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Excited State Intramolecular Proton Transfer in Electron-Rich and Electron-Poor Derivatives of 10-Hydroxybenzo[*h*]quinoline

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Supporting Information

ABSTRACT: Eight previously inaccessible derivatives of 10-hydroxybenzo[*h*]quinoline were prepared via a straightforward strategy comprising formation of the benzo[*h*]quinoline skeleton followed by C−H acetoxylation at position 10. The occurrence of excited state intramolecular proton transfer (ESIPT) was detected in all cases since emission was observed only from the excited keto-tautomer. Studies on derivatives bearing both electron-donating and electron-withdrawing groups adjacent to the pyridine ring allowed us to identify some design patterns giving rise to NIR emission and large Stokes shifts. For a derivative of 10-hydroxybenzo[*c*]acridine, emission at 745 nm was observed, one of the lowest energy fluorescence ever reported for ESIPT system. On the basis of time-resolved measurements, proton transfer was found to be extremely fast with time constants in the range (0.08−0.45 ps).

INTRODUCTION

Excited state inter- and intramolecular proton transfer (ESIPT)[1] has emerged as an interesting phenomenon that can be utilized in the design of fluorescent sensors.[2] Compounds displaying ESIPT include benzoxazoles,[3] flavones,[4] imidazoles,[5] benzothiazoles,[6] and anthraquinones.[7] These compounds possess a large Stokes shift and hence are suitable for many applications such as laser dyes,[8] fluorescence recording,[9] ultraviolet stabilizers,[10] probes for solvation dynamics,[11] probes for biological environments,[12] and, recently, organic light emitting devices.[13] 10-Hydroxybenzo[*h*]quinoline (HBQ) represents a fundamental heterocyclic systems in which ESIPT occurs. Although this molecule has long been used as a reagent in the preparation of optical filter agents in photographic emulsions, the fundamental studies of Chou and colleagues identified ESIPT as the process responsible for the strongly bathochromically shifted fluorescence of HBQ.[14] Detailed photophysical and theoretical studies of HBQ showed very fast and solvent-independent ESIPT,[15] but broader studies were hampered by considerable difficulties with the preparation of its more elaborated derivatives.[16] The recent discovery by Sanford and co-workers of coordination-assisted acetoxylation of derivatives and analogues of 2-phenylpyridine opened up new possibilities.[17] Acetate derivatives of 10-hydroxybenzo[*h*]-quinoline prepared by this method can be easily hydrolyzed to the corresponding phenol. It is noteworthy that, in 6-, 7-, and 8-hydroxyquinolines, excited state proton transfer also occurs in intra- or intermolecular fashion.[18] These analogues of HBQ are known to be photoacids.[19] We envisioned that the combination of the rich chemistry of quinolines (and their benzoanalogues) with this modern synthetic tool could provide easy access to an almost unlimited variety of structural analogues of 10-hydroxybenzo[*h*]quinoline, which would then allow studies of the structure−photophysical properties relationship. While many heterocyclic systems have been reported to display ESIPT, only a few reports have been devoted to the systematic study of the optical properties of any of these scaffolds. Little is known about the properties of the HBQ derivatives, especially those bearing strongly electron-withdrawing and -donating groups at various positions. The aim of this study was to apply this new synthetic strategy to obtain a range of unique derivatives of HBQ and to investigate their fundamental optical properties. This approach would allow us to address the tunability of chromophore absorption as well as proton transfer emission, some of the most important issues of the ESIPT system.

