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# Excited State Intramolecular Proton Transfer in $\pi$ -Expanded Phenazine-Derived Phenols

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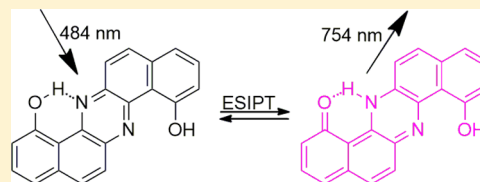
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**ABSTRACT:** Two previously inaccessible analogs of 10-hydroxybenzo[*h*]-quinoline were prepared via a straightforward strategy comprising the formation of  $\pi$ -expanded phenazines skeleton followed by C–H acetoxylation at position 10. Two bis-phenols possessing  $C_2$  and  $D_2$  symmetry were obtained in yields of 52% and 15%, respectively. The occurrence of excited state intramolecular proton transfer (ESIPT) was detected in all cases because steady state emission was observed only from the excited keto-tautomer.

Additionally, a short-lived,  $\sim 0.1$  ps, emission decay was resolved by the femtosecond up-conversion technique at the blue side of the keto-tautomer emission band, 610 nm, and was attributed to the ESIPT, i.e., conversion from enol to keto tautomer. In comparison with the corresponding 10-hydroxybenzo[*h*]quinoline emissions, the emission spectrum of the  $\pi$ -expanded phenazine analogues were weaker but displayed a characteristic bathochromically shift into NIR region. These phenazine analogues constitute one of largest heterocycles for which ESIPT was unambiguously detected.



## INTRODUCTION

Excited state inter- and intramolecular proton transfer (ESIPT)<sup>1–11</sup> has emerged as an interesting phenomenon that can be utilized in the design of fluorescent sensors.<sup>12–15</sup> Compounds displaying ESIPT include benzoxazoles,<sup>16–21</sup> flavones,<sup>22–24</sup> imidazoles,<sup>25–34</sup> imidazo[1,2-*a*]pyridines,<sup>35–42</sup> and anthraquinones.<sup>43–47</sup> The photophysical characteristics of ESIPT-capable compounds make them excellent candidates for applications in such diverse areas as laser dyes,<sup>48,49</sup> fluorescence recording,<sup>50,51</sup> ultraviolet stabilizers,<sup>52</sup> probes for solvation dynamics,<sup>53</sup> probes for biological environments,<sup>54</sup> and recently, organic light emitting devices.<sup>55,56</sup> Although 10-hydroxybenzo[*h*]quinoline (HBQ) represents one of the fundamental heterocyclic systems, in which ESIPT occurs, it was only in 1992 when the fundamental studies of Martinez, Chou, and colleagues identified ESIPT as the process responsible for the strongly bathochromically shifted fluorescence of HBQ.<sup>57,58</sup> Detailed photophysical and theoretical studies of HBQ showed very fast and solvent-independent ESIPT,<sup>59–62</sup> and recently more elaborated derivatives were also investigated.<sup>63–68</sup>

Although the photophysical properties of dibenzo[*a,c*]-phenazine have been extensively studied,<sup>69–76</sup> more comprehensive studies involving its more complex derivatives have yet to be made. This situation can be partly attributed to its problematic derivatization.<sup>77–82</sup> The recent discovery of coordination-assisted acetoxylation of derivatives and analogues of 2-phenylpyridine, by Sanford and co-workers, opened up new possibilities in heterocyclic chemistry.<sup>83–91</sup> Acetate derivatives of 10-hydroxybenzo[*h*]quinoline prepared by this method can be easily hydrolyzed to the corresponding phenols. We envisioned that the combination of the rich photophysics of

$\pi$ -expanded pyrazine analogues with these new synthetic methodologies could provide easy access to novel structural analogues of 10-hydroxybenzo[*h*]quinoline. The aim of this study was to apply the new synthetic strategy to obtain a range of unique analogues of HBQ and to investigate their fundamental optical properties. This approach addresses the tunability of chromophore absorption as well as proton transfer emission, key features involved in the ESIPT system

