

Excited State Intramolecular Proton Transfer in π -Expanded Phenazine-Derived Phenols

Joanna Piechowska,^{†,‡} Kirsi Virkki,[§] Bartłomiej Sadowski,[†] Helge Lemmetyinen,[§] Nikolai V. Tkachenko,^{*,§} and Daniel T. Gryko^{*,†}

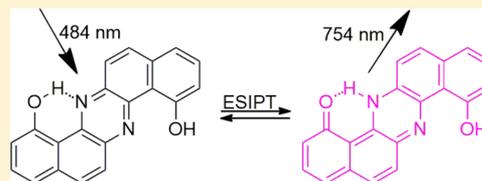
[†]Institute of Organic Chemistry of the Polish Academy of Sciences, 01-224 Warsaw, Poland

[‡]Institute of Physical Chemistry of the Polish Academy of Sciences, 01-224 Warsaw, Poland

[§]Department of Chemistry and Bioengineering, Tampere University of Technology, 33720 Tampere, Finland

ABSTRACT: Two previously inaccessible analogs of 10-hydroxybenzo[*h*]-quinoline were prepared via a straightforward strategy comprising the formation of π -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, ~ 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 π -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)^{1–11} has emerged as an interesting phenomenon that can be utilized in the design of fluorescent sensors.^{12–15} Compounds displaying ESIPT include benzoxazoles,^{16–21} flavones,^{22–24} imidazoles,^{25–34} imidazo[1,2-*a*]pyridines,^{35–42} and anthraquinones.^{43–47} The photophysical characteristics of ESIPT-capable compounds make them excellent candidates for applications in such diverse areas as laser dyes,^{48,49} fluorescence recording,^{50,51} ultraviolet stabilizers,⁵² probes for solvation dynamics,⁵³ probes for biological environments,⁵⁴ and recently, organic light emitting devices.^{55,56} 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.^{57,58} Detailed photophysical and theoretical studies of HBQ showed very fast and solvent-independent ESIPT,^{59–62} and recently more elaborated derivatives were also investigated.^{63–68}

Although the photophysical properties of dibenzo[*a,c*]phenazine have been extensively studied,^{69–76} more comprehensive studies involving its more complex derivatives have yet to be made. This situation can be partly attributed to its problematic derivatization.^{77–82} 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.^{83–91} 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

π -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 (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 hertz. The UV/vis absorption spectra were recorded in CH_2Cl_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)⁹² 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**⁹³ was prepared according to established

Received: November 20, 2013

Revised: December 18, 2013

Published: December 18, 2013

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 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 CH_2Cl_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 Na_2SO_4 and removed under vacuum. The solid was chromatographed (DCVC, Al_2O_3 , hexanes \rightarrow hexanes/ CH_2Cl_2 4:1, 3:1, 3:2). The pure product was obtained after crystallization from hot acetone (40.6 mg, 52%): ^1H NMR (400 MHz, CDCl_3 , δ) 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}C NMR (125 MHz, CDCl_3 , δ) 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 ($\text{C}_{20}\text{H}_{13}\text{N}_2\text{O}_2$); λ_{abs} (CH_2Cl_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 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 CHCl_3 . The organic layer was dried over Na_2SO_4 and removed under vacuum. The solid was chromatographed (DCVC, Al_2O_3 , hexanes \rightarrow hexanes/ CH_2Cl_2 4:1, 3:1, 3:2 \rightarrow CHCl_3). The pure product was obtained after crystallization using THF and filtrated hot mixture through crepe filter paper (52 mg, 15%); ^1H NMR (600 MHz, DMSO, δ) 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}C NMR (150 MHz, DMSO, δ) 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 [M^+], calcd 312.0899 ($\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_2$); λ_{abs} (CH_2Cl_2 , $\epsilon \times 10^{-3}$) 484 (8.7), 266 (26.2) nm.

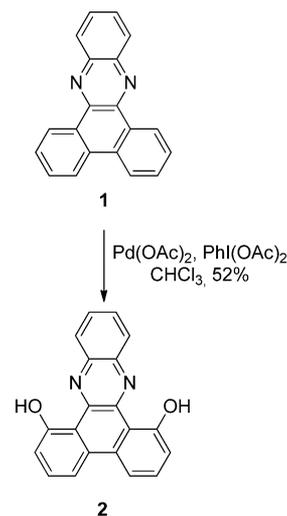
Spectroscopy Measurements. Steady state absorption spectra were measured using a Shimadzu UV-3600 spectrophotometer. Corrected emission spectra were acquired using a Fluorolog 3 fluorometer (SPEX Inc.), with excitation at 328–409 nm, depending on the compound. Emission quantum yields of 2 and 5 were 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.⁹⁴ 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.⁹⁴ 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 π -expanded pyrazines with appropriate architecture namely dibenzo[*a,c*]phenazine (1)⁹³ 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.⁹⁵ 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 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

