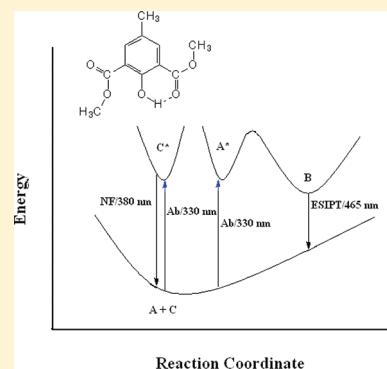


Spectral Response of 4-Methyl-2,6-dicarbomethoxyphenol, an Excited-State Intramolecular Proton-Transfer Probe in Cyclohexane–Ethanol Mixtures: Signatures of Medium Microheterogeneity

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ABSTRACT: In this paper, we explore the role of microscopic heterogeneity of the medium on the spectral response of an excited-state proton-transfer (ESIPT) probe, namely, 4-methyl-2,6-dicarbomethoxyphenol (CMOH) using steady-state and time-resolved emission spectroscopy. The mixtures of two solvents with widely different properties, viz., cyclohexane, a nonpolar, and ethanol, a polar protic solvent, were used as microheterogeneous media for spectroscopic studies. Dual fluorescence (normal and tautomer fluorescence) is observed in the nonpolar solvent (cyclohexane), while only a single peak is observed in the protic solvent, ethanol. The spectral responses of CMOH in the binary mixtures have been found to be dependent on the solvent composition and excitation wavelength. The emission spectral properties of CMOH in the cyclohexane–ethanol mixture have been seen to be superposition of spectral properties in their bulk counterparts, indicating the presence of microscopic heterogeneity in the system. A zwitterionic species of CMOH appears to have been detected in binary solvent mixtures with higher ethanol content only through low-energy excitations. The species is converted into an anionic species as excitation energy increases. Density functional theory calculations indicate that two intramolecularly hydrogen bonded rotamers of CMOH have a small energy difference. The formation of a hydrogen bonded 1:1 molecular cluster of CMOH with ethanol has been investigated in the ground state at the same level of theory. Our findings are expected to shed light on the mechanism of many acid–base reactions occurring in microscopically inhomogeneous media that often mimic many biologically relevant processes.



1. INTRODUCTION

Of late, effects of microscopic heterogeneity of the medium on physicochemical processes have been a hot topic of research in the field of chemistry and biology^{1–4} because many biological processes occur in interfaces rather than in homogeneous media. Uses of micelles, reverse micelles, and ionic liquids have become very common as microscopically heterogeneous media for studying photophysical or photochemical behavior of organic molecules.^{5,6} Excited-state intramolecular proton transfer (ESIPT), which is one of the most fundamental phenomena, consists of a reversible transfer of a proton from a proton donor to a proton acceptor located at a particular distance.^{7,8} In the excited state, the acidity constant of a species can be significantly different from that of the parent ground-state species and structure. The ESIPT phenomenon has drawn the attention of the scientific community due to similarity with many biological processes, including organization of cell membranes, action of ion channels and enzyme catalysis, and so forth.^{7–10} The proton-transfer reaction is a fundamental step in many hydrogen bonded systems. Studying proton transfer in different media provides us with unprecedented insight into these biological processes. The molecules that give rise to fluorescent tautomers through ESIPT are used as laser dyes, in molecular energy storage systems, and in high-energy radiation detectors, etc. In recent times,^{9–23} the

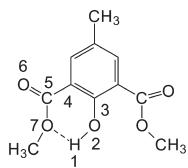
proton-transfer reaction has been studied in different media including binary solvent mixtures, micelles, reverse micelles and ionic liquids.

In the present study 4-methyl-2,6-dicarbomethoxyphenol (CMOH, Scheme 1), an *o*-hydroxybenzaldehyde type of compound is used as a proton-transfer probe.^{24–26} In the ground state, the H-atom of the hydroxyl group remains hydrogen bonded with the oxygen atom of one of the adjacent carbonyl groups or one of the methoxy groups, located at the ortho position with respect to the hydroxyl group. In molecules of this type, proton transfer has been seen mainly in the excited state. Our previous studies have revealed^{24–26} that CMOH can exist in different forms, which are shown in Scheme 2. The probe seems to be more abundant as the intramolecularly hydrogen bonded closed conformer (conformer A) in the ground state. Conformer B in Scheme 2 is the proton-transferred conformer of the probe. CMOH also exists as another closed conformer (which is a rotamer of conformer A), where the hydroxyl proton is hydrogen bonded to the methoxy (-OCH₃) oxygen of CMOH (conformer C) and it forms anions (conformer D) in basic media or due to

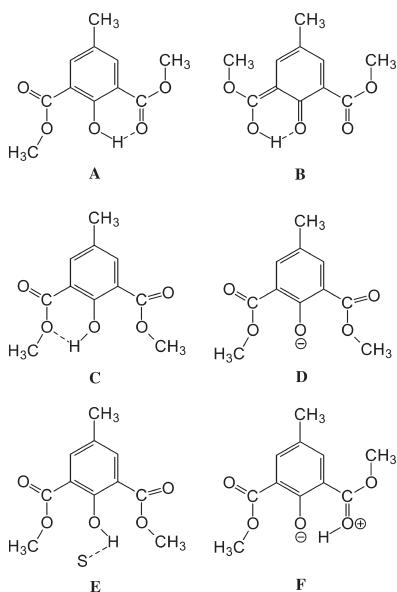
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Scheme 1. Structure of the Probe (CMOH)^a

^a The numbering of selected atoms is done for reference. The hydrogen bond between the hydrogen atom of the hydroxyl hydrogen and the oxygen atom of the ester group has been shown with the dotted line.

Scheme 2. Possible Conformers of the Probe (CMOH)^a

^a The A form is the hydrogen bonded closed form, and the B is the ESIPT form of CMOH. The C form is another hydrogen bonded closed form rotamer, and the D is the anion formed due to loss of a proton from CMOH. E is the hydrogen bonded form of CMOH with solvent while the F form is the zwitterionic form of CMOH.

abstraction of proton by the solvent. The probe molecule forms intermolecular hydrogen bonds with polar solvents, and the structure is depicted as conformer E in Scheme 2. Conformer F in Scheme 2 stands for the zwitterionic form of the probe. The probe molecule can exist in different forms, depending on the properties of the media. So, it will be interesting to decipher the role of the media in stabilizing a particular form. It is a well-studied²⁴ fact that CMOH shows dual fluorescence in nonpolar and weakly polar solvents, and the longer wavelength peak arises due to proton transfer in the excited state (ESIPT). The effect of the media on a particular type of behavior has been keenly studied by the scientific community because it helps provide an understanding of environmental implications of many biologically important processes.^{27,28} Sometimes it is not possible to study a particular property of a molecule using pure solvents alone. In such cases one explores the possibility of using binary solvent mixtures.^{29,30}

For our present study, we have taken two solvents with widely varying properties to explore the role of the medium in the excited-state proton-transfer process of this probe. The properties of the cyclohexane–ethanol binary mixture have been studied

using steady-state and time-resolved spectroscopic techniques. It has been reported that cyclohexane and ethanol give rise to macroscopic heterogeneity in their binary solutions.^{31,32} This makes this medium ideal for photophysical studies because medium microheterogeneity induces preferential solvation that could affect the proton-transfer process. The role of solvent microheterogeneity, if any, on the intramolecular proton transfer of CMOH has remained hitherto unresolved.

In this contribution, we have explored the role of microscopic homogeneity as well as heterogeneity of the medium in the excited-state proton-transfer reaction of CMOH using pure solvents and cyclohexane–ethanol binary mixtures. The outline of the paper is as follows. In section 2, the materials used and the methods adopted for this work have been described. In section 3a, the results obtained from the steady-state absorption and emission studies of the probe in microscopically homogeneous media have been discussed. In section 3b, the results of our density functional theory (DFT) calculations have been discussed and formation of a 1:1 molecular cluster by the probe with ethanol has been confirmed. Using experimental results and theoretical calculations on CMOH, the potential energy surfaces of CMOH in cyclohexane have been drawn and described in section 3c. Section 3d deals with spectral responses in a cyclohexane–ethanol binary mixture, a microscopically heterogeneous medium. The results of our time-resolved experiments have been discussed in section 3e. The conclusions drawn from the present work have been described in section 4.

