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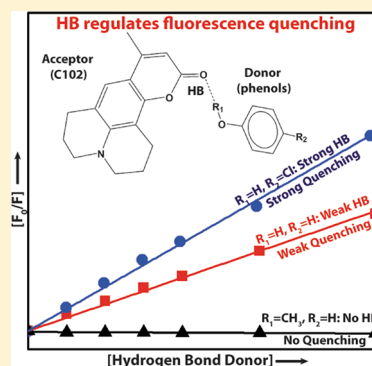
Fluorescence Quenching of Hydrogen-Bonded Coumarin 102-Phenol Complex: Effect of Excited-State Hydrogen Bonding Strength

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Supporting Information

ABSTRACT: The fate of intermolecular hydrogen bond (H-bond) upon electronic excitation of a H-bonded complex has been debated in literature. For a model H-bonded complex, coumarin 102 (C102)-phenol in a noninteracting solvent ethylene tetrachloride, time-resolved infrared spectroscopy experiment of Nibbering and coworkers suggests that the H-bond between the C102 and phenol ruptures upon electronic excitation (C. Chudoba et al. *J. Phys. Chem. A* **1999**, *103*, 5625–5628). On the contrary, Zhao and Han have demonstrated for the first time that the intermolecular hydrogen bond is significantly strengthened, while not disrupted, in the electronically excited states of the hydrogen-bonded complexes upon electronic excitation using the time-dependent density functional theory method (G. J. Zhao and K. L. Han *J. Phys. Chem. A* **2007**, *111*, 2469–2474). The two excited-state hydrogen bonding dynamics mechanisms have widely different predictions of the emission or electronic relaxation of the excited H-bonded complex. The excited-state hydrogen-bond strengthening mechanism proposed by Zhao and Han anticipates a stronger intermolecular interaction, while the H-bond breaking mechanism speculates no interaction between C102 and phenol. The speculation has been tested here on the same system (H-bonded C102-phenol complex) in another noninteracting solvent cyclohexane. We found a strong quenching of the C102 emission in the H-bonded complex. Selectively excited ($\lambda_{\text{ex}} = 405$ nm) H-bonded complex relaxes on a fast time scale of 400–600 ps and may be attributed to the conversion of the locally excited (LE) state to a nonfluorescent charge transfer (CT) state assisted by the strong excited-state H-bond formation. A minor component ($\sim 10\%$) of 2.5 to 1.8 ns is ascribed to the LE complex without a H-bond. The findings are in accordance with the new fluorescence quenching mechanism that the excited-state intermolecular hydrogen bond strengthening facilitates CT from phenol to coumarin in the excited state (G. J. Zhao et al. *J. Phys. Chem. B* **2007**, *111*, 8940–8945). Fluorescence quenching was absent for anisole, where H-bond formation is not possible and was more pronounced for *p*-Cl-phenol, where even stronger H-bonding is expected.



1. INTRODUCTION

The fate of an intermolecular hydrogen bond (H-bond) of a photoexcited complex may have a key role in tuning the photochemistry and dynamics.¹ Photoexcitation alters charge distribution of the molecules (donor and/or acceptor) that participate in the H-bond formation. The H-bond coordinates readjust with this new charge density on a time scale governed by the vibrational motion of the groups forming the H-bond. The process known as the excited-state hydrogen-bonding dynamics was first probed by Nibbering and coworkers on a model acceptor molecule coumarin 102 (102) with many hydrogen-bonded donors including phenol in a nonpolar solvent ethylene tetrachloride (C_2Cl_4).^{1a,2} The $\text{C}=\text{O}$ group of C102 is involved in site-specific hydrogen-bond formation with H-bond donating group of the donors (e.g., $\text{HO}-$ group for phenol), and downshifting of its vibrational frequency from that in the free state (no H-bond) serves as an indicator of the H-bonding strength. Using femtosecond visible excitation and IR probe, their pioneering work demonstrates that the vibrational frequency of the $\text{C}=\text{O}$ group, which was already downshifted in the ground state due to H-bond formation, recovers quickly (within ~ 200 fs after excitation) to the vibrational frequency of

the free $\text{C}=\text{O}$ group, indicating rupture of the hydrogen bond in the excited state.^{1a,2} Later, Zhao et al. performed the time-dependent density functional theory (TD-DFT) calculations and demonstrated that the intermolecular hydrogen bond between C102 and phenol becomes remarkably stronger and shorter in the electronic excited state of the hydrogen-bonded C102-phenol complex.³ The excited-state hydrogen-bonding dynamics have also been investigated by many other groups, and intermediate situations rather than these two extremes (H-bond breaking or strengthening) were also prescribed. In a hydrogen-bonded system C102-aniline in tetrachloroethylene, Yoshihara and coworkers found that the H-bond between C102 and aniline breaks within 250 fs of photoexcitation, followed by reformation of H-bond between excited C102 and aniline within 30 ps.⁴ Palit and coworkers considered dynamic equilibrium between H-bond breaking and reformation in the excited state of fluorenone and amino-fluorenes in many H-bond donating solvents.⁵ Blank and coworkers studied the

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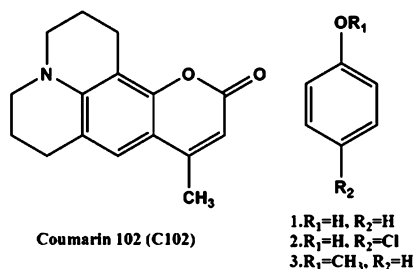


effect of H-bond on the excited C102 in acetonitrile–water binary mixture by both experiment and simulation.⁶ Their model suggests a concurrent strengthening and weakening of the hydrogen bond between C102 and water. The C=O group of C102 forms two hydrogen bonds with two water molecules in the ground state, out of which one H-bond weakens while the other strengthens upon electronic excitation.