EXPERIMENTAL SECTION

All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2, hexanes) were distilled prior to use. All reported ^1H NMR and ^{13}C NMR spectra were collected using 600, 500, 400, or 200 MHz spectrometers. Chemical shifts (δ ppm) were determined with TMS as the internal reference; J values are given in Hz. The UV/vis absorption spectra were recorded in CH_2Cl_2 or TFA. The absorption wavelengths are reported in nm with the extinction

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coefficient in M^{-1} cm^{-1} in parentheses. The melting points of compounds were determined using a capillary type apparatus. Chromatography was performed on silica (230−400 mesh) or neutral alumina. Dry column vacuum chromatography (DCVC)[20] was performed on preparative thin-layer chromatography alumina. The mass spectra were obtained via field desorption MS (FD-MS), electrospray ionization (ESI-MS), and electron impact MS (EI-MS). Compounds **1**,[21] **9**,[22] **15**,[23] and **17**[23] were prepared according to the literature procedures. A spectrophotometer and a spectrofluorimeter were used to acquire the absorption and emission spectra. Spectrophotometric grade solvents were used without further purification.

Optical Studies. Steady-state absorption spectra were measured by Shimadzu UV-3600 spectrophotometer. Corrected emission spectra were acquired by Fluorolog 3 fluorimeter (SPEX Inc.), with excitation at 328−409 nm, depending on the compound. Emission quantum yields of **2**, **14**, and **18** was determine using Rhodamine 6G as a standard. The quantum yields of other compounds were too low to use a highly emissive standard; therefore, **14** was used as the standard for other compounds. Emission decays were measured using two methods, femtosecond up-conversion and picosecond time-correlated single-photon counting (TCSPC). The up-conversion instrument has been described elsewhere.[24] In brief, the femtosecond pulses (ca. 50 fs) were generated by tunable Ti:sapphire laser, which provided the excitation wavelengths in the range 380−400 nm and the time resolution of approximately 150 fs. The emission decays were measured at three wavelengths when possible: at the expected emission maximum of the enol form and close to the maximum and at the red sides of the keto form emission band. The longest delay time is limited by 1.2 ns for the up-conversion instrument. Therefore, the samples with emission lifetime longer than a few hundredths of picoseconds were also measured using TCSPC instrumentation described elsewhere.[24] In brief, the samples were excited with a pulsed diode laser at 405 nm (LDH-P-C-405B, PicoQuant GmbH), the emission detection range was 450−840 nm, and the time resolution was 60−70 ps.

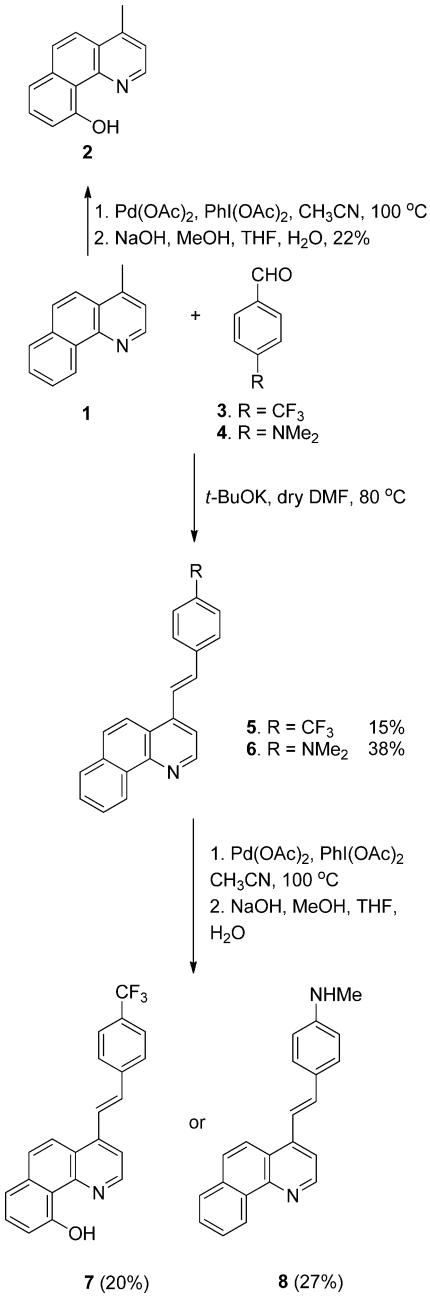
RESULTS AND DISCUSSION

Design and Synthesis. Until recently, only a few derivatives and analogues of 10-hydroxybenzo[*h*]quinoline were known.[16] We were interested in the effect of structural modifications on photophysical properties. The design of our small library was driven by two considerations: (a) introduction of strongly electron-withdrawing and electron-donating substituents at this core and (b) expansion of the chromophore itself. Along these lines, by combination of known methods for the construction of quinolines, we synthesized eight analogues of 10-hydroxybenzo[*h*]quinolines **2**, **7**, **8**, **13**, **14**, **16**, **18**, and **22** (Schemes 1−5).[21−31] Details of the synthesis are presented in the Supporting Information.