2. MATERIALS AND METHODS

2a. Materials and Solutions. CMOH was prepared in the Inorganic Chemistry department of this institute using the procedure described elsewhere.^{33,34} The compound was recrystallized from methanol and dried before use. The solvents used were of spectroscopic grade (Merck/Spectrochem). Triply distilled water was used throughout the experiment. Analytical grade NaOH and triethylamine (TEA) were used. All of the solvents were checked for residual fluorescence, if any, before use. To avoid the effect of concentration, very dilute solutions were used for all spectral measurements of the probe ($(2\text{--}3) \times 10^{-5}$ mol/L). All of the spectral data were collected at an ambient temperature of 298 K.

2b. Instruments. Absorption and emission spectra of CMOH were recorded on a Shimadzu UV-vis spectrophotometer, UV-2401 (PC) S220 V and Fluoro Max 3 (Horiba Jobin Yvon) fluorescence spectrophotometer, respectively. The lifetime measurements have been performed by using time-correlated single-photon counting (TCSPC) technique in a Horiba Jobin Yvon instrument. The details of this instrument have been reported elsewhere.³⁵ Briefly, the system was excited using two different lights with wavelengths of 340 and 375 nm, and the emissions were monitored as corresponding steady-state emission wavelengths. The detector was a Hamamatsu MCP plate photomultiplier (R3809U). The single-photon counting technique was comprised of an Ortec 9327 discriminator (CFD, Tenelec TC 454) and Fluoro Hub single-photon counting controller. The data were collected with a DAQ card as a multichannel analyzer. The spectra obtained were analyzed by using the Software IBH DAS6 at Data Station v2.3 through exponential fitting to yield the corresponding excited-state lifetimes of CMOH. The quality of fit was judged in terms of a Durbin–Watson (DW) parameter, weighted residuals, and reduced χ^2 values.

2c. Theoretical Calculations. The ground-state geometries of rotamers A and C of the probe (CMOH) have been optimized fully using DFT employing Becke's—three parameter—Lee—Yang—Parr (B3LYP) hybrid functional and Dunning type correlation consistent valence triple- ζ (cc-pVTZ) basis set.³⁶ Calculations based on time-dependent density functional theory

(TDDFT) have been performed to compute energies and oscillator strengths of first 10 vertical transitions. Because cyclohexane cannot form a hydrogen bond with CMOH (rotamer C), the effect of this solvent on the electronic structure of the probe has been taken into consideration using the self-consistent reaction field (SCRF) theory that takes care of the macroscopic solvation of the probe. The structure of the 1:1 molecular cluster of CMOH (rotamer C) with ethanol (CMOH·C₂H₅OH) in the ground state has been optimized at the same level of theory. The SCRF calculations have been performed on the CMOH·C₂H₅OH cluster to study the effect of microscopic as well as mesoscopic solvation of the probe in ethanol. All of the calculations have been performed using the quantum chemical software, Gaussian 03.³⁷

3. RESULTS AND DISCUSSION

3a. Steady-State Absorption and Emission Studies of CMOH in Pure Solvents. To understand the spectral response of CMOH in the cyclohexane—ethanol binary mixture, the properties of this probe in pure counterparts must be analyzed first. We have recorded the steady-state spectra of the probe at room temperature in pure cyclohexane as well as in pure ethanol. The absorption and emission spectra of the probe in cyclohexane have been displayed in Figure 1, while the absorption and emission maxima of the probe in different media have been reported in Table 1 for ready reference. It has been observed that in cyclohexane the absorption spectrum of CMOH shows a single peak at 330 nm. The emission spectrum of the probe in cyclohexane, when excited (λ_{ex}) at 330 nm, shows large

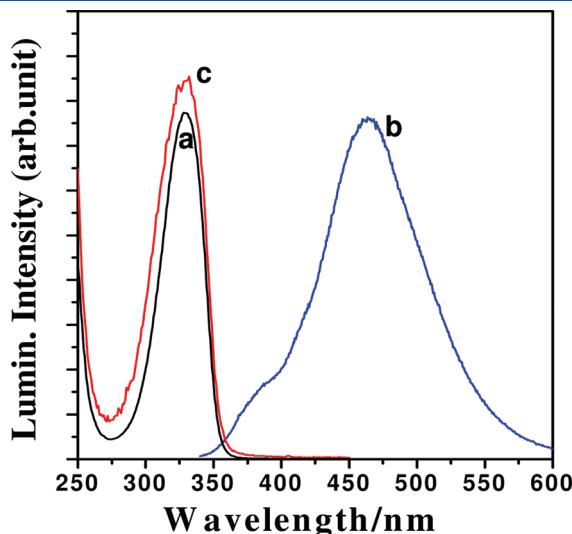


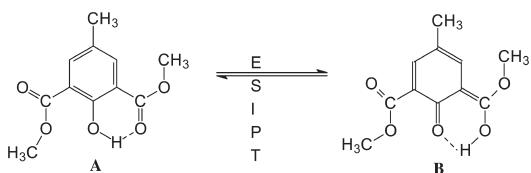
Figure 1. Steady-state absorption (a) and emission (b) and excitation (c) spectra of CMOH in cyclohexane. The excitation wavelength was 330 nm. The excitation spectrum (c) was collected by monitoring the emission at 465 nm.

Table 1. Recorded Steady-State Absorption (λ_{abs}) and Emission (λ_{emm}) Maxima (Cross Marked) of CMOH in Cyclohexane (C), Ethanol (E), and Their Binary Mixtures Corresponding to 330 and 360 nm Excitation (First and Second Row, Respectively)^a

media	χ_P	λ_{abs} (nm)			λ_{emm} (nm)					
		330	370 (D)	380 (C)	402 (F)	430 (E)	450 (D)	460 (B)	465 (B)	
cyclohexane	0.00	×		×						×
				×						×
95% C + 5% E	0.09	×		×						×
				×						×
90% C + 10% E	0.17	×		×						×
				×						×
80% C + 20% E	0.32	×		×						×
				×						×
60% C + 40% E	0.55	×		×						×
				×						×
50% C + 50% E	0.65	×		×						×
				×						×
40% C + 60% E	0.73	×		×						×
				×						×
20% C + 80% E	0.88	×		×						×
				×						×
ethanol	1.00	×								×
										×
water	—	×		×						×
				×						×
aqueous NaOH	—	×	×	×	×					×

^a The different species formed have been cross (×) marked. The mole fraction of the polar solvent (χ_P) in the cyclohexane—ethanol binary mixture of the media are also reported.

Scheme 3. Mechanism of Intramolecular Proton-Transfer Reaction of CMOH in Different Media



Stokes-shifted emission at 465 nm with a shoulder appearing around 380 nm. The 465 nm emission band has been assigned to the enol tautomer (Scheme 2B) formed through ESIPT. The mechanism of formation of the ESIPT form in the excited state has been depicted in Scheme 3. The relatively weak fluorescence band at 380 nm is assigned to the intramolecularly hydrogen bonded closed conformer of CMOH (Scheme 2C), where the hydroxyl proton is hydrogen bonded to the methoxy (-OMe) oxygen of CMOH. Similar assignments exist in literature in the cases of salicylamide³⁸ and methyl salicylate.³⁹ We have recorded the excitation wavelength dependent emission spectra of the CMOH in cyclohexane and found that it is independent of the excitation wavelength.