It is very important to understand how the ultrafast H-bonding dynamics could influence the photophysics or electronic relaxation of a hydrogen-bonded complex. Zhao and coworkers have demonstrated that excited-state H-bond strengthening effect may have a stronger influence on controlling the emission characteristics of the hydrogen-bonded complex³ and subsequently applied the excited-state hydrogen bond strengthening and weakening concept on many ultrafast nonadiabatic dynamic processes, such as internal conversion,⁷ intersystem crossing,⁸ photoinduced electron and carrier transfer,⁹ intramolecular charge transfer (CT) and site-specific solvation,¹⁰ excited-state proton transfer and dihydrogen bonding,¹¹ twisted intramolecular CT,¹² and metal–ligand CT.¹³ The effect of H-bonding on the photophysics of many other complexes has been studied, but the case of C102-phenol complex remains ambiguous.^{7,14}

In this article, we revisited the C102-phenol system (Scheme 1) in another noninteracting solvent cyclohexane. We have

Scheme 1. Structure of Coumarin 102 (C102) and Phenol Derivatives (Phenol, 1; *p*-Cl-Phenol, 2 and Anisole, 3)



applied steady-state and time-resolved emission spectroscopy to characterize the excited states of the H-bonded system, in particular, to observe the effect of the excited-state hydrogen-bond strengthening or weakening in the excited-state relaxation. In addition to phenol, we have also used another two derivatives, anisole and *p*-Cl-phenol (Scheme 1). Anisole lacks the donor hydrogen for H-bond formation as the –OH group is replaced by –OCH₃ while *p*-Cl-phenol may be a better H-bond donor than phenol, as an electron-withdrawing –Cl group is at the para position. The lower pK_a value of *p*-Cl-phenol (9.38) than phenol (9.98) suggests that *p*-Cl-phenol may form a stronger H-bond than phenol with C102.¹⁵ The oxidation potential of the three phenol derivatives is similar.¹⁶ Hence, interaction with C102 may be dominated by the effect of the excited-state H-bond rather than by the free energy of electron transfer.¹⁷ We found that anisole has negligible or no effect on the fluorescence spectra of C102, while phenol significantly quenches the fluorescence of C102. For C102-*p*-Cl-phenol the fluorescence quenching is even more drastic. Density functional theory (DFT) and TD-DFT calculations were also performed to understand the nature of the excited states and to estimate the strength of the H-bond in the ground and in the excited states.

To understand the role of solvent in controlling the H-bond formation, we perform the study in two more solvents: acetonitrile and methanol. These solvents may directly involve in hydrogen bonding with either C102 or phenol or both. Interestingly, fluorescence quenching by phenol was completely absent in those solvents within the concentration range of phenol studied.

The article is organized as follows. First, we present our theoretical calculation to characterize the spectroscopic states in the H-bonded complex, followed by steady-state and time-resolved results in the absence and in the presence of the H-bond donors. Subsequently, we analyze our results based on the excited-state H-bonding effect on the electronic states.

2. EXPERIMENTAL AND CALCULATION METHODS

The structures of C102, phenol, and *p*-Cl-phenol were first optimized separately with DFT using B3LYP functional and 6-31G** basis set, followed by optimization of their 1:1 complexes at the same level of computation. Only the H-bond length (i.e., distance between the oxygen atom of the C=O group of C102 and the hydrogen atom of the –OH group of phenol or *p*-Cl-phenol) was scanned with a step of 0.05 Å to calculate the potential energy surface of the H-bonded complex, and single-point energy calculations were done on each configuration by DFT and TDDFT methods with B3LYP/6-31G**. All of the calculations were done with the Gaussian 03 package¹⁸ in the gas phase.

Coumarin 102 (C102) and phenol were purchased from Sigma-Aldrich and used as received. *p*-Cl-phenol was obtained from Hi-Media. Cyclohexane, acetonitrile, and methanol were supplied by Merck Chemicals.

The UV–vis spectra were recorded in a Perkin-Elmer Lambda-35 spectrophotometer. Emission spectra were collected on Jobin-Yvon FluoroMax4 spectrofluorometer. Time-resolved fluorescence measurements were performed on a time-correlated single photon counting (TCSPC) setup LifeSpec2 (Edinburgh Instruments). For 375 and 405 nm excitations, picosecond laser diodes EPL-375 (Edinburgh Instruments) and LDH-P-C-405 (PicoQuant) were used, respectively. Typical fwhm of the setup was ~100 ps.