Optical Studies. An examination of the spectral characteristics of compounds **2**, **7**, **9**, **12**, **13**, **15**, **18**, and **22** as compared to those of the parent 10-hydroxybenzo[*h*]quinoline[14,16a] (Table 1; Figures 1 and 2) revealed that ESIPT occurred in all compounds. Steady-state fluorescence emission maxima measurements showed emission by the keto-tautomer in the spectral range 450−750 nm.

The positions of absorption and emission maxima were virtually solvent independent with the exceptions of **7** and **16**. For **7**, the absorption maximum shifted slightly to the blue in more polar solvents. The intensities of the fluorescence

Scheme 1. Preparation of 10-Hydroxybenzo[*h*]quinolines 2 and 7



emission spectra and the positions of the emission maxima were strongly solvent dependent (Figure 2b). The absorption spectra of **16** in THF and acetonitrile displayed no clear band, which could be attributed to the lowest energy excited state (Figure 1c); therefore, only a rough estimation of the maximum positions were made for this compound, and consequently, the calculated Stokes shift values are also estimations (Table 1). The third compound with a clear solvent dependence on the emission was **18** with the 7-nitro group, for which the emission quantum yield was almost 20-fold lower in acetonitrile than in toluene. However, the position of the emission maximum was practically independent of the nature of the solvent.

In his fundamental paper, Chou and co-workers stated that the addition of electron-withdrawing substituents at the pyridine ring of HBQ should result in a decrease of the lowest

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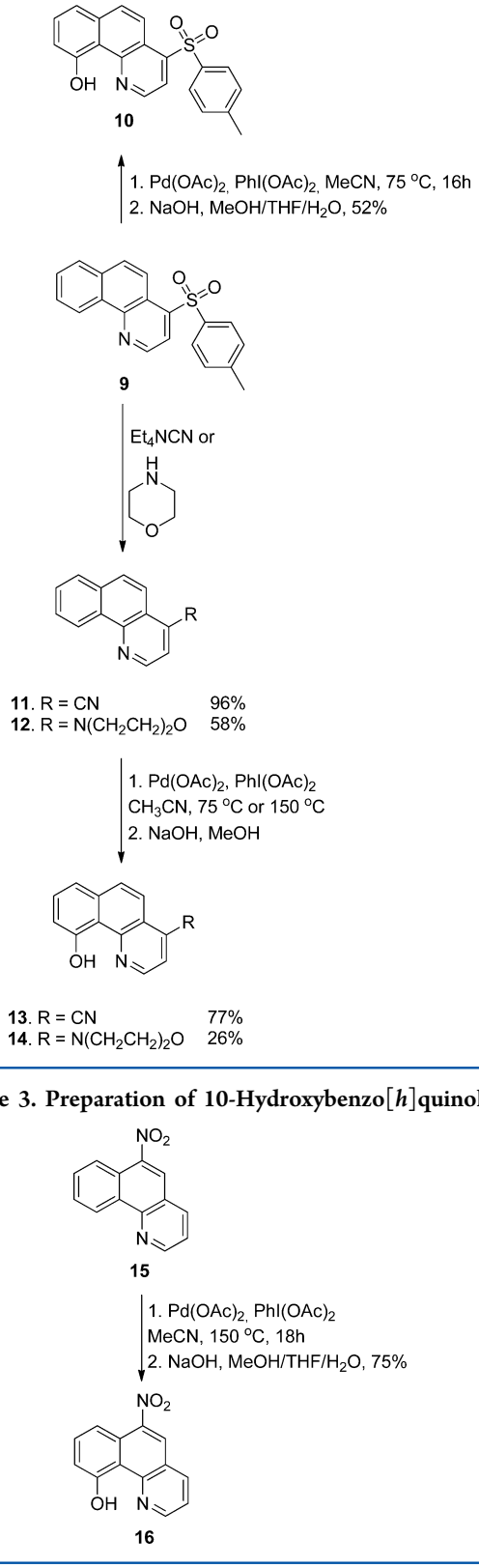
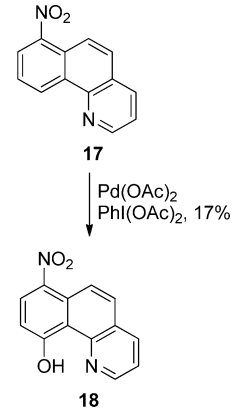
Scheme 2. Preparation of 10-Hydroxybenzo[*h*]quinolines 10, 13, and 14