The absorption spectra of CMOH in pure ethanol and in the presence of base in ethanol have been recorded and displayed in Figure 2A. The absorption spectrum of the probe in ethanol shows a single peak at 330 nm. Although the absorption maximum of CMOH in ethanol is energetically same with that in cyclohexane, the origins of these two species are different. The 330 nm species in ethanol presumably arises due to the formation of an intramolecular hydrogen bonded closed conformer of CMOH.²⁵ This is due to formation of a stable 1:1 molecular complex by CMOH with ethanol, as described in section 3b of this paper. By the addition of a strong base such as NaOH or TEA, another relatively weak absorption band appeared at 370 nm in ethanol (Figure 2A). The emission spectra of the probe in ethanol have been recorded with varying excitation wavelengths and displayed in Figure 2B. The emission spectrum of the probe in ethanol shows a peak at 450 nm when excited with 330 nm light. The emission maximum of the probe gets blue-shifted with an increase in the excitation wavelength, and a new peak is generated at 430 nm while exciting the sample at 360 nm or higher wavelengths. It has been seen that the intensity of the 450 nm band increases with the gradual addition of base without any change in the position of the band. The excitation spectra corresponding to the 450 nm emission peak in pure water and ethanol show peaks at 330 nm. To establish the nature of the species formed in ethanol in the ground and excited states, we compared the spectral behavior of CMOH in ethanol with that of CMOH in pure water and in the presence of base. The absorption spectra in pure water and in the presence of base have been shown in Figure 3A. The absorption spectrum of CMOH in pure water shows a peak at 330 nm. The addition of base in pure water gives rise to another peak at 370 nm, the intensity of which has been seen to increase due to further addition of base in the medium with a concomitant decrease in the intensity of the 330 nm peak. It shows an isosbestic point at 340 nm (Figure 3A), indicating that the species involved (closed conformer and anion) are in equilibrium. The emission spectrum (Figure 3B) of the probe in water shows a single peak at 450 nm. The emission spectra of CMOH in water are found to be independent

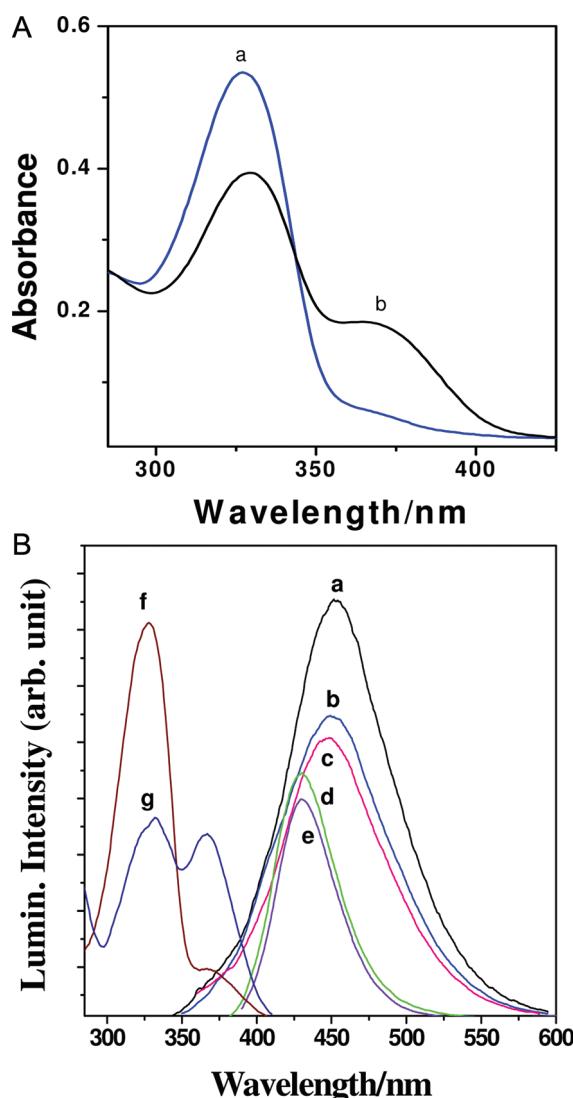


Figure 2. (A) Absorption spectra of CMOH in pure ethanol (a) and in the presence of base (b). (B) Excitation wavelength dependent emission spectra (a–e) and excitation spectra (f and g) of CMOH in ethanol at room temperature. Excitation wavelengths were as follows: (a) 330, (b) 340, (c) 350, (d) 360, and (e) 370 nm. Excitation spectra of CMOH in pure ethanol (f) and in presence of TEA (g) using λ_{mon} of 450 nm.

of excitation wavelength. Addition of base to this solution increases the intensity of the 450 nm peak, confirming the fact that the single emission peak is indeed due to the anionic form of CMOH, which is formed in the excited state. The spectral observations in ethanol and water indicate the presence of anion in pure solvents in the excited state. The excitation spectrum in basic water shows a single band at 370 nm, which is indeed similar to the absorption spectra of anion. From this observation we propose that the 450 nm emission band is due to the anion of CMOH. These observations also indicate that the ionization of CMOH, i.e., the formation of the anion in the excited state, is complete only in water. Because of the presence of an electron-donating ethyl group, ethanol can accept a proton from CMOH, particularly in the excited state. Water is a stronger proton acceptor than ethanol (the Brønsted acidity, pK_a , of ethanol and water are 15.9 and 14, respectively). So, water can rupture the intramolecular hydrogen bond of CMOH to form the

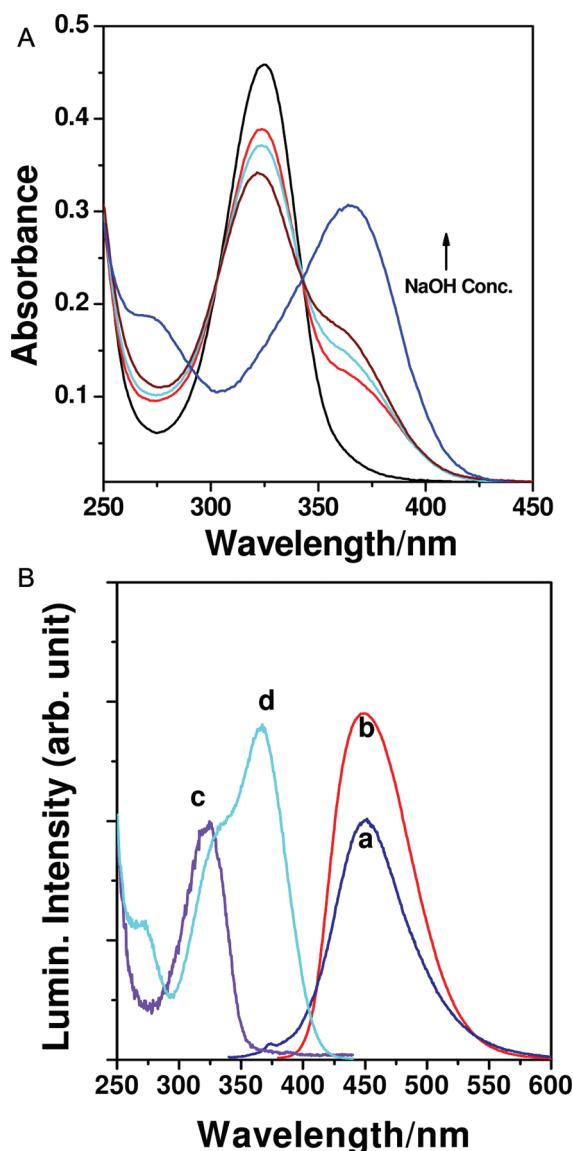


Figure 3. (A) Steady-state absorption spectra of CMOH in water with increasing concentration of NaOH. With addition of base the intensity of the anion (370 nm) increases. (B) Emission (a and b) and excitation (c and d) spectra of aqueous CMOH in the absence (a and c) and presence (b and d) of dilute base (NaOH). Excitation spectra of the probe were collected by monitoring their corresponding emission maxima.

solvated open conformer (Scheme 2E), and upon photoexcitation the open conformer is converted to the anion through the elimination of proton. Formation of the anion through rapid proton dissociation accounts for the absence of open conformer emission in water. On the addition of a base such as TEA or NaOH the emission intensity increases without any change in position of the band and is independent of excitation wavelength only in water. Due to the similarity in spectral features in water and ethanol, we tend to conclude that the 450 nm species of CMOH detected from the emission spectra of the probe in ethanol is indeed the anionic form of CMOH. The 430 nm band is assigned to the intermolecularly hydrogen bonded complexes with ethanol (Scheme 2E) that has been formed at the excited state.