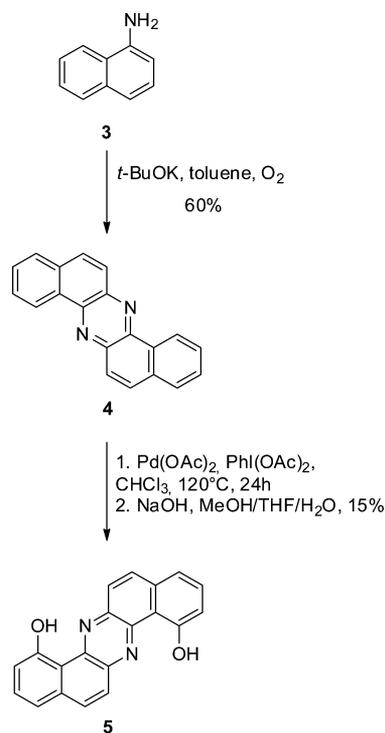
Scheme 1. Preparation of Hydroxyphenazine 2



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.^{96,97} 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 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.^{57–59} 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.⁹⁸ 10-Hydroxybenzo[*h*]quinoline and all its derivatives and analogues possessing various functional groups have rather low fluorescence quantum yields.^{63–68} For this reason the parent compound has been used as an optical filter agent in photographic emulsions, for many years.⁹⁹ ESIPT-based functional dyes characterized by low fluorescence quantum yields can find applications in research aiming at switch-on

probing¹⁰⁰ compounds, because coordination of various cations disables proton transfer and in turn usually leads to a significant increase in fluorescence quantum yields.^{66,67,101,102} 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 (~ 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%)

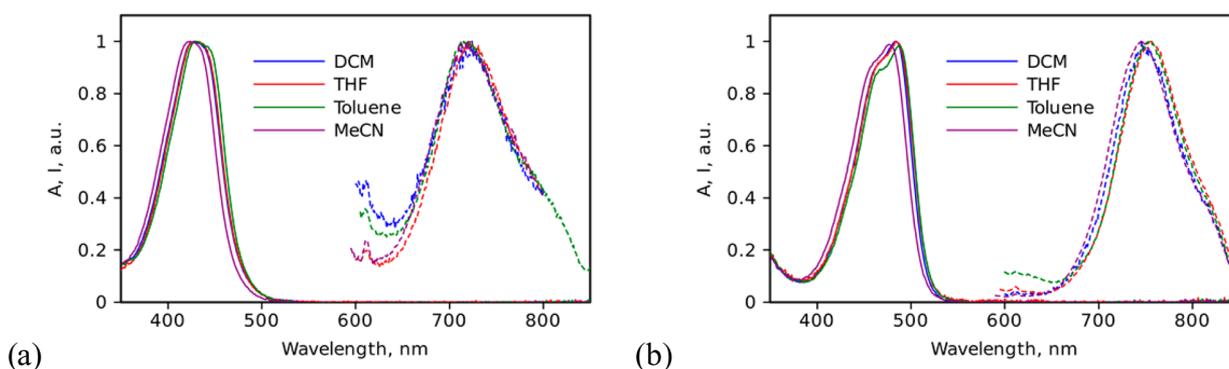
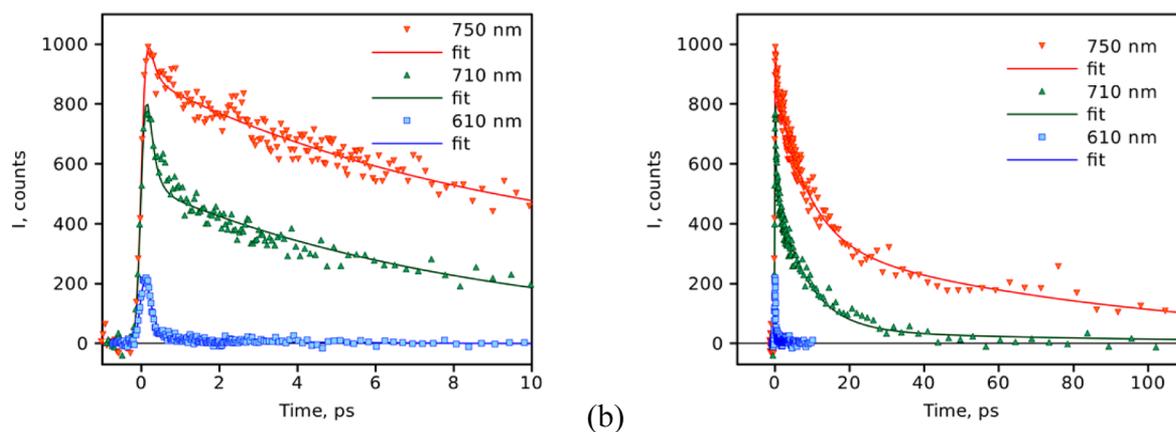