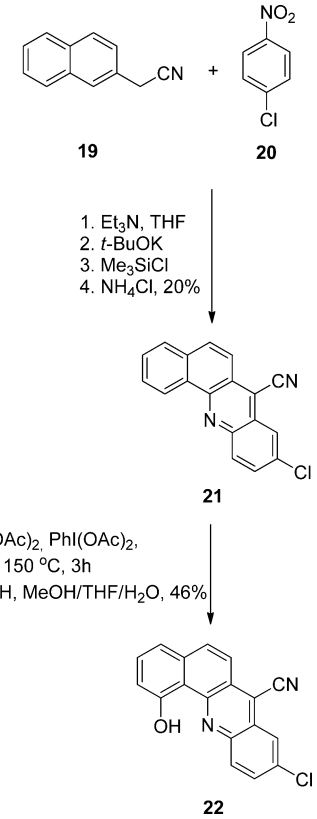
Scheme 3. Preparation of 10-Hydroxybenzo[*h*]quinoline 16

unoccupied molecular orbital (LUMO), hence a decrease of the energy gap of the keto-tautomer.[16a] This hypothesis, based on DFT calculations, was never experimentally proved. Our results are in agreement with this proposal. For derivatives substituted at the pyridine ring, moving from tertiary amine through

Scheme 4. Preparation of 10-Hydroxybenzo[*h*]quinoline 18



Scheme 5. Preparation of Compound 22



methyl to cyano and SO_2Ph group at position 4 of HBQ (**14**, **2**, **13**, and **10**, respectively), we observed a small bathochromic shift in absorption maxima (from 373 to 402 nm in CH_2Cl_2). In agreement with the predictions of Chou, with the addition of stronger electron-withdrawing substituents, the emission maxima showed significant red-shifting from 599 nm for 4-morpholino **14** to 720 nm for compounds **10** (4-tosyl) and **13** (4-cyano) (Table 1, Figure 1). Simultaneously, we detected decreases in fluorescence quantum yields ranging 1.5−2.5% for methyl derivative **2** and tertiary amine **14** to ∼0.05% for derivatives **10** and **13**, the compounds bearing electron-withdrawing groups. This is also in line with observations of Chou and co-workers and was attributed to energy gap law predicting exponential increase of nonradiative relaxation rate constant with a decrease of the emission energy gap.[16a]