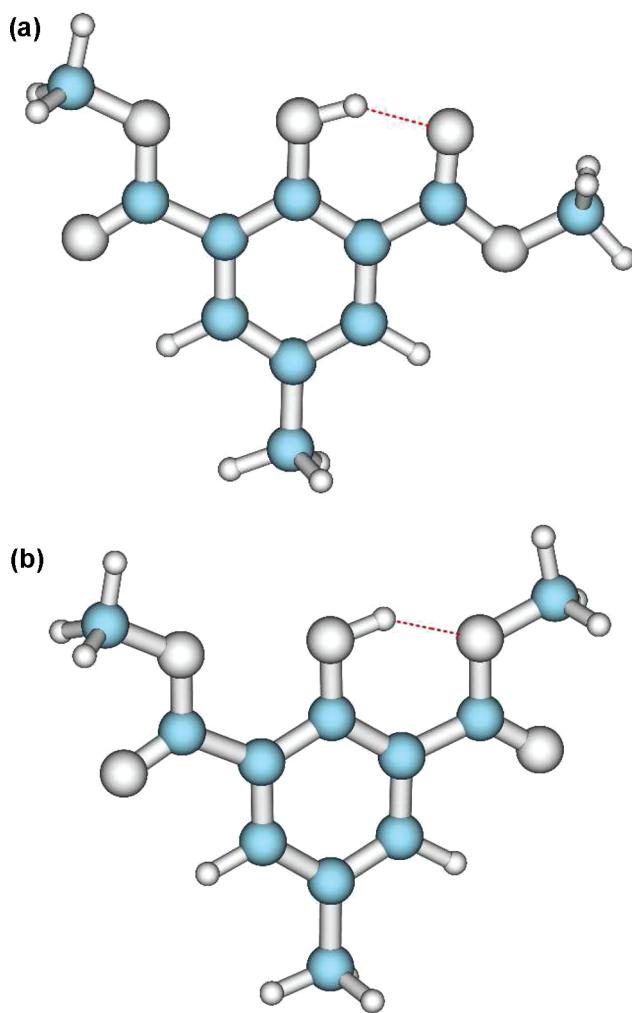


Figure 4. Gas-phase optimized geometry of rotamer A (A) and rotamer C (A) of CMOH in the ground state as obtained using DFT calculation, employing the B3LYP functional and the cc-pVTZ basis set.

3b. Ground-State Geometry of CMOH in the Gas Phase, in Cyclohexane, and in Ethanol. The ground-state geometries of CMOH rotamers A and C in the gas phase have been optimized fully using density functional theory employing the B3LYP hybrid functional and the cc-pVTZ basis set. The structures obtained have been shown in Figure 4A,B. The equilibrium distances between pairs of atoms of conformers A and C have been reported in Table 2 for ready reference. In the ground state, the hydrogen atom of the hydroxyl group (-OH) of rotamer A forms an intramolecular hydrogen bond with the carbonyl oxygen atom while in rotamer C the hydrogen of the hydroxyl (-OH) group forms an intramolecular H-bond with the oxygen of the methoxy (-OCH₃) groups. For this reason, the equilibrium bond lengths and the electronic charge distribution over the atoms of these two conformers are somewhat different. For example, the H₁-O₂, O₂-C₃, and C₃-C₄ bond lengths in rotamer A have been seen to be 0.986, 1.332, and 1.422 Å, respectively, while those in rotamer C have been seen to be 0.972, 1.340, and 1.419 Å, respectively. The electronic charges over the atoms of the molecule have been displayed in Table 3. The Mulliken charges over the H₁, O₂, and C₃ atoms of conformer A have been found to be +0.227, -0.252, and +0.172 electronic

Table 2. Distances (\AA) between Pairs of Atoms in CMOH (Rotamers A and C), the Rotamer C of CMOH in SCRF ($\epsilon = 2$) of Cyclohexane [CMOH (C) + Cyc], in 1:1 Molecular Cluster with Ethanol, Considering Microscopic and as Well as Macroscopic Solvations (1:1 Cluster + SCRF)^a

system	H_1-O_2	O_2-C_3	C_3-C_4	C_4-C_5	C_5-O_6	C_5-O_7	$\text{H}_1-\text{O}_\text{H}$ ^b	$\text{O}_7-\text{H}_\text{S}$
CMOH (A)	0.986	1.332	1.422	1.470	1.226	1.339	1.680	
CMOH (C)	0.972	1.340	1.419	1.483	1.205	1.369	1.726	
CMOH (C) + Cyc	0.973	1.341	1.419	1.484	1.207	1.364	1.718	
1:1 cluster	0.974	1.346	1.413	1.484	1.204	1.368	1.715	2.018
1:1 cluster + SCRF	0.976	1.347	1.413	1.484	1.209	1.358	1.709	2.111

^a The intramolecular hydrogen bonding distances (\AA) and the distances (\AA) between H_7 and the alcoholic hydrogen of ethanol (marked as H_S), whenever applicable, have also been reported. ^b The oxygen atom to which the H_1 is attached through hydrogen bond. It is O_6 in rotamer A of CMOH while it is O_7 in case of rotamer C.

Table 3. Mulliken Atomic Charges (Atomic Unit) over Some Atoms in CMOH (Rotamers A and C), the Rotamer C of CMOH in SCRF ($\epsilon = 2$) of Cyclohexane [CMOH (C) + Cyc], in 1:1 Molecular Cluster with Ethanol, Considering Microscopic and as Well as Macroscopic Solvations (1:1 Cluster + SCRF)

system	H_1	O_2	C_3	C_4	C_5	O_6	O_7
CMOH (A)	0.227	-0.252	0.172	-0.093	0.335	-0.370	-0.225
CMOH (C)	0.213	-0.248	0.160	-0.112	0.337	-0.323	-0.267
CMOH (C) + Cyc	0.219	-0.257	0.160	-0.106	0.345	-0.342	-0.263
1:1 cluster	0.227	-0.289	0.190	-0.115	0.339	-0.320	-0.267
1:1 cluster + SCRF	0.238	-0.304	0.195	-0.096	0.361	-0.369	-0.259

unit, respectively, while those in conformer C are seen to be $+0.213$, -0.248 , and $+0.160$ electronic unit, respectively. The hydrogen bond distance in rotamer A turns out to be 1.680 \AA while that in rotamer C is 1.726 \AA . This indicates that rotamer A forms a stronger intramolecular hydrogen bond compared to rotamer C. The energies of both rotamers have been calculated, and it has been found that the energies of both rotamers are comparable. Rotamer A is 1451 cm^{-1} less in energy compared to rotamer C. Because cyclohexane cannot form a hydrogen bond with the probe, we have optimized the geometry of CMOH in SCRF of cyclohexane ($\epsilon = 2$). It has been observed that the geometry and the electronic charges over the atoms of CMOH change due to solvation in cyclohexane. The geometry of 1:1 molecular cluster of CMOH with ethanol (CMOH-EtOH) has been optimized using the DFT B3LYP functional and cc-pVTZ basis set, and the fully optimized structure has been displayed in Figure 5A. To consider the macroscopic solvation of the probe by ethanol, the geometry of the 1:1 molecular cluster has been further optimized using SCRF of ethanol ($\epsilon = 36$), and the optimized structure is displayed in Figure 5B. Marginal changes have been seen in the key geometrical parameters due to macrosolvation. The H_1-O_2 distance is seen to be marginally elongated from 0.972 to 0.973 \AA due to macroscopic solvation by cyclohexane. The H_1-O_2 bond distance further increases to 0.974 \AA as a result of 1:1 molecular cluster formation with ethanol and to 0.976 \AA when macrosolvation of the 1:1 cluster is accounted for. It has been observed that the solvents assist in the intramolecular hydrogen bonding of the probe in the ground state. The intramolecular hydrogen bond distances predicted in the SCRF of cyclohexane, in the 1:1 CMOH-EtOH microcluster and with consideration of both the microscopic and the macroscopic solvation by ethanol, have been seen to be 1.718 , 1.715 , and 1.709 \AA , respectively. It has been observed that the electronic charge distribution over the key atoms in the molecule changes due to microscopic as well as macroscopic solvation of

the probe by ethanol. For example, the Mulliken charge over the H_1 atom increases from 0.213 electronic unit to 0.219 electronic unit due to macroscopic solvation by cyclohexane. The electronic charge over H_1 is 0.227 electronic unit after formation of a 1:1 molecular cluster with ethanol which increases to 0.233 electronic unit as a result of macroscopic solvation by ethanol. On the other hand, the Mulliken charges over the O_7 atom decreases from -0.267 electronic unit to -0.263 electronic unit due to macroscopic solvation by cyclohexane. The decrease in Mulliken charge from -0.267 electronic unit to -0.259 electronic unit has been observed due to macroscopic solvation of the CMOH- $\text{C}_2\text{H}_5\text{OH}$ cluster by ethanol. The distance between the O_7 atom of the probe and the alcoholic hydrogen (H_S) of ethanol has been seen to change due to macroscopic solvation by ethanol. The $\text{O}_7-\text{H}_\text{S}$ distance in the CMOH- $\text{C}_2\text{H}_5\text{OH}$ cluster has been calculated to be 2.018 \AA while that in the SCRF of ethanol has been seen to be 2.111 \AA . So, we can conclude that the probe forms a 1:1 molecular cluster with ethanol in the ground state due to the formation of strong hydrogen bonds between the probe and the solvent.