3. RESULTS

3.1. Time-Dependent Density Functional Theory Calculations. Figure 1 shows the optimized ground-state geometry of the H-bonded complex of C102-phenol and C102-*p*-Cl-phenol. We have considered only the 1:1 complex because we report only on the low-concentration range of the donors (phenol and *p*-Cl-phenol), and at these concentrations higher order complexes (C102-(donor)_{n=2,3...}) may be ignored. The C=O group of C102 forms a H-bond with the HO– group of phenol. The H-bond distance, that is, the distance between the O atom of the C=O group and the H atom of the HO– group of phenol, is found to be 1.845 Å (Table 1). The H-bond formation leads to lengthening of the acceptor and donor bonds. The C=O bond (1.211 Å) of isolated C102 is elongated by 0.015 Å on the formation of 1:1 H-bonded complex with phenol (Table 1). The molecular planes of C102 and phenol are nearly orthogonal to each other in the 1:1 complex. The optimized geometry and the H-bond parameters of the C102-phenol complex agree well with Zhao et al.³ The geometry of the C102-*p*-Cl-phenol complex is similar to the C102-phenol complex (Figure 1). The H-bond length is

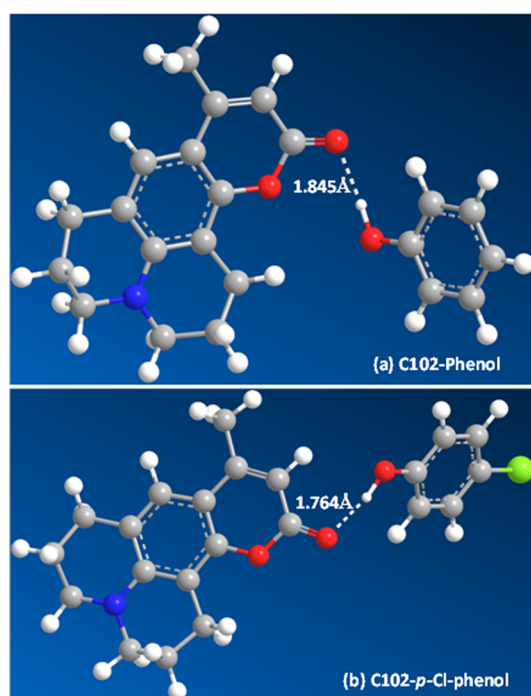


Figure 1. Optimized ground-state (S_0) structure of 1:1 C102-phenol (a) and C102-*p*-Cl-phenol (b) hydrogen-bonded complexes. The shorter hydrogen bond length in the C102-*p*-Cl-phenol complex indicates stronger H-bond formation than in the C102-phenol complex.

shorter by 0.081 Å in the C102-*p*-Cl-phenol than in the phenol complex. This was expected from the superior H-bond-donating ability of *p*-Cl-phenol.

To estimate the H-bonding parameters in the excited state, we varied H-bond distance (i.e., distance between the O atom of the C=O group of C102 and the H atom of the HO-group of phenol) by a step of 0.05 Å starting from the optimized ground-state complex, keeping all other bond parameters same. At each step, single-point energy calculation was done by TDDFT/B3LYP/6-31G** method. Figure 2 shows the potential energy curve of the first three singlet electronic states of the C102-phenol and C102-*p*-Cl-phenol complexes, respectively. As evident from the curves, the minima of the S_1 and S_2 potential curves shift to a shorter distance than that of the ground state (S_0). This shortening is similar to that observed by Zhao et al. for C102-phenol using BP86 functional with TZVP basis set.³ The potential energy curve, $U(r)$ along the hydrogen-bonding coordinate (r) was fitted with a Morse-type equation for each of the electronic states

$$U(r) = U(r_0) + D_e[1 - e^{-a(r-r_0)^2}] \quad (1)$$

where r_0 , $U(r_0)$, and D_e represent equilibrium H-bond distance, equilibrium potential energy, and H-bond dissociation energy, respectively, and a is an adjustable Morse parameter. The

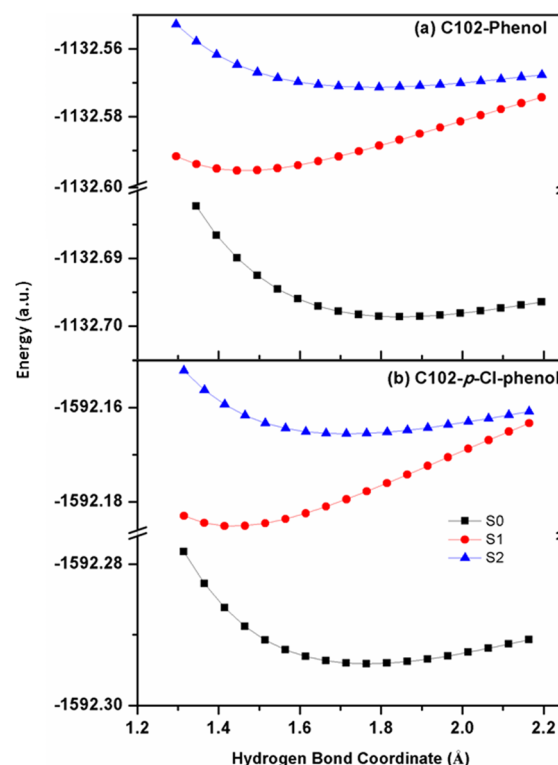


Figure 2. Potential energy variation along the H-bond coordinates (i.e., the distance C=O·····H–O in angstroms) for the C102-phenol (a) and C102-*p*-Cl-phenol (b) complexes in the three electronic states. The minima of the S_2 and S_1 potentials correspond to shorter H-bond than in the ground state. For *p*-Cl-phenol, H-bond is shorter than phenol in all electronic states. The H-bond shortening is more drastic in the S_1 state for both phenol and *p*-Cl-phenol.

fitted results for the three electronic states S_0 , S_1 , and S_2 for C102-phenol and C102-*p*-Cl-phenol are given in Table 2. The H-bond is shorter and H-bond energy is larger for *p*-Cl-phenol than that of phenol. The fitted values for H-bond energy for C102-phenol complex in S_0 and S_2 states are 8.40 and 11.36 kcal M^{-1} , respectively, which are in very good agreement with the calculated values (8.67 and 12.26 kcal M^{-1} respectively) of Zhao et al.³ The excited-state H-bond strengthening is most dramatic in the S_1 state for both of the complexes (Table 2).