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Table 1. Optical Properties of Compounds 2, 7, 10, 13, 14, 16, 18, and 22

compound	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift (cm^{-1})	φ_F (%)
2				
CH_3CN	370	604	10500	1.43
DCM	372	602	10300	1.73
toluene	376	609	10200	1.38
7				
CH_3CN	390	470	4400	0.194
DCM	394	511	5800	0.181
toluene	399	447	2700	0.213
10				
CH_3CN	396	716	11300	0.059
DCM	402	714	10900	0.067
toluene	406	714	10600	0.077
13				
CH_3CN	402	712	11100	0.057
DCM	408	714	10500	0.057
toluene	411	717	10500	0.063
14				
CH_3CN	370	596	10200	2.23
DCM	373	599	10100	2.50
toluene	376	604	10000	1.96
16				
CH_3CN	420[a]	582	6600	0.05
DCM	434[a]	580	5800	0.06
toluene	442[a]	587	5600	0.13
18				
CH_3CN	368	566	9500	0.16
DCM	371	566	9300	0.58
toluene	370	577	9700	3.05
22				
CH_3CN	458	740	8300	0.076
DCM	461	745	8300	0.074
toluene	464	745	8100	0.075

[a]Approximate value for a maximum corresponding to the lowest energy band.

According to expectations, the bathochromic shift of absorption was visible when going from simple derivatives of benzo[*h*]quinoline to its π-expanded analogues (Table 1; Figures 1−2; λ_{abs}(**13**) = 411 nm (toluene); λ_{abs}(**22**) = 464 nm (toluene)). However, the Stokes shift for π-expanded derivative **22** is smaller than that for derivative **13**, which indicates that enlarging conjugation of the pyridine moiety has an effect similar to the attachment of an electron donating group.

Surprisingly, the π-expanded derivative **7** lacked a bathochromic shift of absorption. Its absorption maximum was located around 395 nm (depending on the solvent). Its emission was observed at 511 nm in CH_2Cl_2, a much shorter wavelength value than any other HBQ derivative studied, and this compound is characterized by the smallest Stokes shift in this series. Probably steric flexibility of the styryl group is responsible for rather different properties of this compound.

The 6-nitro **16** and 7-nitro **18** derivatives showed a minor shift in fluorescence emission maxima to shorter wavelengths in more polar solvents, but the emission quantum yield was clearly solvent dependent. In more polar solvents, the fluorescence emission intensity is weaker than in nonpolar solvents. This effect is the most pronounced for 10-hydroxy-6-nitrobenzoquinoline (**16**), one of the first derivatives with a substituent at the middle ring ever studied (Figure 2c). The addition of an electron withdrawing nitro group at position 7 (derivative **18**), which belongs to dienone moiety and affects mainly the highest occupied molecular orbital (HOMO) of keto-tautomer, increases the energy gap for the keto-tautomer (hypsochomic shift of the emission), as expected. The same nitro group at position 6 (derivative **16**) is expected to affect mostly LUMO of the keto-tautomer, which should lead to reduction of the energy gap and bathochromic emission shift. However, the actual effect of nitro group at position 7 is a hypsochromic emission shift as compared to nonsubstituted benzo[*h*]quinoline and only minor bathochromic shift compared to **16**. Apparently, substitution at position 7 affects both HOMO and LUMO with a net effect of a minor increase of the energy gap of keto-tautomer.

Fluorescence quantum yields of products **2**, **7**, **10**, **13**, **14**, **16**, **18**, and **22** were found to be generally very low (0.05−2.3) in CH_3CN (Table 1) and solvent independent, except compounds **18** and **16** to a lesser degree. Fluorescence spectra were obtained by exciting the molecules at 328−409 nm depending on the compound. When compared to parent compound HBQ, the Stokes shifts of many substituted derivatives were lower (11 000 cm^{-1} for HBQ and 4400−9500 cm^{-1} for compounds **7**, **16**, **18**, and **22**). Both absorption and emission of π-expanded compound **22** were bathochromically shifted versus HBQ, which resulted in the lowest energy emission (~745 nm) ever reported for a ESIPT-capable system (Table 1).

(As indicated in Table 1, as a general trend, the polarity of the solvent had little effect on the fluorescence quantum yield (φ_F). As illustrated by compounds **2** and **14**, the quantum yields were relatively high and independent of solvent polarity.