## EXPERIMENTAL SECTION

All chemicals were used as received unless otherwise noted. Reagent grade solvents ( $\text{CH}_2\text{Cl}_2$ , hexanes) were distilled prior to use. All reported  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were collected using 600, 500, 400, or 200 MHz spectrometers. Chemical shifts ( $\delta$  ppm) were determined with TMS as the internal reference;  $J$  values are given in hertz. The UV/vis absorption spectra were recorded in  $\text{CH}_2\text{Cl}_2$ , toluene, TFA, and MeCN. The absorption wavelengths are reported in nanometers with the extinction coefficient in  $\text{M}^{-1} \text{cm}^{-1}$  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)<sup>92</sup> 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). Compound **1**<sup>93</sup> was prepared according to established

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protocols. A spectrophotometer and a spectrofluorometer were used to acquire the absorption and emission spectra. Spectrophotometric grade solvents were used without further purification.

**1,8-Dihydroxydibenzo[*a,c*]phenazine (2).** A sealed tube was charged with dibenzo[*a,c*]phenazine (1) (70 mg, 0.25 mmol),  $\text{PhI}(\text{OAc})_2$  (330 mg, 1 mmol),  $\text{Pd}(\text{OAc})_2$  (4.6 mg, 0.02 mmol), and  $\text{CHCl}_3$  (2.1 mL). The reaction was stirred at 120 °C for 24 h. The mixture was transferred to a round-bottom flask and evaporated to dryness. The precipitate was dissolved in MeOH, and NaOH (5 equiv) was added to hydrolyze the formed bis-acetate. After stirring at room temperature for a few hours, the mixture was acidified with 10% HCl until neutral pH was achieved. The solvent was removed under reduced pressure and extracted between  $\text{CH}_2\text{Cl}_2$  and water. A thin layer of diatomaceous earth was used to remove the insoluble black solid from the formed emulsion. The organic layer was dried over  $\text{Na}_2\text{SO}_4$  and removed under vacuum. The solid was chromatographed (DCVC,  $\text{Al}_2\text{O}_3$ , hexanes  $\rightarrow$  hexanes/ $\text{CH}_2\text{Cl}_2$  4:1, 3:1, 3:2). The pure product was obtained after crystallization from hot acetone (40.6 mg, 52%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ) 3.23–5.10 (br s, 1H, NH), 7.28 (d, 1H,  $J$  = 0.7), 7.68 (t, 2H,  $J$  = 8.0), 7.82–7.98 (m, 2H), 8.06 (d, 2H,  $J$  = 7.7), 8.15–8.34 (m, 2H), 14.81 (s, 1H, OH);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$ ) 112.9, 114.6, 116.7, 127.3, 130.5, 132.7, 133.7, 137.2, 145.5, 161.6; ESI-LR found 313.1 [ $\text{M} + \text{H}^+$ ], calcd 313.1 ( $\text{C}_{20}\text{H}_{13}\text{N}_2\text{O}_2$ );  $\lambda_{\text{abs}}$  ( $\text{CH}_2\text{Cl}_2$ ,  $\epsilon \times 10^{-3}$ ) 428 (17.9), 263 (64.8) nm.