The energy, strength, and nature of the transitions in the H-bonded complex can be calculated from the TD-DFT calculations. Table 3 shows two lowest energy transitions in C102 and C102-phenol and C102-*p*-Cl-phenol complex. C102 has a strong $S_0 \rightarrow S_1$ transition band at 341 nm. For C102-phenol complex, our calculation predicts a strong transition ($S_0 \rightarrow S_2$) at 357 nm along with a very weak low-energy transition ($S_0 \rightarrow S_1$) at 407 nm, which may be ascribed as a dark state. In the C102-*p*-Cl-phenol complex, the transitions are similar to those of the C102-phenol complex. From the frontier molecular orbitals (Supporting Information, Figure S1) of the

Table 1. H-Bond Length ($L_{O,H}$) and the Bond Lengths of the H-Bond Accepting ($L_{C=O}$) and Donating Groups (L_{H-O}) in the Ground State (S_0) before and after Formation of the H-Bonded Complex^a

phenol	<i>p</i> -Cl-phenol	C102	C102-phenol			C102- <i>p</i> -Cl-phenol		
L_{H-O}	L_{H-O}	$L_{C=O}$	$L_{C=O}$	$L_{O,H}$	L_{H-O}	$L_{C=O}$	$L_{O,H}$	L_{H-O}
0.966	0.966	1.211	1.226	1.845	0.981	1.228	1.764	0.985

^aAll of the lengths are reported in angstroms.

Table 2. Fit Results According to Equation 1 to the Calculated Potential Energy Curve of the 1:1 C102-Phenol Complex in Three Electronic States^a

states	$r_0/\text{\AA}$	$U(r_0)/\text{a.u.}$	$D_e/\text{kcal M}^{-1}$	$a/\text{\AA}^{-2}$
S_0	1.845 (1.762)	-1132.6986 (-1592.2941)	8.40 (10.26)	1.47 (1.52)
S_1	1.467 (1.439)	-1132.5958 (-1592.1851)	31.21 (31.51)	1.47 (1.48)
S_2	1.777 (1.712)	-1132.5713 (-1592.1656)	11.36 (12.41)	1.42 (1.50)

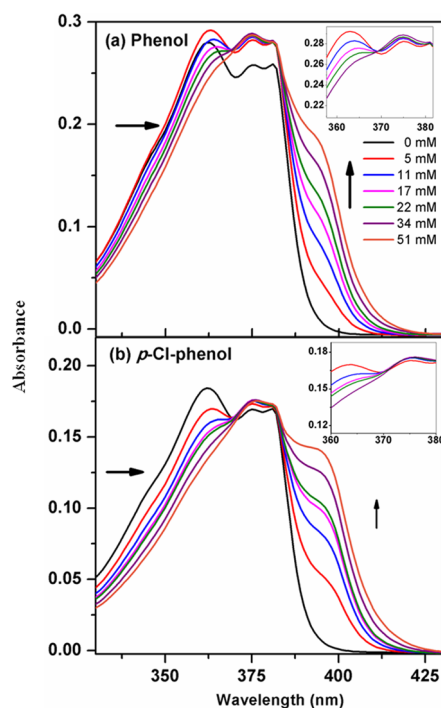
^aResults for the C102-*p*-Cl-phenol complex are given in the parentheses.**Table 3.** TDDFT/B3LYP/6-31G** Calculated Electronic Transition Wavelength (nm) of Free C102, C102-Phenol, and C102-*p*-Cl-Phenol Complexes in Gas Phase^a

transitions	C102	C102-phOH	C102- <i>p</i> ClphOH
$S_0 \rightarrow S_1$	341 (0.3391)	407 (0.0011)	391 (0.0004)
$S_0 \rightarrow S_2$	298 (0.0045)	357 (0.3262)	354 (0.3938)

^aCorresponding oscillator strengths are given in the parentheses.

H-bonded complex, it may be stated that the $S_0 \rightarrow S_1$ transition is of CT character, where electron density dominantly moves from the phenol moiety to C102. Because the excited-state hydrogen bond shortening is most dramatic in the S_1 state of the complex, this CT may be aided by the excited-state hydrogen bonding. In the case of $S_0 \rightarrow S_2$ transition, electron density remains on C102 before and after excitation, and hence it is locally excited (LE) in nature and possess a strong oscillator strength. This observation is also in accordance with that of Zhao et al.³

3.2. Steady-State Absorption and Emission Measurements. Figure 3 shows absorption spectrum of $\sim 12 \mu\text{M}$ C102 in cyclohexane in the presence of different concentrations of the H-bond donors (phenol or *p*-Cl-phenol). In the absence of any donor, the absorption spectrum of C102 displays

**Figure 3.** Absorption spectra of C102 in cyclohexane in the presence of different concentrations (0–51 mM) of phenol (a) and *p*-Cl-phenol (b). The inset shows the magnification of the isosbestic region in both cases.