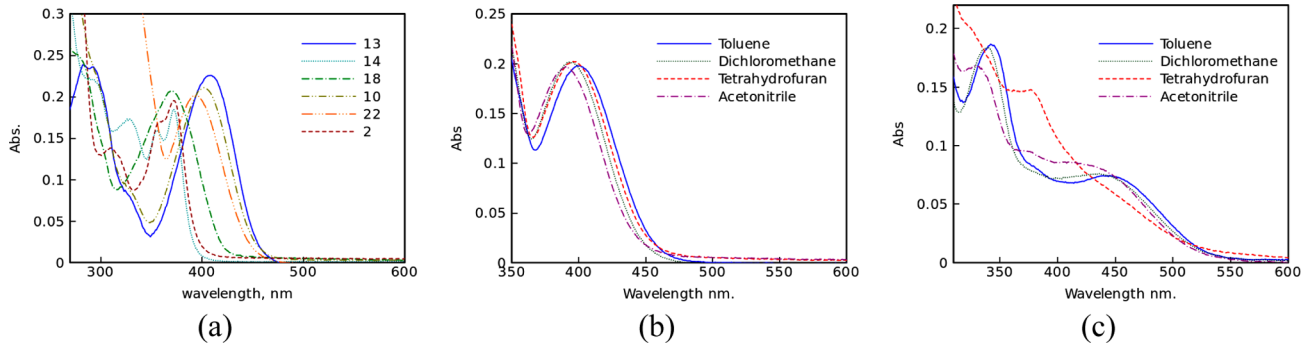

Figure 1. (a) Absorption spectra of **2**, **10**, **13**, **14**, **18**,and **22** in DCM. (b) Absorption spectra of **7** in four solvents. (c) Absorption spectra of **16** in four solvents.

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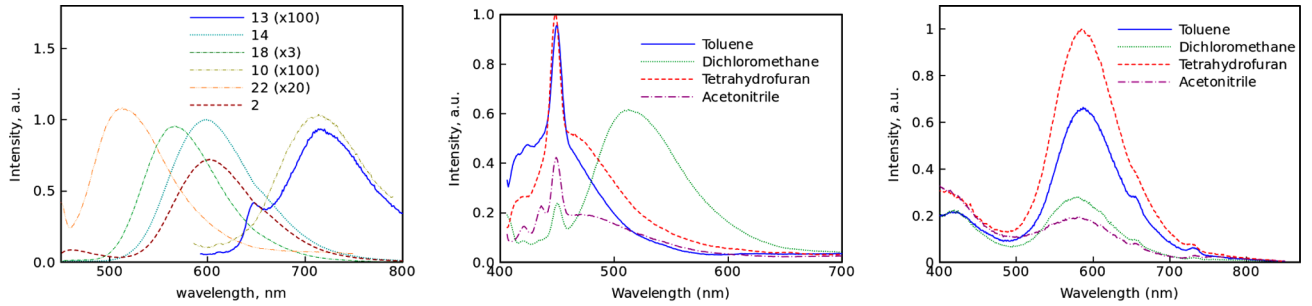

Figure 2. (a) Emission spectra of **2**, **13**, **14**, **18**, **10**, and **22** in DCM; multiplication factors are indicated in brackets. (b) Emission spectra of **7** in four solvents (the sharp bands around 450 nm are due to Raman scattering by the solvents). (c) Emission spectra of **16** in four solvents.