**1,8-Dihydroxydibenzo[*a,h*]phenazine (5).** A sealed tube was charged with dibenzo[*a,h*]phenazine (4) (300 mg, 1.07 mmol),  $\text{PhI}(\text{OAc})_2$  (1.38 g, 4.28 mmol),  $\text{Pd}(\text{OAc})_2$  (24 mg, 0.107 mmol), and  $\text{CHCl}_3$  (10 mL). The reaction was stirred at 120 °C for 24 h. The mixture was transferred into a round-bottom flask and evaporated to dryness. The precipitate was dissolved in MeOH/THF, and NaOH (5 equiv) was added to hydrolyze the formed bis-acetate. After stirring at room temperature for a few hours, the mixture was acidified with 10% HCl until neutral pH was achieved. The solvent was removed under reduced pressure and extracted with  $\text{CHCl}_3$ . The organic layer was dried over  $\text{Na}_2\text{SO}_4$  and removed under vacuum. The solid was chromatographed (DCVC,  $\text{Al}_2\text{O}_3$ , hexanes  $\rightarrow$  hexanes/ $\text{CH}_2\text{Cl}_2$  4:1, 3:1, 3:2  $\rightarrow$   $\text{CHCl}_3$ ). The pure product was obtained after crystallization using THF and filtrated hot mixture through crepe filter paper (52 mg, 15%);  $^1\text{H}$  NMR (600 MHz, DMSO,  $\delta$ ) 7.55 (d, 2H,  $J$  = 7.9), 7.76 (d, 2H,  $J$  = 7.6), 7.89 (t, 2H,  $J$  = 7.8), 8.17 (d, 2H,  $J$  = 9.1), 8.40 (d, 2H,  $J$  = 9.3), 11.43 (s, 2H);  $^{13}\text{C}$  NMR (150 MHz, DMSO,  $\delta$ ) 110.1, 116.6, 119.4, 122.4, 133.7, 134.0, 135.0, 136.9, 138.7, 156.1; EI-HR found 312.0905 [ $\text{M}^+$ ], calcd 312.0899 ( $\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_2$ );  $\lambda_{\text{abs}}$  ( $\text{CH}_2\text{Cl}_2$ ,  $\epsilon \times 10^{-3}$ ) 484 (8.7), 266 (26.2) nm.

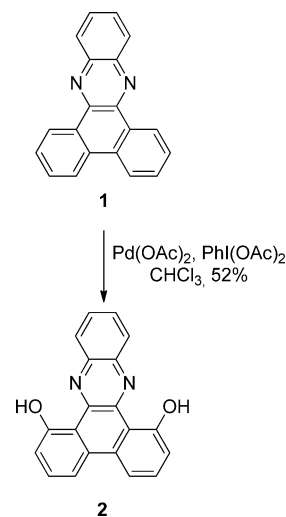
**Spectroscopy Measurements.** Steady state absorption spectra were measured using a Shimadzu UV-3600 spectrophotometer. Corrected emission spectra were acquired using a Fluorolog 3 fluorometer (SPEx Inc.), with excitation at 328–409 nm, depending on the compound. Emission quantum yields of 2 and 5 were determined using Rhodamine 6G as a standard (ethanol, quantum yield 0.95). 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.<sup>94</sup> Excitation wavelengths were 380–400 nm with a time resolution of approximately 150 fs. 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 few hundredths of picoseconds were also measured using TCSPC instrumentation described elsewhere.<sup>94</sup> In brief, the samples were excited with a pulsed diode laser at 405 nm, the emission detection range was 450–840 nm, and the time resolution was 60–70 ps.

## RESULTS AND DISCUSSION

**Design and Synthesis.** No pyrazine derivatives undergoing ESIPT were known prior to this study. We designed two  $\pi$ -expanded pyrazines with appropriate architecture namely dibenzo[*a,c*]phenazine (1)<sup>93</sup> and dibenzo[*a,h*]phenazine (5) as precursors of the corresponding bis-phenols. Phenazine 4 has been synthesized by air-controlled oxidation of 1-aminonaphthalene following procedure by Itoho and Kosugi.<sup>95</sup> Initially, compound 1 was subjected to optimized conditions (i.e., MeCN, 150 °C, 14 h) with 2 equiv of oxidant ( $\text{PhI}(\text{OAc})_2$ ). Although a high conversion did occur, the reaction led to the formation of numerous products and therefore required optimization. On the basis of this result, we tested other solvents and determined that using  $\text{CHCl}_3$  at 120 °C in conjunction with higher concentration of  $\text{Pd}(\text{OAc})_2$  (3 times) resulted in full conversion (Scheme 1). After purification