vibrational structures (characteristics of absorption bands of most fluorophores in nonpolar solvents) with absorption maximum at 362 nm. Our calculation in the gas phase predicts the lowest energy $S_0 \rightarrow S_1$ transition at 341 nm (405 nm by Zhao et al.³). On addition of phenol the absorption band gradually shifts to longer wavelength and an additional shoulder develops at ~ 395 nm. Similar observation was noticed for the C102-phenol in C_2Cl_4 .^{2a} Our theoretical calculation suggests that the absorption band is a superposition from both the absorption from the $S_0 \rightarrow S_2$ transition of the H-bonded complex and the $S_0 \rightarrow S_1$ transition of the free C102. The calculated absorption maximum of the $S_0 \rightarrow S_2$ transition of the complex is 16 nm red-shifted from the $S_0 \rightarrow S_1$ absorption band of coumarin. The relative contribution of the complex increases to that of the free C102 as the amount of phenol increases. This accounts for the gradual red shifting of the absorption band at progressively higher phenol concentration. Another noticeable feature is that at low phenol concentration (≤ 34 mM) a clear isosbestic point is observed at 368 nm. The isosbestic point indicates the formation of the 1:1 C102-phenol complex between C102 and phenol at low concentration of phenol.^{14c} At the higher phenol concentration the isosbestic region becomes defocused. This may be due to the formation of higher order C102-(phenol)_{*n*} complex ($n = 2, 3$ etc). For *p*-Cl-phenol the 395 nm band increases more rapidly on increasing the *p*-Cl-phenol concentration, and the isosbestic point is found to be at 369 nm. The red-shifting the absorption band is more prominent in *p*-Cl-phenol, indicating better H-bonding donating ability of *p*-Cl-phenol over phenol (Figure 3). Anisole does not have any effect on the absorption spectrum of C102 in the same concentration range (Supporting Information, Figure S2). In polar solvents, acetonitrile and methanol, phenol does not alter the absorption spectrum of C102 (Supporting Information, Figure S2). This may be due to direct involvement of the solvent molecules in H-bond formation with either C102 or phenol or both, and hence intermolecular C102-phenol H-bonding is masked.

Figure 4 displays emission spectra of C102 in the presence of various concentrations of phenol at an excitation wavelength of 370 nm. Because this wavelength is close to the isosbestic point of the absorption spectra, the transition probability of the both species (free C102 and 1:1 C102-phenol) is the same, and hence excited-state population will be proportional to the ground-state population of each species. The emission intensity will depend on the quantum yield of the free C102 and C102-phenol complex. We observe that the fluorescence intensity gradually diminishes on the addition of phenol. For *p*-Cl-phenol, the fluorescence quenching is even stronger. For example, at 34 mM *p*-Cl-phenol the fluorescence intensity decreases by a factor of 2.4, while for the same phenol concentration fluorescence intensity reduces by a factor of 1.7 from that in the absence of any donor. From the theoretical calculation we found that *p*-Cl-phenol forms a stronger H-bond with C102. On the contrary, anisole does not quench the

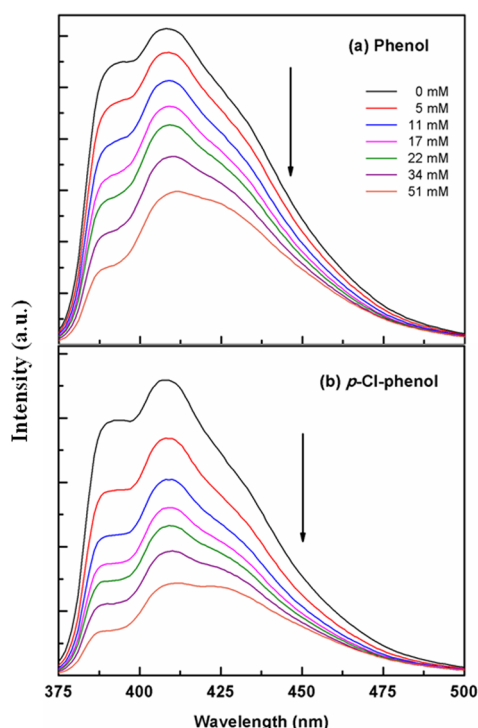


Figure 4. Emission spectra of C102 in cyclohexane in the presence of different concentrations (0–51 mM) of phenol (a) and *p*-Cl-phenol (b) at an excitation wavelength (λ_{ex}) of 370 nm.

emission spectrum of C102 (Supporting Information, Figure S4). Stronger fluorescence quenching by *p*-Cl-phenol and no quenching in anisole may imply that the H-bonding-assisted mechanism is responsible for fluorescence quenching. Phenol does not alter the emission spectrum of C102 in polar solvents: acetonitrile and methanol (Supporting Information, Figure S5).

The quenching effect can be quantified by the use of the Stern–Volmer equation

$$\frac{F_0}{F} = 1 + K_{\text{SV}}[Q] \quad (2)$$

where F_0 and F are the fluorescence intensities of C102 in the absence and in the presence of quencher (phenol or *p*-Cl-phenol). Figure 5 shows the Stern–Volmer plot for phenol and *p*-Cl-phenol. The quenching constant (K_{SV}) for the phenol and *p*-Cl-phenol are 25.8 and 42.7 M^{-1} , respectively. The higher quenching constant of *p*-Cl-phenol than phenol indicates that H-bonding should have a major role in fluorescence quenching.

Excitation at 405 nm will have negligible contribution from the unbound C102 and the emission spectrum will be representative of the H-bonded C102-phenol complex alone. On the addition of 11 mM phenol the emission intensity of C102 decreases dramatically by a factor of 16. Further addition of phenol has little effect on the emission spectra (Supporting Information, Figure S6).