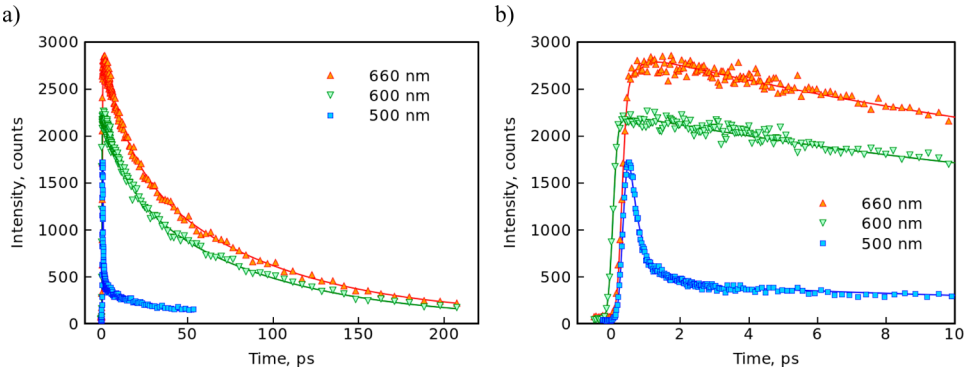

Figure 3. Emission decays of **18** in acetonitrile monitored at three wavelengths, 500, 600, and 660 nm. Solid lines present global fit curves. Panel b shows the same data as that in panel a but in an expanded time scale. Sample was excited at 390 nm.

Table 2. Decay Time Constants of Enol- (τ_{enol}) and Keto-Tautomers (τ_{keto}) Obtained from Emission Time-Resolved Measurements, Emission Quantum Yields (φ_F), and Radiative Rate Constants (k_r)

	acetonitrile				THF				toluene			
compound	τ_{enol} (ps)	τ_{keto} (ps)	φ_f (%)	k_r (10^9 s^{-1})	τ_{enol} (ps)	τ_{keto} (ps)	φ_f (%)	k_r (10^9 s^{-1})	τ_{enol} (ps)	τ_{keto} (ps)	φ_f (%)	k_r (10^9 s^{-1})
2	0.31	627[a]	1.4	0.022	0.30	654[a]	1.4	0.022	0.45	690[a]	1.4	0.02
10	0.14	36	0.06	0.017	0.12	47	0.07	0.015	0.19	56	0.08	0.014
13	0.21	32	0.06	0.019	0.13	35	0.05	0.014	0.24	45	0.06	0.013
14	0.36	863[a]	2.2	0.025	0.39	876[a]	2.1	0.024	0.45	818[a]	2.0	0.024
18	0.33	82	0.16	0.02	0.49	993[a]	2.4	0.024	0.35	1490[a]	3.1	0.021

[a]Measured by TCSPC instrument.

For **18**, however, the emission yield was highest in nonpolar toluene, 3.05%, but fell to 0.16% in more polar acetonitrile.)

We considered that low emission yield could arise from fast nonradiative relaxation. To verify this hypothesis, we measured emission decays for **2**, **10**, **13**, **14**, and **18** in acetonitrile, THF, and toluene. The primary excited state for the compounds should be the singlet excited state of the enol-tautomer. One can expect to observe the fluorescence of the enol-tautomer at the red edge of the absorption band since the Stokes shift for the enol-tautomer should be relatively small. Therefore, we measured the fluorescence emission decays at three wavelengths: close to the red edge of the absorption band representing the enol-tautomer, close to the emission maximum of the keto-tautomer, and at the red edge of the keto emission band. As an example, the emission decays are shown for **18** in acetonitrile in Figure 3. The decays at all three wavelengths were fitted simultaneously using a three-exponential model, which gave lifetimes of 0.33, 14, and 82 ps. The fast component dominates the decay at 500 nm, which is expected to be the decay of the singlet excited state of the enol-tautomer. At 600 and 660 nm, the decay is almost monoexponential with time constant of 82 ps, which is the lifetime of the keto-tautomer, and the 0.33 ps component is seen as formation of the emission. This observation has a straightforward interpretation: the singlet excited enol-tautomer has a very short lifetime and undergoes rapid conversion to the keto-tautomer. Thus, the time constant for the proton transfer in this case is 0.33 ps, and the lifetime of the excited state of keto- tautomer is 82 ps. An intermediate component, with lifetime of 14 ps, is relatively weak at all wavelengths and presumably originates from the solvent relaxation dynamics.[32,33] Similar emission decays were obtained for all compounds, and the lifetimes are summarized in Table 2.