3c. Excited-State Potential Energy Surfaces of CMOH in Cyclohexane. We have used the results obtained from different experiments and from our calculations using TDDFT to explore the potential energy surface of CMOH in cyclohexane, a medium where ESIPT reaction of CMOH has been seen to occur. The TDDFT calculation has been performed on the gas-phase optimized geometries of CMOH (rotamers A and C) using the B3LYP functional and the cc-pVTZ basis set. The set of the first 10 vertical excited states was considered for our calculations. It has been predicted that, in rotamer A, the $\text{S}_0 \rightarrow \text{S}_1$ transition occurs at 317 nm . The oscillator strength (f) of $\text{S}_0 \rightarrow \text{S}_1$ transition is 0.14 . The transition from the S_0 to S_2 (264 nm), S_3 (247 nm), S_4 (245 nm), and S_5 (232 nm) states in rotamer A have oscillator strengths of 0.001 , 0.001 , 0.001 , and 0.16 , respectively. In rotamer C, it is predicted that the $\text{S}_0 \rightarrow \text{S}_1$ transition occurs at

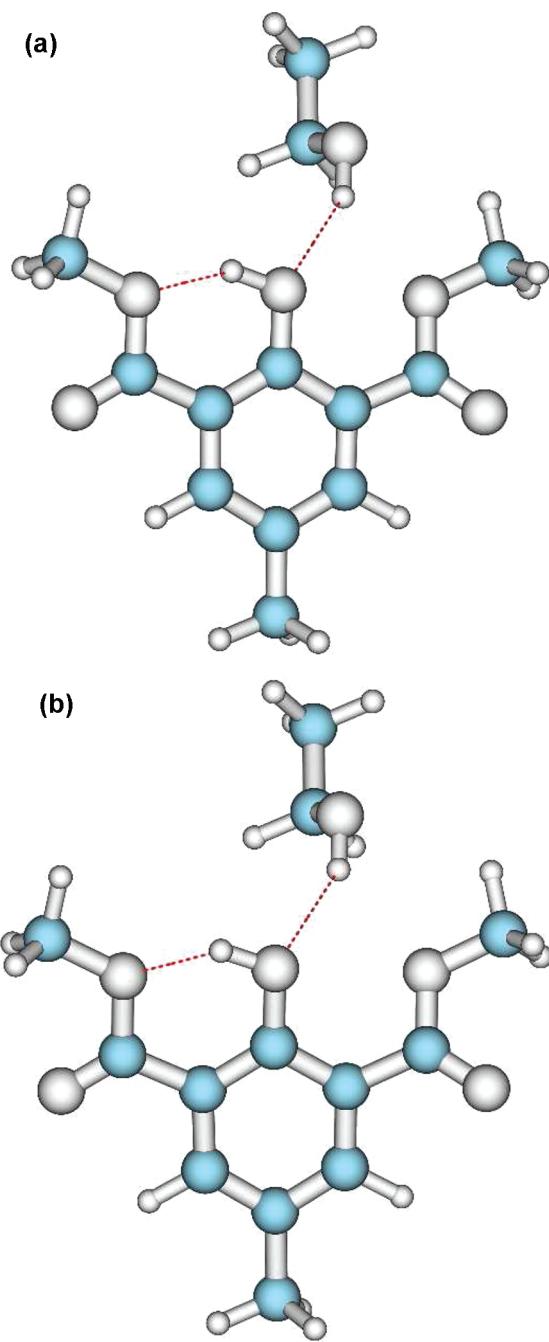
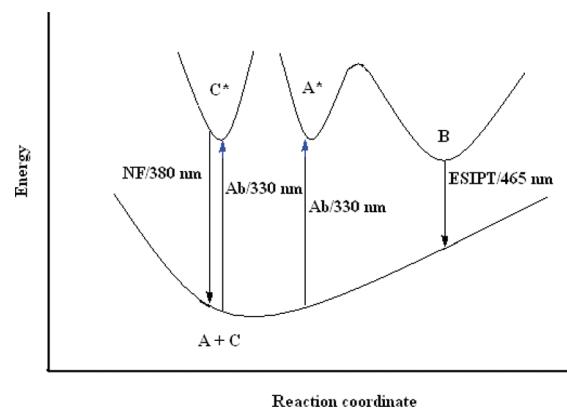


Figure 5. (A) Ground-state optimized geometry of 1:1 cluster of CMOH with ethanol (A) in the gas phase and (B) with consideration of both microscopic and macroscopic solvation by ethanol. DFT B3LYP functional and cc-pVTZ basis set were used for the calculation.

309 nm and f of this transition is 0.12. The transition from the S_0 to S_2 (262 nm), S_3 (246 nm), S_4 (246 nm), and S_5 (231 nm) states have oscillator strengths of 0.001, 0.001, 0, and 0.17, respectively. So, it is obvious that the ground state as well as the first five excited states of rotamer A and rotamer C are comparable in energies and oscillator strengths of transitions are also comparable. Hence, both rotamer A and rotamer C of CMOH can coexist and take part in the absorption process. Comparing the experimental values of absorption wavelengths in cyclohexane, which is a nonpolar solvent ($\epsilon = 2$) and the

Scheme 4. Potential Energy Diagram of the Proton-Transfer Reaction of CMOH in Cyclohexane^a



^a In the ground state both A and C conformers of CMOH are present, which absorbs energy. The C form is responsible from the normal fluorescence (NF) while A form tautomerizes in the excited state to give proton transferred B form which gives the emission spectra for ESIPT.

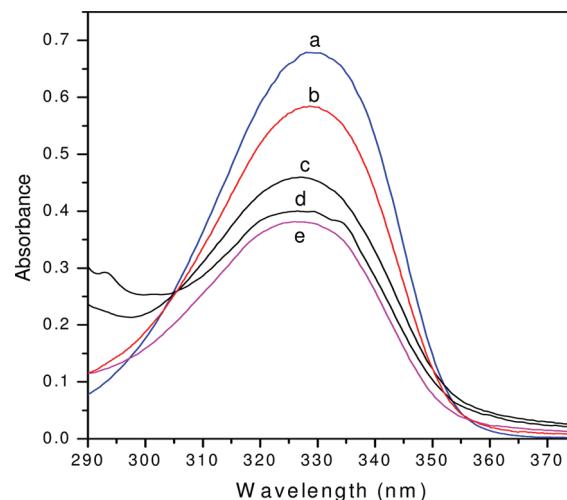


Figure 6. Absorption spectra of CMOH in (a) cyclohexane, cyclohexane–ethanol mixtures [$\chi_P = 0.32$ (b), 0.65 (c), and 0.88 (d)] and in pure ethanol (e). No change in absorption maximum has been observed due to change in the solvent.