3.3. Time-Resolved Fluorescence. For time-resolved measurements the samples were excited at two wavelengths: 375 and 405 nm. At 375 nm, both the free C102 and the H-bonded C102 may be excited, and relative contributions of the excited species depend on their ground-state population (as the molar extinction coefficient at this wavelength is similar). In the absence of any donor (phenol or *p*-Cl-phenol), fluorescence decay of C102 is exponential with a decay time of 2.7 ns, which is in agreement with literature.¹⁹ From Figure 6, it is clear that

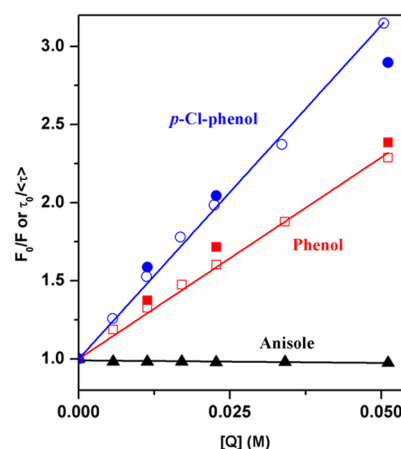


Figure 5. Stern–Volmer plot of the fluorescence quenching of C102 in cyclohexane in the presence of the quenchers: phenol (square), *p*-Cl-phenol (circle), and anisole (triangle). Fluorescence quenching is absent for anisole and most drastic for *p*-Cl-phenol. Time-resolved data ($\tau_0/\langle\tau\rangle$) for phenol and *p*-Cl-phenol are displayed as filled symbols.

on gradual addition of the H-bond donor (phenol or *p*-Cl-phenol) the fluorescence decays gradually become faster. The fluorescence transients at $\lambda_{\text{ex}} = 375$ nm could be fitted by a sum of two exponentials

$$F(t) = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} \quad (3)$$

In the presence of 11 mM phenol, the fluorescence transient displays a fast component of 400 ps and a slow component of 2500 ps. On further addition of phenol the time constants do not change much but the relative contribution of the components increases. With increase in the phenol concentration from 11 to 51 mM the contribution of the fast component increases from 25 to 54%. Because the fast component was absent in free C102, the decay time could be assigned to the H-bonded complex, and the amplitude corresponds to their relative excited-state population. The slow component is close to the lifetime of free C102 and decreases slightly on the addition of phenol. This decay time may be attributed to the directly excited free C102 or a LE complex, where the H-bond has been ruptured. As the concentration of phenol increases, the local environment of the excited C102 may be preferentially solvated by the polar phenol, and hence decay time decreases slightly.

The effect of excited-state H-bonding on the electronic relaxation is more evident if we compare the fluorescence decays of phenol with *p*-Cl-phenol at the same concentration of each (Figure 7). The decay times for both phenol and *p*-Cl-phenol are similar, but the relative contribution of the fast and slow components differs. At 22 mM phenol, the contribution of the fast (410 ps) component is 38%, while at same concentration of *p*-Cl-phenol the fast component increases to 56%. This implies that the fluorescence decay is governed by the H-bond-regulated mechanism.

The decrease in the relaxation times could be correlated to the Stern–Volmer quenching by

$$\frac{\tau_0}{\langle\tau\rangle} = 1 + K_{\text{SV}}[Q] \quad (4)$$

where τ_0 is the decay time of C102 in the absence of any quencher (phenol or *p*-Cl-phenol) and $\langle\tau\rangle$ is the average decay

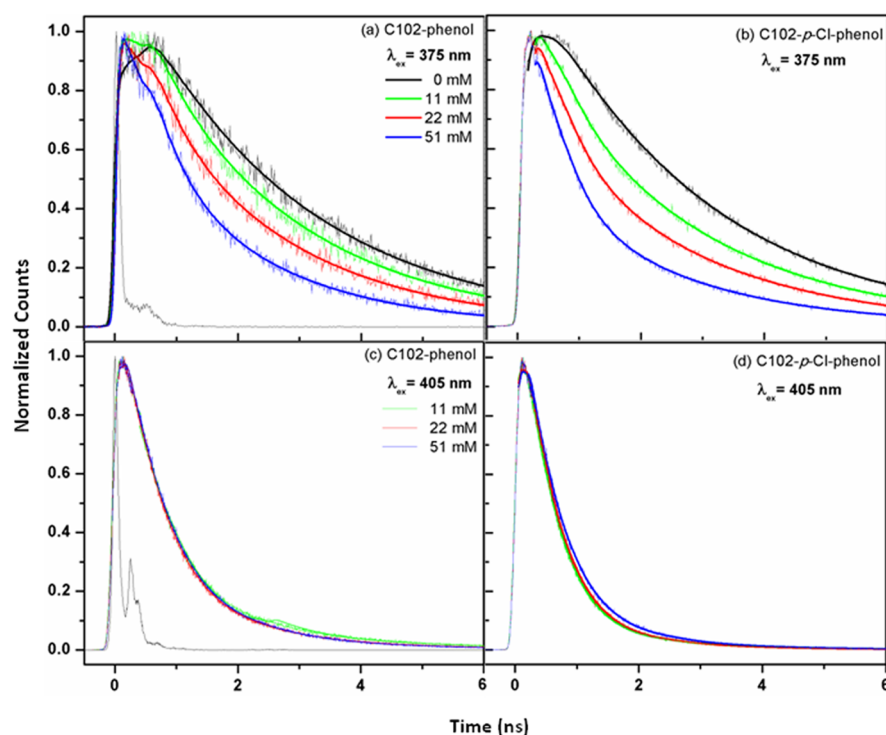


Figure 6. Fluorescence transients of C102 in cyclohexane in the presence of different concentrations (0–51 mM) of phenol or *p*-Cl-phenol excited at two different wavelengths: 375 and 405 nm. Fluorescence decays (at $\lambda_{\text{em}} = 405$ nm) at 375 nm excitation gradually become faster on the addition of phenol or *p*-Cl-phenol, but at 405 nm excitation, fluorescence decays (at $\lambda_{\text{em}} = 430$ nm) remain almost invariant of phenol or *p*-Cl-phenol concentration.