Figure 1. Normalized absorption (solid lines) and emission (dashed lines) spectra of **2** (a) and **5** (b) in different solvents.

Table 1. Summary of the Absorption and Emission Properties of Compounds **2** and **5** in MeCN, THF, Toluene, and CH₂Cl₂–MeOH mixture

| compound | solvent | λ_{abs} (nm) | $10^{-3}\epsilon$ | λ_{em} (nm) | $\Delta\nu$ (cm ⁻¹) | Φ (%) |
|----------|---|-----------------------------|-------------------|----------------------------|---------------------------------|------------|
| 2 | 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 ₂ Cl ₂ /MeOH 1:1 | 431 | 17.0 | 708 | 9100 | 0.03 |
| 5 | 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 ₂ Cl ₂ /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.^{59–68}

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⁻¹ (2.60 eV), which correspond to a difference of 2680 cm⁻¹ (0.36 eV), whereas the energies of the emission bands are 13 800 (1.71 eV) and 13 500 cm⁻¹ (1.67 eV) for **2** and **5**, respectively, which result in a difference of only 300 cm⁻¹ (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, ES IPT occurs and the formation of each keto group displaces the aromaticity of the connecting ring, effectively removing it from the extended π -system. The decreased degree of conjugation diminishes the extended π -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 ES IPT-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 π -conjugated system on the optical properties of ES IPT dyes? A limited number of papers published on this aspect^{103–107} revealed that the π -expansion of basic ES IPT-capable chromophores can, in some cases, lead to quenching of excited state intramolecular proton transfer.¹⁰⁴ Our earlier studies of this aspect led to the conclusion that in the case of π -expanded benzo[*h*]quinoline analogues, the energetics of ES IPT depends on the actual position of π -expansion.^{65–68} Park and co-workers³³ proved that the observed behavior concerning ES IPT of π -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).^{108,109} In the case of dyes **2** and **5** the weak keto-tautomer emission is parallel to many other ES IPT 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 π -expanding of the chromophore of 10-hydroxybenzo[*h*]quinoline in the presented way does not interfere with ES IPT. 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 π -expansion of HBQ leads to a drastic change of energy levels, hence disabling ES IPT.^{65,68} In conjunction with our previous studies on π -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 π -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^{57,58,63} 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⁻¹. 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⁻¹. 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.

AUTHOR INFORMATION

Corresponding Authors

*N. V. Tkachenko: e-mail, nikolai.tkachenko@tut.fl.

*D. T. Gryko: e-mail, dtgryko@icho.edu.pl.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was funded by the Foundation for Polish Science (TEAM-2009-4/3). We thank Jillian Larsen (UC Riverside) for amending manuscript.