oscillator strength of absorptions with the TDDFT counterparts shows that absorption of light excites the molecule to an S_1 state. A combined result from our theoretical calculations and experimental studies help us to construct an energy diagram for absorption and emission of CMOH in cyclohexane. It can be surmised that both conformer A and conformer C are responsible for the absorption of the probe. The excitation spectra of CMOH show peaks at 330 and 327 nm, when the emissions of the probe in cyclohexane were monitored at 460 and 380 nm, respectively. So, the difference in energy of the A and C rotamers are 3 nm only, which is comparable to that obtained from TDDFT calculation (8 nm). The small difference in energy in the gas phase and in solution may be assigned to the solvent stabilization of the probe. The normal fluorescence of the probe in cyclohexane has been seen to be at 380 nm, which is from the C form of the probe. It can be proposed that the excited form of

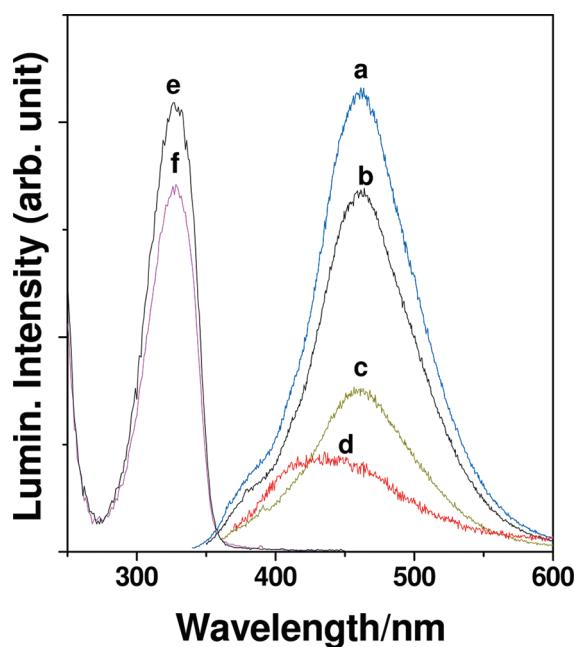


Figure 7. Emission spectra of CMOH in an 80:20 cyclohexane–ethanol binary mixture at different excitation wavelengths: (a) 330, (b) 340, (c) 350, and (d) 370 nm. Excitation spectra were obtained by monitoring the emission wavelengths at 380 (e) and 465 nm (f).

rotamer C (C^*) has no crossing with the excited form of rotamer A (A^*) and that is why it gives rise to normal fluorescence at 380 nm rather than getting converted to A^* to give emission from the ESIPT form of the probe. The A form gets excited to A^* due to absorption of 330 nm light and tautomerizes in the excited state to produce form B (ESIPT state), which is responsible for the 465 nm emission of the probe. These observations have been depicted in Scheme 4.

3d. Steady-State Absorption and Emission Studies of CMOH in Cyclohexane–Ethanol Binary Mixtures. The absorption spectra of CMOH in cyclohexane–ethanol solvent mixtures with varying compositions have been recorded at room temperature and have been displayed in Figure 6. The absorption maxima of the probe in different media have been reported in Table 1 along with the respective emission maxima. The percentage of each of the solvents and the mole fraction (χ_p), which has been calculated using the following equation

$$\chi_p = \frac{n_p}{n_n + n_p} \quad (I)$$

where n_n and n_p are the mole numbers of the nonpolar and polar solvents present in the binary mixture, respectively, have been reported in the same table. It has been observed that the probe shows an absorption maximum at 330 nm both in cyclohexane and ethanol. The absorption maximum of the probe in cyclohexane–ethanol binary mixtures does not shift with the change in solvent composition. Rather, with gradual increase in the ethanol content, the ESIPT peak vanishes. The emission spectra of CMOH at 80:20 cyclohexane–ethanol binary mixture ($\chi = 0.32$) has been recorded by exciting the solution with varying excitation wavelengths (Figure 7). At an excitation wavelength of 330 nm, the emission spectrum of CMOH shows a peak at 465 nm with a shoulder at 380 nm. The large Stokes-shifted emission peak at 465 nm is assigned to the ESIPT band of

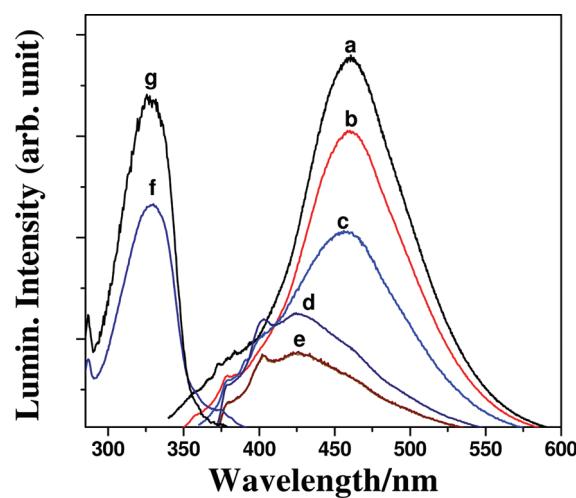


Figure 8. Emission spectra of CMOH in a 50:50 cyclohexane–ethanol binary mixture at different excitation wavelengths: (a) 330, (b) 340, (c) 350, (d) 360, and (e) (370 nm). Excitation spectra were obtained by monitoring the emission wavelengths at 400 (f) and 460 nm (g).

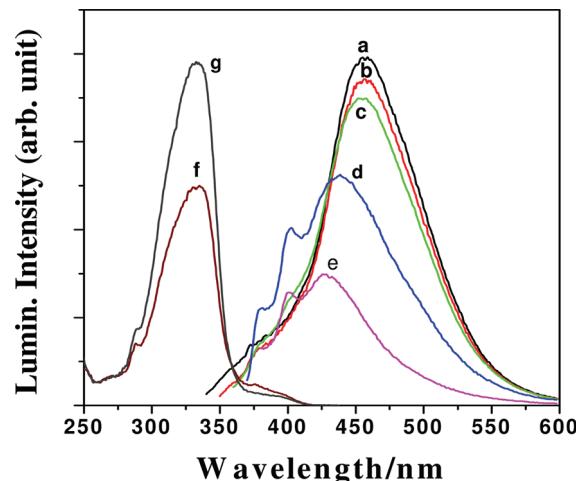


Figure 9. Emission spectra of CMOH in the 20:80 cyclohexane–ethanol binary mixture at different excitation wavelengths (nm): (a) 330, (b) 340, (c) 350, (d) 360, and (e) 370 nm. Excitation spectra were obtained by monitoring the emission wavelengths at 400 (f) and 460 nm (g).

CMOH, and the shorter wavelength (380 nm) species is assigned to the normal form of the probe (Scheme 2C). The excitation spectra of CMOH obtained by monitoring the emission at 380 and 460 nm have been displayed in Figure 7. The recorded excitation spectra of the probe show a peak at 330 nm, while monitoring at 460 and 380 nm, indicating the fact that both species have originated in the ground state. Excitation of the probe at 340 nm does not alter the emission maxima of the probe, but there is a small decrease in intensity compared to that of the spectrum obtained through the 330 nm excitation. CMOH in an 80:20 cyclohexane–ethanol binary mixture shows emission peaks at 380 and 430 nm when the probe is excited at 370 nm. The new peak at 430 nm probably originates from the intermolecularly hydrogen bonded species of the probe (Scheme 2E).

The emission spectra of CMOH in a 50:50 cyclohexane–ethanol binary mixture ($\chi_p = 0.65$) have been recorded and

displayed in Figure 8. Excitation at 330 or 340 nm shows spectral behavior similar to that seen in the 80:20 cyclohexane–ethanol binary mixture ($\chi = 0.32$). In the 50:50 cyclohexane–ethanol binary mixture, an excitation wavelength (λ_{ex}) of 360 nm gives an additional peak at around 402 nm along with the 380 and 430 nm peaks. We have recorded the excitation spectra of the probe in the 50:50 cyclohexane–ethanol binary mixture by monitoring the emission at 400 and 460 nm. The recorded excitation spectra have been displayed in Figure 8. The 330 nm peak appears in each case, indicating that all of the species responsible for the emission spectra of the probe at this composition originate in the ground state. The emission spectrum of the probe in a 40:60 cyclohexane–ethanol binary mixture ($\chi_p = 0.73$), for excitation at 330 nm, shows peaks at 380 and 460 nm. When the sample is excited at 360 nm, the probe does not show any peak at 430 nm, indicating that no intermolecular hydrogen bonded complex is formed. Instead, it shows a broad peak at 402 nm which could arise due to the formation of the zwitterionic form of the probe (Scheme 2F) at this solvent composition.