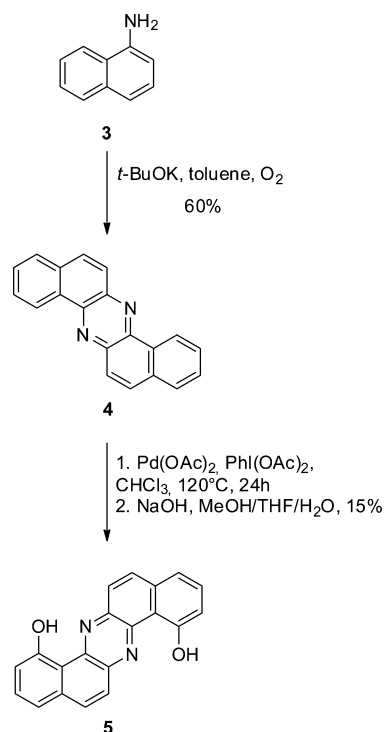
Scheme 1. Preparation of Hydroxyphenazine 2



using chromatography, the newly optimized procedure produced the desired product 2 in 52% yield. The same conditions were applied for phenazine 4 (Scheme 2) to afford compound 5 in 15% yield (after hydrolysis).

**Optical Properties.** Previously reported studies show that pyrazine derivatives do not display a strong fluorescence. Indeed, their photostability results from the loss of excited state energy through vibrational relaxation.<sup>96,97</sup> Absorption and emission spectra of 2 and 5 are presented in Figure 1. Close examination of the spectra revealed a virtual solvent independence with the exception of a slightly higher emission intensity of 2 in toluene in comparison to the cases of other studied solvents. For both compounds large Stokes shifts can be noted at 9800 and 7500  $\text{cm}^{-1}$  for dyes 2 and 5, respectively (Table 1). The optical data collected emphasize that, in analogy

## Scheme 2. Preparation of Hydroxyphenazine 5



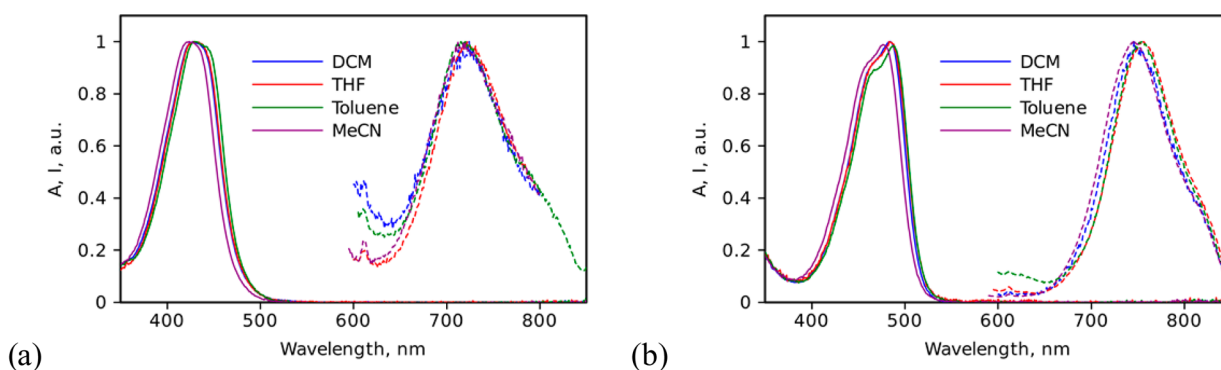
to HBQ.<sup>57–59</sup> ESIPT for phenols **2** and **5** is free from solvent perturbation. Large Stokes shifts (characteristic for ESIPT), along with the lack of emission at the red end of the absorption band indicated that the proton transfer was a fast and efficient process, similar to the parent HBQ compound. Additionally, the fluorescence emission generated from the proton transferred state was relatively weak. Emission quantum yields were estimated to be roughly 0.01% and 0.03% for **2** and **5**, respectively, which indicated a relatively short lifetime of the proton transferred state.

