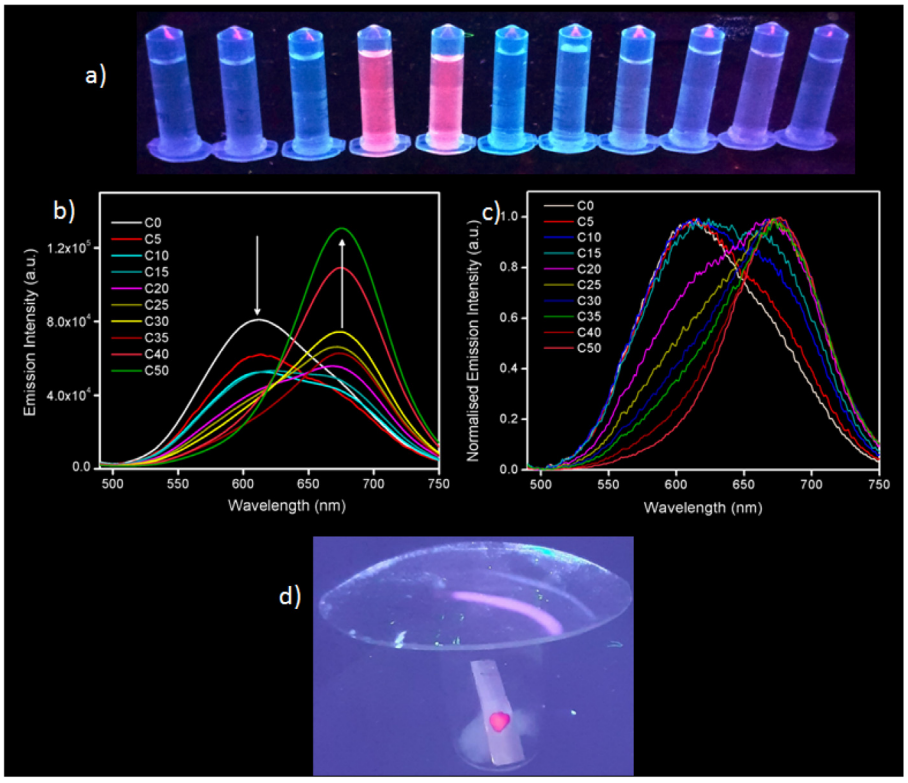


Fig. 4. (a) Color of solutions of **DPPHC** under UV-light (from left) heptane, cyclohexane, MethylcycloHexane, chloroform, dichloromethane, acetonitrile, dimethylsulfoxide, methanol, isopropanol, tertiary butanol and water. (b) Emission titration profile of **DPPHC** in ethanol upon increasing Chloroform content. (c) Normalized Emission titration profile of **DPPHC** in ethanol upon increasing Chloroform content. (C0 to C50 indicate 0% to 50% chloroform content) (d) Detection of Chloroform vapor by **DPPHC** observed under UV light.

chloroform binary mixture was at ~675 nm. This could be due to dipolar stabilization of **DPPHC** in ethanol medium upon introducing chloroform. As **DPPHC** was able to detect chloroform in ethanol, vapor phase detection of chloroform was attempted next (Fig. 4c). A TLC plate coated with **DPPHC** was inserted in a glass beaker containing a piece of cotton soaked in chloroform. The beaker was covered with a watch glass. After 3 min, the color of the TLC plate containing **DPPHC** was observed to be bright red under UV light. Hence, it could be stated that **DPPHC** could efficiently detect chloroform in the vapor phase as well. Hence, apart from a platform showing ICT prevalent over ESIPT, **DPPHC** finds considerable practical utility to detect chloroform in solution as well as vapor phase.

4. Conclusions

Excited state properties of a synthetic coumarin based chalcone 3-((2E, 4E)-5-(4-(dimethylamino) phenyl) penta-2, 4-dienoyl)-4-h ydroxy-2H-chromen-2-one (**DPPHC)** were investigated spectroscopically. From steady state and time resolved spectroscopic analysis, it was concluded that **DPPHC** portrayed ESIPT suppressed ICT process. The occurrence of ICT over ESIPT was confirmed through solvent polarity dependent red shifted low energy emission band. The ICT effect through red emission was most pronounced in chloroform and dichloromethane. Hence, **DPPHC** was utilized to detect chloroform in ethanol. The limit of detection was 3% (v/v). In addition, **DPPHC** could successfully detect chloroform vapor and liquid chloroform in the solid state.

CRediT authorship contribution statement

Arghyadeep Bhattacharyya: Formal analysis, Writing-original draft. **Nikhil Guchhait:** Supervision, Conceptualization, Writing-review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.saa.2021.119578.

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