The emission spectral behavior of the probe in a 20:80 cyclohexane–ethanol binary mixture is shown in Figure 9. We find that it is quite similar to what has been observed in the 50:50 cyclohexane–ethanol binary mixture of the probe. At the excitation wavelength of 330 nm, the emission spectrum of CMOH at this composition shows peaks at 380 and 460 nm, due to the presence of the normal form and of the ESIPT form of CMOH, respectively. The emission profiles as well as peak positions remain the same when the sample is excited at 340 and 350 nm. A slight decrease in the emission intensity is noted. When the sample is excited at 360 nm, the emission spectrum shows peaks at 380, 402, and 430 nm. The peak at 380 nm arises due to emission from the normal form of the probe. The 402 and 430 nm peaks are assigned to the zwitterionic form (Scheme 2F) and the intermolecularly hydrogen bonded complex of CMOH with ethanol (Scheme 2E), respectively. The excitation spectra of CMOH in the 20:80 cyclohexane–ethanol mixture that have been recorded by monitoring the emission at 400 and 460 nm are shown in Figure 9. All of the excitation spectra of CMOH show a peak at 330 nm, indicating that all the species detected have originated in the ground state. It has been seen that the zwitterionic species originates only if the sample is excited (λ_{ex}) at 360 nm or lower energy. This can be explained from the stability of the zwitterionic species. The energy of the zwitterionic species (Scheme 2F) is higher than that of the anion (Scheme 2D). So, the stability of the zwitterionic species is less than that of the anion. As we excite the system with higher energy, due to lower stability of the zwitterionic species it is transformed into the anionic species. The effect of medium microheterogeneity on a zwitterionic probe, namely, 2,6-di-chloro-4-(2,4,6-triphenyl-1-pyridino)phenolate, has been studied by El Seoud⁴⁰ and co-workers, and they have concluded that the solvatochromic behavior of the probe in binary mixtures is complex due to preferential solvation and sometimes solvent microheterogeneity. In the case of 4-methyl-2,6-diformylphenol (MFOH), another *o*-hydroxybenzaldehyde type of probe, it has been found that the probe molecule dissociates via an intermolecular proton-transfer reaction and dissociation creates a solvated molecular anion,⁴¹ but formation of zwitterions was not detected. It has also been seen that the rate of proton transfer to solvent can be controlled by varying the solvent composition of such solvent mixtures.

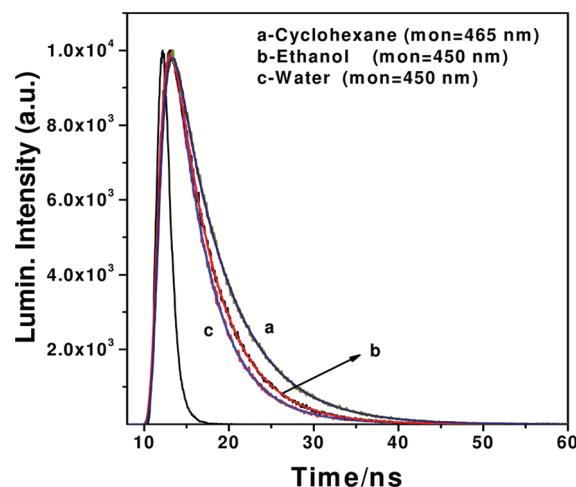


Figure 10. Time-resolved emission spectra of CMOH in cyclohexane, water, and ethanol. The samples were excited at 340 nm, and the emissions were monitored at their corresponding emission maxima. The instrument response function is also shown.

Generally, if a solute is dissolved in a binary solvent mixture that consists of a nonpolar and a polar solvent, the probe tends to remain solvated preferably by one of these components, an effect that is known as preferential solvation.^{42–45} Because the probe molecule (CMOH) interacts with cyclohexane and ethanol in a different fashion in the cyclohexane–ethanol binary mixtures, one can expect to observe preferential solvation in these media. From the spectral features of CMOH in binary solvent mixtures, it has been revealed that the probe seems to be more and more solvated with the polar component with an increase in the ethanol content on the solvent mixture. Moreover, the probe shows spectral profiles in cyclohexane–ethanol binary mixtures that are a superposition of the spectral results obtained in the pure solvents. Because there are no notable changes in absorption and emission maxima of the probe in the binary mixtures with varying composition, the effect of dielectric enrichment^{46,47} could not be ascertained. However, the intensities of absorption or emission of CMOH change with the change in solvent composition, and formation of a zwitterionic species at particular compositions appears to take place.

3e. Time-Resolved Emission Studies of CMOH in Pure Solvents and Binary Solvent Mixtures. The time-resolved emission spectra of CMOH have been recorded in bulk cyclohexane, ethanol, and their binary mixtures of varying compositions. The samples were excited at 340 nm and monitored at their corresponding steady-state emission maxima. The time-resolved emission data have been fitted to eq ii, yielding the corresponding excited-state lifetime of the probe.

$$I(t) = A + A_i \sum_i e^{-t/\tau_i} \quad (\text{ii})$$

where τ_i and A_i are the lifetimes and the relative amplitude of the excited-state species of CMOH. The recorded emission decays of the probe in cyclohexane, ethanol, and water have been displayed in Figure 10. The time-resolved decay curve of CMOH fits to a triexponential. The excited-state lifetimes of the probe in different media have been reported in Table 4. It can be seen that in pure cyclohexane, when monitored at 380 nm, two species with lifetimes of 2.93 and 3.80 ns are formed with relative amplitudes of 91.71 and 7.14%, respectively. As in pure cyclohexane, the

Table 4. Lifetime of Each Species (ns) and the Relative Amplitude (RA) of CMOH in Cyclohexane, Ethanol, and Their Binary Mixtures of Varying Composition^a

		$\lambda_{\text{mon}} = 380 \text{ nm}$						$\lambda_{\text{mon}} = 450-460 \text{ nm}$							
medium		lifetimes (ns)			RA (%)			lifetimes (ns)			RA (%)				
E (%)	χ_P	τ_1	τ_2	τ_3	a_1	a_2	a_3	χ^2	τ_1	τ_2	τ_3	a_1	a_2	a_3	χ^2
0	0.0	0.14	2.93	3.80	1.15	91.71	7.14	1.04	0.52	2.36	3.04	0.46	7.14	92.4	1.04
10	0.17	0.97	2.45	13.51	6.56	91.80	1.64	1.11	0.31	2.40	9.52	0.95	0.51	98.54	1.04
20	0.32	0.16	2.37	10.04	4.07	92.19	3.75	1.10	1.24	2.36	9.44	0.85	98.18	0.97	1.06
50	0.65	0.11	2.31	13.47	6.99	84.21	8.81	1.12	1.96	2.52	24.72	45.05	52.97	1.98	1.01
80	0.88	1.61	2.62	14.48	39.47	51.46	9.08	1.14	1.87	2.55	16.74	63.28	34.43	2.29	1.15
90	0.94	2.11	6.72	17.99	84.55	5.58	9.87	1.17	1.94	3.66	27.40	89.69	7.69	2.63	1.03
100	1.0								1.80	3.24	23.45	82.3	13.75	3.95	1.03
water									0.5	2.94	5.30	59.04	23.06	17.91	1.07

^a The systems were excited at 340 nm and monitored at corresponding steady-state emission wavelengths. The percentage of ethanol and the ratio of mole fraction of the polar solvent (χ_P) in the cyclohexane–ethanol binary mixture and the χ^2 values of fitting have also been reported.

formation of the ESIPT is favored; the 2.93 ns component has been assigned to the ESIPT form (B form, Scheme 2) of the probe. The 3.80 ns species is due to the presence of the normal form (A form, Scheme 2) of CMOH. The picosecond component formed in pure cyclohexane and binary mixtures with low ethanol content presumably arise due to solvent relaxation. A new species has been seen to form in the binary mixtures with higher ethanol content and is due to formation of an ethanol–CMOH complex. This has been better understood while monitoring the emission of the probe at the 450–460 nm region (depending on the corresponding steady-state emission maxima) following excitation by 340 nm light. In pure cyclohexane, two species have been formed of lifetimes 2.36 and 3.04 ns with relative amplitudes of 7.14 and 92.4%, respectively. Due to higher relative amplitude, the 3.04 ns species has been assigned to the ESIPT form of the probe. The 2.36 ns component arises from the normal form of the probe. The lifetime of the normal form (Scheme 2) is seen to be less sensitive to the change in composition in the binary mixture than that of the ESIPT form. A new species has been formed with lifetime ranging from 1.24 to 1.94 ns in binary mixtures with ethanol content of 20% or higher. The relative amplitude of this species has been seen to increase with an increase in ethanol content in the medium, being the highest in the 90:10 ethanol–cyclohexane binary mixture. To understand the origin of this species, we have recorded the time-resolved emission spectra of the probe in water. It has been seen that in water two species of lifetimes 2.94 and 5.30 ns with relative amplitudes of 23.06 and 17.91%, respectively, are formed. Because the formation of anion is complete in water in the excited state, no solvent–CMOH complex has been seen to form. So, the new species formed can be assigned to the ethanol–CMOH complex.