The fundamental study by Park and co-workers showed that ESIPT-derived fluorescence from the excited keto state is usually low if the six-membered nitrogen containing ring is involved.<sup>98</sup> 10-Hydroxybenzo[*h*]quinoline and all its derivatives and analogues possessing various functional groups have rather low fluorescence quantum yields.<sup>63–68</sup> For this reason the parent compound has been used as an optical filter agent in photographic emulsions, for many years.<sup>99</sup> ESIPT-based functional dyes characterized by low fluorescence quantum yields can find applications in research aiming at switch-on

probing<sup>100</sup> compounds, because coordination of various cations disables proton transfer and in turn usually leads to a significant increase in fluorescence quantum yields.<sup>66,67,101,102</sup> Given relatively high molar-absorption coefficients, one can also envision applications as photostabilizers.

To experimentally determine the fluorescence lifetime emission, we employed both femtosecond up-conversion and picosecond time-resolved emission spectroscopy (Figure 2). As expected, emission decay measurements of phenol **2** confirmed shorter lifetimes composed of two dominating emission decay component having lifetimes of 0.16 and 8.4 ps in THF. The shorter 0.16 ps lifetime is clearly observed at the blue side of the emission band and is the only decay component at 610 nm. These findings can be attributed to the emission of the enol-tautomer, or the singlet excited state with conformation corresponding the ground state. The longer lifetime of 8.4 ps occurred at similar wavelengths observed in the steady state emission spectrum of **2** and therefore can be ascribed to the lifetime of the emission band. The lifetime of 8.4 ps is still rather short and indicates that nonradiative decay is dominating the relaxation process, which is in agreement with the low emission quantum yield of the compound. Similar measurements were also carried out in MeCN and toluene, the results were essentially the same showing a fast ( $\sim 0.1$  ps) emission decay at 610 nm and decays with 11 and 14 ps time constants at longer wavelengths (710 nm) in MeCN and toluene, respectively. The somewhat longer emission lifetime in toluene corroborates with the slightly high emission quantum yield in this solvent as compared to the cases of two other solvents. Unfortunately, similar measurements were impossible for **5** because the limitation imposed by the up-conversion instrument, namely a low signal-to-noise ratio near the fundamental wavelength of the femtosecond laser, 800 nm, as well as a weak absorption of the compound **5** at the excitation wavelength, 400 nm. However, considering that the emission quantum yield of **5** is roughly 3 times larger than that of **2**, one can expect that the nonradiative decay of **5** is slower and its time constant is expected to be close to 25 ps.

Three main solvents used in this study were MeCN, THF, and toluene, which represent polar, moderately polar, and nonpolar media, and all these solvents are nonprotic ones. Unfortunately, good protic solvents, such as methanol or ethanol, could not be used with these compounds because of solubility issues. Therefore, test measurements were carried out in mixtures of dichloromethane and methanol at 1:1 volume ratio. Virtually no change in position or intensity of absorption and emission bands was observed, and only a slight (<20%)