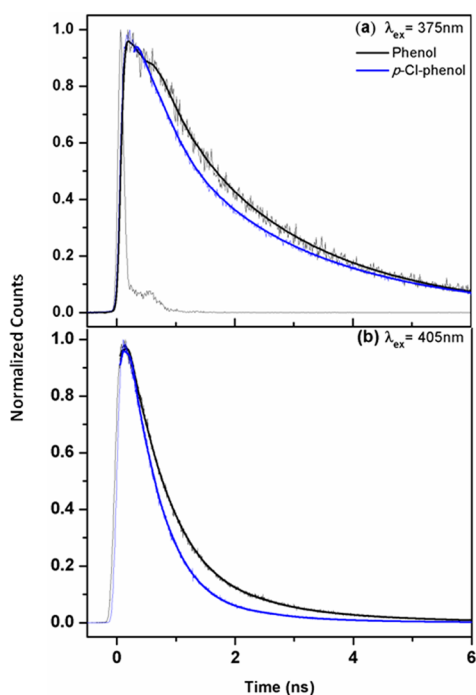


Figure 7. Comparison of the effect of phenol versus *p*-Cl-phenol on the fluorescence decay of C102 in cyclohexane at same concentration (22 mM) of phenol or *p*-Cl-phenol. The fluorescence decays are faster in the presence of *p*-Cl-phenol than in phenol at both of the excitation wavelengths (375 and 405 nm).

time in the presence of the quencher. The time-resolved data agree well with the steady-state quenching (Figure 5).

At 405 nm, the H-bonded complex will be excited exclusively as free C102 has negligible absorption at this wavelength. Hence the fluorescence decay at 405 nm will be characteristics of relaxation of the hydrogen-bonded complex only. Interestingly, the fluorescence decay (at $\lambda_{\text{ex}} = 405$ nm) in the presence of phenol (or *p*-Cl-phenol) is markedly different from the free C102 and remains almost unchanged on further addition of phenol. The fluorescence decay of the C102-phenol complex is biexponential with a fast component of 610–630 ps and a slow component of 2.7–1.8 ns. The contribution of the slow component is very small (10–16%) and may be due to directly excited free C102 or the C102-phenol complex with broken H-bond in the excited state. In the case of *p*-Cl-phenol, the fluorescence decay is slightly faster than phenol at the same concentration of the donors (Tables 4 and 5).

4. DISCUSSION

The most important finding in this work is the observation of strong fluorescence quenching of C102 in the presence H-bond donors- phenol or *p*-Cl-phenol in cyclohexane but no quenching in the case of anisole where H-bond formation is

Table 4. Fluorescence Decay Analysis of C102 in Cyclohexane at Various Concentrations of Phenol at Two Excitation Wavelengths (λ_{ex}): 375 and 405 nm

[phenol]	$\lambda_{\text{ex}} = 375$ nm		$\lambda_{\text{ex}} = 405$ nm	
	τ_1/ps (a_1)	τ_2/ps (a_2)	τ_1/ps (a_1)	τ_2/ps (a_2)
0 mM		2700(1.00)		2700(1.00)
11 mM	400(0.25)	2500(0.75)	640(0.90)	2500(0.10)
22 mM	410(0.38)	2300(0.62)	610(0.86)	1800(0.14)
51 mM	420(0.54)	2000(0.46)	630(0.84)	1700(0.16)

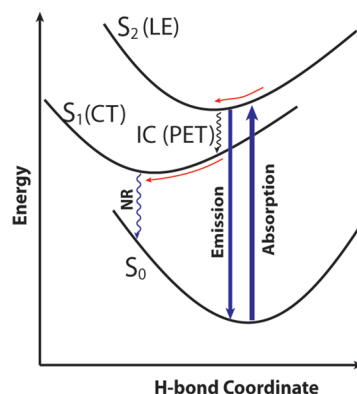
Table 5. Fluorescence Decay Analysis of the C102 in Cyclohexane at Various Concentrations of *p*-Cl-Phenol at Two Excitation Wavelengths (λ_{ex}): 375 and 405 nm

[<i>p</i> -Cl-phenol]	$\lambda_{\text{ex}} = 375 \text{ nm}$		$\lambda_{\text{ex}} = 405 \text{ nm}$	
	$\tau_1/\text{ps}(a_1)$	$\tau_2/\text{ps}(a_2)$	$\tau_3/\text{ps}(a_1)$	$\tau_4/\text{ps}(a_2)$
0 mM		2700(1.00)		2700(1.00)
11 mM	350(0.40)	2600(0.60)	470(0.94)	1700(0.06)
22 mM	400(0.56)	2500(0.44)	480(0.92)	1400(0.08)
51 mM	390(0.71)	2200(0.29)	510(0.91)	1500(0.09)