REFERENCES

- (1) Herbich, J.; Dobkowski, J.; Thummel, R. P.; Hegde, V.; Waluk, J. Intermolecular Excited State Double Proton Transfer in Dipyrro-carbazole:Alcohol Complexes. *J. Phys. Chem. A* **1997**, *101*, 5839–5845.
- (2) Kyrchenko, A.; Herbich, J.; Izydorczak, M.; Wu, F.; Thummel, R. P.; Waluk, J. Role of Ground State Structure in Photoinduced Tautomerization in Bifunctional Proton Donor–Acceptor Molecules: 1H-Pyrrolo[3,2-*h*]quinoline and Related Compounds. *J. Am. Chem. Soc.* **1999**, *121*, 11179–11188.
- (3) Herbich, J.; Hung, C. Y.; Thummel, R. P.; Waluk, J. Solvent-Controlled Excited State Behavior: 2-(2'-Pyridyl)indoles in Alcohols. *J. Am. Chem. Soc.* **1996**, *118*, 3508–3518.
- (4) Dobkowski, J.; Herbich, J.; Galievsky, V.; Thummel, R. P.; Wu, F.; Waluk, J. Diversity of Excited State Deactivation Paths in Heterozaaromatics with Multiple Intermolecular Hydrogen Bonds. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 469–475.
- (5) Kyrchenko, A.; Herbich, J.; Wu, F.; Thummel, R. P.; Waluk, J. Solvent-Induced *syn-anti* Rotamerization of 2-(2'-Pyridyl)indole and the Structure of its Alcohol Complexes. *J. Am. Chem. Soc.* **2000**, *122*, 2818–2827.
- (6) Herbich, J.; Waluk, J.; Thummel, R. P.; Hung, C. Y. Mechanisms of Fluorescence Quenching by Hydrogen Bonding in Various Aza Aromatics. *Photochem. Photobiol. A: Chem.* **1994**, *80*, 157–160.
- (7) Herbich, J.; Kijak, M.; Zielińska, A.; Thummel, R. P.; Waluk, J. Fluorescence Quenching by Pyridine and Derivatives Induced by Intermolecular Hydrogen Bonding to Pyrrole-Containing Heteroaromatics. *J. Phys. Chem. A* **2002**, *106*, 2158–2163.
- (8) Arnaut, L. G.; Formosinho, S. J. Excited-state Proton Transfer Reactions I. Fundamentals and Intermolecular Reactions. *J. Photochem. Photobiol. A: Chem.* **1993**, *75*, 1–20.
- (9) Waluk, J. Hydrogen-Bonding-Induced Phenomena in Bifunctional Heterozaaromatics. *Acc. Chem. Res.* **2003**, *36*, 832–838.

- (10) Kwon, J. E.; Park, S. Y. Advanced Organic Optoelectronic Materials: Harnessing Excited-State Intramolecular Proton Transfer (ESIPT) Process. *Adv. Mater.* **2011**, *23*, 3615–3642.

- (11) Fang, C.; Frontiera, R. R.; Tran, R.; Mathies, R. A. Mapping GFP Structure Evolution During Proton Transfer with Femtosecond Raman Spectroscopy. *Nature* **2009**, *462*, 200–204.

- (12) (a) Kim, J. S.; Quang, D. T. Calixarene-Derived Fluorescent Probes. *Chem. Rev.* **2007**, *107*, 3780–3799.

- (13) *Chemosensors: Principles, Strategies, and Applications*; Wang, B., Anslyn, E. V., Eds.; Wiley: New York, 2011; pp 253–273.

- (14) Roshal, A. D.; Grigorovich, A. V.; Doroshenko, A. O.; Pivovarenko, V. G.; Demchenko, A. P. Flavonols and Crown-Flavonols as Metal Cation Chelators. The Different Nature of Ba²⁺ and Mg²⁺ Complexes. *J. Phys. Chem. A* **1998**, *102*, 5907–5914.

- (15) (d) Sveczkarev, D. A.; Karpushina, G. V.; Lukatskaya, L. L.; Doroshenko, A. O. 2-(Benzimidazol-2-yl)-3-hydroxychromone Derivatives: Spectroscopic Properties and a Possible Alternative Intramolecular Proton Phototransfer. *Cent. Eur. J. Chem.* **2008**, *6*, 443–449.

- (16) Mordziński, A.; Grabowska, A.; Kuhnle, W.; Krowczyński, A. Intramolecular Single and Double Proton Transfer in Benzoxazole Derivatives. *Chem. Phys. Lett.* **1983**, *101*, 291–296.

- (17) Frey, W.; Laermer, F.; Elsaesser, T. Femtosecond Studies of Excited-state Proton and Deuterium Transfer in Benzothiazole Compounds. *J. Phys. Chem.* **1991**, *95*, 10391–10395.

- (18) Das, K.; Sarkar, N.; Majumdar, D.; Bhattacharyya, K. Excited-state Intramolecular Proton Transfer and Rotamerism of 2-(2'-hydroxyphenyl) Benzimidazole. *Chem. Phys. Lett.* **1992**, *198*, 443–448.

- (19) Fores, M.; Duran, M.; Sola, M.; Adamowicz, L. Excited-State Intramolecular Proton Transfer and Rotamerism of 2-(2'-hydroxyvinyl)benzimidazole and 2-(2'-hydroxyphenyl)imidazole. *J. Phys. Chem. A* **1999**, *103*, 4413–4420.

- (20) Wang, H.; Zhang, H.; Abou-Zied, O. K.; Yu, C.; Romesberg, F. E.; Glasbeek, M. Femtosecond Fluorescence Upconversion Studies of Excited-state Proton-transfer Dynamics in 2-(2'-Hydroxyphenyl)-benzoxazole (HBO) in Liquid Solution and DNA. *Chem. Phys. Lett.* **2003**, *367*, 599–608.