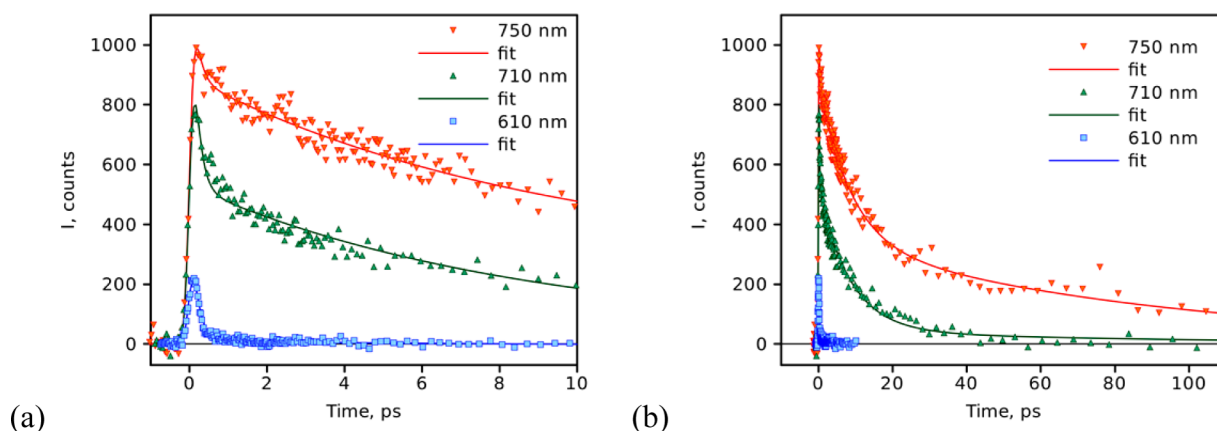


**Figure 1.** Normalized absorption (solid lines) and emission (dashed lines) spectra of **2** (a) and **5** (b) in different solvents.



**Table 1.** Summary of the Absorption and Emission Properties of Compounds **2** and **5** in MeCN, THF, Toluene, and CH<sub>2</sub>Cl<sub>2</sub>–MeOH mixture

| compound | solvent                                   | $\lambda_{\text{abs}}$ (nm) | $10^{-3}\epsilon$ | $\lambda_{\text{em}}$ (nm) | $\Delta\nu$ (cm <sup>-1</sup> ) | $\Phi$ (%) |
|----------|---|-----------------------------|-------------------|----------------------------|---------------------------------|------------|
| <b>2</b> | MeCN                                      | 423                         | 14.2              | 724                        | 9830                            | 0.01       |
|          | THF                                       | 432                         | 15.4              | 722                        | 9300                            | 0.01       |
|          | toluene                                   | 429                         | 15.5              | 722                        | 9500                            | 0.02       |
|          | CH <sub>2</sub> Cl <sub>2</sub> /MeOH 1:1 | 431                         | 17.0              | 708                        | 9100                            | 0.03       |
| <b>5</b> | MeCN                                      | 477                         | 16.7              | 743                        | 7510                            | 0.03       |
|          | THF                                       | 485                         | 19.8              | 756                        | 7390                            | 0.03       |
|          | toluene                                   | 488                         | 22.0              | 754                        | 7230                            | 0.03       |
|          | CH <sub>2</sub> Cl <sub>2</sub> /MeOH 1:1 | 484                         | 22.1              | 740                        | 7150                            | 0.03       |

**Figure 2.** Time-resolved emission decays of **2** in THF at 610, 710, and 750 nm. The colored symbols are experimental data, and the solid lines are exponential fits of the decays. (a) and (b) represents the same data at different time scales.

increase in emission quantum yield was noticed. This agrees with previous reports indicating almost no solvent dependence for similar compounds.<sup>59–68</sup>

Comparison of the emission and absorption spectra of two compounds shows a greater difference between the steady-state absorption bands than that of the emission bands. The absorption band energies for **2** and **5** are 23 640 (2.93 eV) and 20 960 cm<sup>-1</sup> (2.60 eV), which correspond to a difference of 2680 cm<sup>-1</sup> (0.36 eV), whereas the energies of the emission bands are 13 800 (1.71 eV) and 13 500 cm<sup>-1</sup> (1.67 eV) for **2** and **5**, respectively, which result in a difference of only 300 cm<sup>-1</sup> (0.04 eV) (nearly an order of magnitude smaller than the absorption energy difference). This can be rationalized by considering the conjugation systems of the enol- and keto-tautomers. In the ground state, the enol-tautomer is dominant, which results in a conjugation system that spans the entire molecular backbone of both compounds. Because each compound has a distinct arrangement of aromatic systems, the electronic configurations of **2** and **5** are quite different, which leads to the difference in absorbance spectra. Conversely, for the keto-tautomers, ESIPT occurs and the formation of each keto group displaces the aromaticity of the connecting ring, effectively removing it from the extended  $\pi$ -system. The decreased degree of conjugation diminishes the extended  $\pi$ -systems of both bis-phenols to a common tricyclic chromophore. Thus the energy differences of the emissions bands between compounds **2** and **5** are smaller than the steady-state absorbance energies because they are generated by a similar excited state electronic configuration.