not possible. The spectral shift of the absorption and emission of C102 was reported in the presence of phenol in another noninteracting solvent C_2Cl_4 ^{2a} but fluorescence quenching is reported for the first time in this work using cyclohexane as a solvent. Both C_2Cl_4 and cyclohexane are noninteracting solvent without any hydrogen bond accepting or donating ability. Strong fluorescence quenching in cyclohexane but no fluorescence quenching in C_2Cl_4 is somewhat striking. Fluorescence quenching was also absent in interacting solvents—acetonitrile and methanol and is ascribed to the masking of the intermolecular C102-phenol H-bond by the dominant H-bonding interaction of the solvent with either C102 or phenol. Although C_2Cl_4 may not involve in hydrogen bonding it may not be a totally noninteracting solvent. Yoshihara and coworkers observe a broad FTIR spectrum for the $\text{C}=\text{O}$ group of C102 in C_2Cl_4 compared to that in dimethylaniline (DMA).⁴ The π electron of the unsaturated solvent or the chlorine atoms may weakly interact with C102 or phenol through halogen bonding.²⁰ Hence the fluorescence quenching may be obscured in C_2Cl_4 but not in cyclohexane.

The mechanism of fluorescence quenching may be understood from the theoretically predicted potential energy states of the hydrogen-bonded complexes. In the absence of H-bonding, the S_1 states of the isolated C102 are LE in character and the S_0 – S_1 energy gap is large, and hence the excited-state relaxation is almost exclusively radiative. This may be the reason for very high quantum yield of C102 in cyclohexane.¹⁹ The results of H-bonding are to lower the energy of the LE state of the complex and in addition create a new CT state that was absent in the free coumarin. This CT state may be formed due to intermolecular interactions within the strongly H-bonded species in the excited state. On the basis of the theoretical and experimental results, the following relaxation scheme may be proposed for the excited-state relaxation of the hydrogen-bonded complex (Scheme 2). At $\lambda_{\text{ex}} = 405 \text{ nm}$, only the hydrogen-bonded complex is selectively excited, whereas at $\lambda_{\text{ex}} = 375 \text{ nm}$, both the free and the H-bonded complexes are excited. Our TD-DFT calculations suggest that the S_1 state is a dark state and hence nonfluorescent. Optical excitation prepares the complex initially in the S_2 (LE) state, from where it may relax radiatively to the ground state (S_0) or undergo internal conversion (IC) to the S_1 (CT) state. This nonradiative IC may be the main origin of fluorescence quenching, and the fast component ($\sim 600 \text{ ps}$) may be due to the dynamics of the process. This local CT (or photoinduced electron transfer (PET)) within the hydrogen-bonded complex as a possible mechanism of the fluorescence quenching was first proposed by Zhao et al.³ but is observed for the first time here. Fluorescence quenching due to PET in the absence of a hydrogen bond has been extensively studied in coumarin–dimethylaniline (DMA) systems.²¹ However, the oxidation potential of the phenol derivatives is much less favorable for

Scheme 2. Relaxation Scheme of the H-Bonded Complex^a



^aUpward and downward solid arrows indicate absorption and emission, respectively; excited-state hydrogen-bonding dynamics is shown as red curved arrow; internal conversion (IC) and nonradiative transitions are represented as wavy arrows.

PET than DMA, and C102 is known to be less susceptible to PET among all other coumarins.²¹ Hence fluorescence quenching through PET without a H-bond could be neglected for the phenol derivatives. This may be the reason for lack of fluorescence quenching for anisole in cyclohexane and all the of phenol derivatives in acetonitrile and methanol. Photoinduced electron transfer in the H-bonded system could be very facile due to the proximity of the donor–acceptor and proper orientation of the donor–acceptor compared with the non-hydrogen-bonded system. Hence, fluorescence quenching is observed only in the H-bonded C102-phenol or C102-*p*-Cl-phenol pairs but not for anisole, although all have similar oxidation potential.

5. SUMMARY AND CONCLUSIONS

The theoretical speculation that excited-state hydrogen-bond strengthening or shortening may lead to the fluorescence quenching has been observed here for the first time for C102-phenol complex in cyclohexane. Fluorescence quenching was correlated well with the strength of hydrogen bond. The quenching was completely absent for the C102-anisole system, where no H-bonding is possible, and was more prominent for the *p*-Cl-phenol, which forms stronger hydrogen bond with C102 than phenol. Time-resolved fluorescence measurement suggests that the observed quenching is mostly dynamics quenching and aided by excited-state hydrogen-bond strengthening. Theoretical calculations indicated that a dark CT state exists in the hydrogen-bonded complex and plays a major role in the fluorescence quenching mechanism. The observed fluorescence quenching of the selectively excited hydrogen bonded C102-phenol complex may be due to the internal conversion (or PET) from the S_2 (LE) to S_1 (CT) state, and the transfer occurs on a much faster time scale ($\sim 600 \text{ ps}$) than the electronic relaxation of the unbound C102. The H-bond may persist for most of the excited-state complex, and only a small fraction (10%) of the complex may dissociate in the excited state and display a slow relaxation similar to unbound C102. This study shows that excited-state hydrogen-bonding dynamics, which are typically proposed to occur on an ultrafast time scale, may alter the fluorescence characteristics of a H-bonded complex on much slower time scale as well.

■ ASSOCIATED CONTENT

■ Supporting Information

Frontier molecular orbitals of the H-bonded complexes, absorption spectra of C102 in the presence of anisole in cyclohexane, absorption spectra of C102 in the presence of phenol in acetonitrile and methanol, emission spectra of C102 in the presence of anisole in cyclohexane, emission spectra of C102 in the presence of phenol in acetonitrile and methanol, and emission spectra of C102 in presence of phenol and *p*-Cl-phenol in cyclohexane at an excitation wavelength of 405 nm. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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