To study the excitation wavelength dependence on the time-resolved emission spectra of CMOH, we also have excited the sample at 375 nm and monitored their corresponding steady-state emission maxima. The recorded emission decays of the probe in different media have been displayed in Figure 11A,B. It has been found that the decay curve of the probe is biexponential. The excited-state lifetimes of the probe in different media that have been yielded using eq ii have been reported in Table 5. In pure cyclohexane the decay shows formation of two species of lifetimes of 3.4 and 13.9 ns with relative amplitudes of 81 and

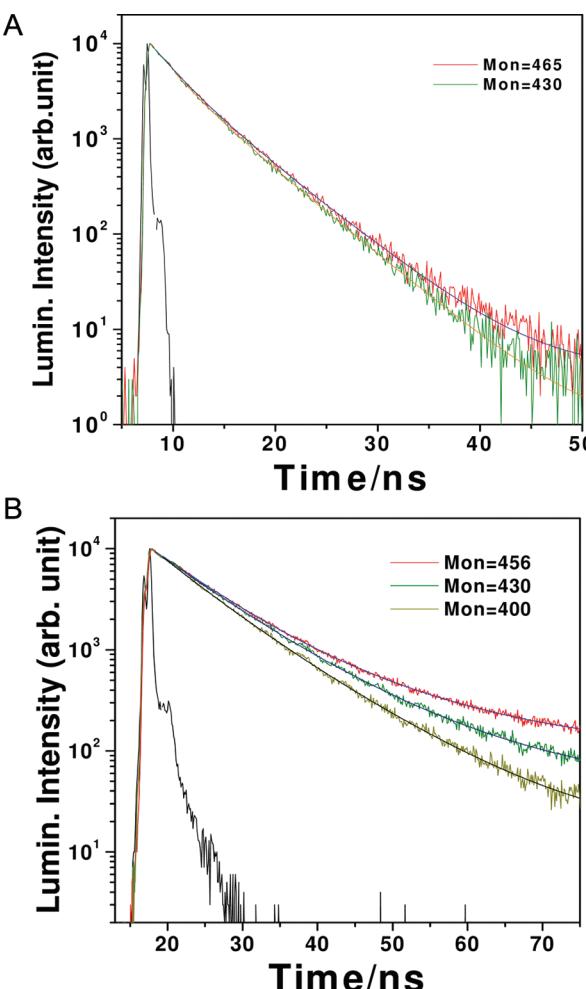


Figure 11. Time-resolved emission spectra of CMOH in (A) 80:20 and (B) 20:80 cyclohexane–ethanol binary mixtures. The samples were excited at 375 nm, and the emissions were monitored at their corresponding emission maxima. The instrument response function is also shown.

19%, respectively. As in pure cyclohexane, formation of the ESIPT species is more favorable (Scheme 2): the 3.4 ns species is

Table 5. Lifetime of Each Species (ns) of the Probe (CMOH) in Cyclohexane (Cyc), Water, Aqueous NaOH, Ethanol (EtOH), and Binary Mixtures of Cyclohexane and Ethanol with Varying Composition^a

medium	χ_P	τ_1 (ns)	τ_2 (ns)	a_1 (%)	a_2 (%)	χ^2
cyclohexane	0.00	3.4	13.9	81	19	1.13
95% Cyc + 5% EtOH	0.09	2.8	12.6	77	23	1.05
90% Cyc + 10% EtOH	0.17	2.8	11.0	73	27	1.08
80% Cyc + 20% EtOH	0.32	2.6	11.3	67	33	1.16
60% Cyc + 40% EtOH	0.55	2.7	8.0	70	30	1.18
50% Cyc + 50% EtOH	0.65	2.1	7.5	65	35	1.06
40% Cyc + 60% EtOH	0.73	2.3	7.1	71	29	1.11
20% Cyc + 80% EtOH	0.88	2.0	6.9	63	37	1.05
ethanol	1.00	2.1	4.5	46	54	1.13
water		1.4	4.5	53	47	1.19
aqueous. NaOH		1.8	3.7	7	93	1.17

^aThe systems were excited at 375 nm and monitored at corresponding steady-state emission wavelengths. The ratio of mole fraction of the polar solvent (χ_P) in the cyclohexane–ethanol binary mixture and the χ^2 values of fitting have also been reported.

assigned to the ESIPT form of the probe. The more stable species with lifetime of 13.9 ns has been assigned to the C form of CMOH, which is responsible for the 380 nm emission of the probe. As we add ethanol to the cyclohexane, the lifetimes of both of these species decrease. It has also been observed that, with an increase in concentration of ethanol in the binary mixture, the relative amplitude of the ESIPT species decreased. For example, the lifetime of the ESIPT species decreases to 2.8 ns with a relative contribution of 77% in the binary mixture containing 5% ethanol and 95% cyclohexane, and the lifetime of conformer A decreases to 12.6 ns with an increase in relative amplitude to 23%. In pure ethanol, the fluorescent decay of CMOH obtained by monitoring the emission at 450 nm is biexponential, with lifetime values of 2.1 and 4.5 ns. In pure ethanol, the lifetimes of the A and B species are 2.1 and 4.5 ns, respectively. The decrease in the relative amplitude of the A form with a concomitant increase in the B form with an increase in ethanol content in the binary mixture is due to the formation of the B form. In the steady-state emission spectra of the probe it has been observed that the ESIPT peak vanishes with an increase in ethanol mole fraction. So, the time-resolved emission spectra of the probe are consistent with what has been seen in the steady-state experiments.

4. CONCLUSIONS

The effects of solvent microheterogeneity on the excited-state proton-transfer reaction of CMOH has been studied in pure solvents as well as cyclohexane–ethanol binary mixtures. The excited-state proton-transfer (ESIPT) reaction of CMOH has been observed in a nonpolar and aprotic solvent, namely, cyclohexane, while in a polar aprotic solvent, ethanol, no ESIPT reaction has been observed. The emission spectral behaviors of the probe in cyclohexane–ethanol binary mixtures have been seen to be dependent on the solvent composition and on excitation wavelengths. With the increase in ethanol content in the cyclohexane–ethanol binary mixtures, the emission intensity of the ESIPT form decreases with a concomitant increase in the intramolecularly hydrogen bonded closed conformer of the probe. In cyclohexane–ethanol binary mixtures with higher

ethanol content, a zwitterionic form of the probe is detected if the sample is excited with 360 nm or lower energy light. The zwitterion is converted to the anion if excited with higher energy. The time-resolved spectra of the probe are consistent with the observations obtained from the steady-state spectroscopic studies of the probe. Density functional theory calculations reveal that the closed form rotamers of CMOH are comparable in their ground-state energy although they differ in their electronic structures and intramolecular hydrogen bond strengths. It has been found that both microscopic solvation and macroscopic solvation play an important role in the spectral response of the probe. The formation of a 1:1 molecular cluster by CMOH with ethanol has been confirmed in the ground state. These results are expected to unravel the medium implications on the energetics, that is, stabilities, of the different species of the CMOH, an important ESIPT probe.

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