The vast majority of ESIPT-related studies performed within last the 60 years focused on the small heterocyclic systems. This leaves an intriguing question unanswered: what is the influence

of extension of the  $\pi$ -conjugated system on the optical properties of ESIPT dyes? A limited number of papers published on this aspect<sup>103–107</sup> revealed that the  $\pi$ -expansion of basic ESIPT-capable chromophores can, in some cases, lead to quenching of excited state intramolecular proton transfer.<sup>104</sup> Our earlier studies of this aspect led to the conclusion that in the case of  $\pi$ -expanded benzo[*h*]quinoline analogues, the energetics of ESIPT depends on the actual position of  $\pi$ -expansion.<sup>65–68</sup> Park and co-workers<sup>33</sup> proved that the observed behavior concerning ESIPT of  $\pi$ -expanded derivatives of imidazoles and related molecules can be explained by considering the nodal pattern of the wave function along with the delocalization of the electrons in the excited state (so-called nodal-plane model developed by Nagaoka).<sup>108,109</sup> In the case of dyes **2** and **5** the weak keto-tautomer emission is parallel to many other ESIPT molecules and can be generally interpreted in terms of either rapid intersystem crossing or other fast nonradiative pathways. As was proved by Chou and co-workers for HBQ, the excited state resonance charge transfer triggers the proton transfer reaction, which simultaneously enhances the degree of resonance charge transfer effect. The optical properties of compounds **2** and **5** (Table 1, Figures 1 and 2) made it clear that  $\pi$ -expanding of the chromophore of 10-hydroxybenzo[*h*]quinoline in the presented way does not interfere with ESIPT. The presence of neither additional benzene rings nor additional nitrogen atoms interferes with the favorable relative energy levels of E\* and K\*. This is in strong contrast with the case of 12-hydroxy-1-azaperylene, when  $\pi$ -expansion of HBQ leads to a drastic change of energy levels, hence disabling ESIPT.<sup>65,68</sup> In conjunction with our previous studies on  $\pi$ -expanded analogs of HBQ, the current pyrazine-

derived phenols emphasize further that large, polycyclic systems can also undergo ESIPT in analogy to small model compounds.

In conclusion, we proved that double coordination-assisted acetoxylation can be used to transform  $\pi$ -expanded pyrazine derivatives into bis-phenols. An examination of the spectral characteristics of two large aromatic polycyclic pyrazine derivatives as compared to those of the parent 10-hydroxybenzo[*h*]quinoline<sup>57,58,63</sup> as well as to known phenazines revealed that ESIPT occurred in both compounds. Steady-state fluorescence emission maxima measurements showed emission by the keto-tautomer in the NIR spectral range. The two compounds have different symmetries, and the positions of their absorption maxima differ by 2680 cm<sup>-1</sup>. Transition to keto-tautomer after ESIPT changes the symmetry of both chromophores into a similar conjugation system, which reduced the difference in emission band positions to 300 cm<sup>-1</sup>. The presence of two ESIPT-capable moieties decreases the fluorescence quantum yield of the keto tautomer and at the same time induces the red shift of the emission, in comparison to the case for 10-hydroxybenzo[*h*]quinolone.

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### Notes

The authors declare no competing financial interest.

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