In all cases, the proton transfer was found to be extremely fast with time constants in the range 0.08−0.45 ps. The proton transfer leads to the formation of the singlet excited keto-tautomer. The time constant of the relaxation of the excited state of the keto tautomer was much slower, with the most

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rapid being 32 ps for **13** in acetonitrile and the slowest at 1.5 ns for **18** in toluene. The longest delay time available from our up-conversion instrument was 1 ns; therefore, to obtain accurate lifetimes in time scales longer than a few hundredths of a picosecond, the TCSPC instrument was used. An example of the emission decays measured by TCSPC instrument is presented in Figure 4 and shows the measurements of **18** in

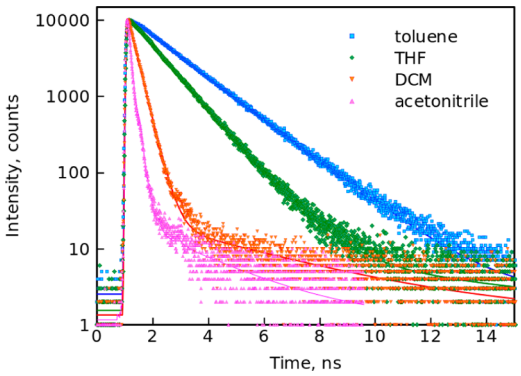

Figure 4. Emission decays of **18** at 600 nm in the indicated solvents as measured by TCSPC instrumentation.

four solvents. Compound **18** was the only candidate with strong solvent dependency for the emission lifetime. The wide variations in decay rates with respect to solvent polarity were expected, considering that the emission intensities and the quantum yields were greater in more nonpolar solvents.

Emission quantum yield divided by the lifetime of the emissive state gives the radiative rate constant. Notably, for all measured samples, the radiative rate constants for the keto-tautomer are in the range $(1.3–2.4) \times 10^7$ s^{-1}, despite rather large structural and photophysical differences between compounds. Apparently, the similarity in chromophore backbone is the main determinant of the radiative rate constants, and this fact accounts for the consistency of the results obtained by different methods. The large variation in emission lifetimes and thus emission quantum yields is due to the large difference in nonradiative decay rate constants for this series of compounds. Previously, a good correlation between the nonradiative rate constant and energy gap of keto tautomer was reported by Chou and co-workers.[16a] A similar trend can be seen for compounds **2**, **10**, **13**, and **14**. Derivatives **2** and **14** have a larger energy gap for the keto-tautomer and a longer emission lifetime than derivatives **10** and **13**. However, behavior of derivative **18** is more complex. In toluene, the compound has the longest emission lifetime compared to compounds **2**, **10**, **13**, and **14**, which is in agreement with the fact that derivative **18** has the highest energy gap, but the lifetime decreases sharply with an increase in solvent polarity, whereas the energy gap remains almost independent of the solvent. This type of behavior is indicative for an opening of another relaxation channel in polar solvents. One of the processes sensitive to the solvent polarity is intramolecular charge transfer, which may take place considering strong electron withdrawing character of the nitro group and highly uneven electron density distribution in core HBQ structure, but at present, we have no firm experimental proof for this hypothesis.

CONCLUSIONS

Using novel compounds, we systematically studied the effect of both electron-donating and electron-withdrawing substituents on the optical properties of derivatives and analogues of 10-hydroxybenzo[*h*]quinoline. Insertion of electron-withdrawing groups at the pyridine-ring of HBQ resulted in extending the fluorescence emission to the NIR region and affording large Stokes shifts. Conversely, a strongly electron-donating amino group influenced neither the emission nor the absorption maxima. Derivatives bearing electron-donating groups displayed higher fluorescence quantum yields. The strongly electron-withdrawing nitro group had various effects on absorption maxima depending on the actual site of insertion. We proved that, as far as the radiative rate constants are concerned, similarity in chromophore scaffold is a more important factor than large structural variations at its periphery. These results are not only of theoretical significance in that they provide new insight into factors influencing the ESIPT phenomenon but they may also open doors to practical applications in biological imaging.

ASSOCIATED CONTENT

Supporting Information

Syntheses and complete experimental section. 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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