- (21) Rini, M.; Dreyer, J.; Nibbering, E. T. J.; Elsaesser, T. Ultrafast Vibrational Relaxation Processes Induced by Intramolecular Excited State Hydrogen Transfer. *Chem. Phys. Lett.* **2003**, *374*, 13–19.

- (22) McMorro, D.; Kasha, M. Intramolecular Excited-state Proton Transfer in 3-Hydroxyflavone. Hydrogen-bonding Solvent Perturbations. *J. Phys. Chem.* **1984**, *88*, 2235–2243.

- (23) Strandjord, A. J. G.; Smith, D. E.; Barbara, P. F. Structural Effects on the Proton-Transfer Kinetics of 3-hydroxyflavones. *J. Phys. Chem.* **1985**, *89*, 2362–2366.

- (24) Chou, P.-T.; Chen, Y.-C.; Yu, W.-S.; Chen, Y.-M. Spectroscopy and Dynamics of Excited-state Intramolecular Proton-Transfer Reaction in 5-Hydroxyflavone. *Chem. Phys. Lett.* **2001**, *340*, 89–97.

- (25) Druzhinin, S. I.; Rodchenkov, G. M.; Uzhinov, B. M. Intermolecular Excited State Proton Transfer Reactions of Diaryloxazoles. *Chem. Phys.* **1988**, *128*, 383–394.

- (26) LeGourrierc, D.; Kharlanov, V. A.; Brown, R. G.; Rettig, W. Excited-State Intramolecular Proton Transfer (ESIPT) in 2-(2'-Hydroxyphenyl)-oxazole and thiazole. *J. Photochem. Photobiol. A: Chem.* **2000**, *130*, 101–111.

- (27) Chen, K.-Y.; Cheng, Y.-M.; Lai, C.-H.; Hsu, C.-C.; Ho, M.-L.; Lee, G.-H.; Chou, P.-T. Ortho Green Fluorescence Protein Synthetic Chromophore; Excited-State Intramolecular Proton Transfer via a Seven-Membered-Ring Hydrogen-Bonding System. *J. Am. Chem. Soc.* **2007**, *129*, 4534–4535.

- (28) Huang, G.; Zhang, G.; Wu, Y.; Liao, Q.; Fu, H.; Zhang, D. Modification of the Green Fluorescent Protein Chromophore with Large Aromatic Moieties: Photophysical Study and Solid-State Emission. *Asian J. Org. Chem.* **2012**, *1*, 352–358.

- (29) Kaczmarek, Ł.; Balicki, R.; Lipkowski, J.; Borowicz, P.; Grabowska, A. Structure and Photophysics of Deazabipyridyls. Excited Internally Hydrogen-bonded Systems with One Proton Transfer Reaction Site. *J. Chem. Soc., Perkin Trans.* **1994**, *2*, 1603–1610.

- (30) Inouchi, T.; Nakashima, T.; Kawai, T. The Origin of the Emission Properties of π -Conjugated Molecules that have an Acid-responsive Benzimidazole Unit. *Asian J. Org. Chem.* **2013**, *2*, 230–238.
- (31) Skonieczny, K.; Ciuciu, A. I.; Nichols, E.; Hugues, V.; Blanchard-Desce, M.; Flamigni, L.; Gryko, D. T. Bright, Emission Tunable Fluorescent Dyes Imidazole and π -Expanded Imidazole. *J. Mater. Chem.* **2012**, *22*, 20649–20664.
- (32) Park, S.; Kwon, J. E.; Kim, S. H.; Seo, J.; Chung, K.; Park, S.-Y.; Jang, D.-J.; Medina, B. M.; Gierschner, J.; Park, S. Y. A White-Light-Emitting Molecule: Frustrated Energy Transfer between Constituent Emitting Centers. *J. Am. Chem. Soc.* **2009**, *131*, 14043–14049.
- (33) Park, S.; Kwon, J. E.; Park, S. Y. Strategic Emission Color Tuning of Highly Fluorescent Imidazole-Based Excited-state Intramolecular Proton Transfer Molecules. *Phys. Chem. Chem. Phys.* **2012**, *14*, 8878–8884.
- (34) Kim, S.; Park, S. Y. Photochemically Gated Protonation Effected by Intramolecular Hydrogen Bonding: Towards Stable Fluorescence Imaging in Polymer Films. *Adv. Mater.* **2003**, *15*, 1341–1344.
- (35) Douhal, A.; Amat-Guerri, F.; Acuña, A. U. Photoinduced Intramolecular Proton Transfer and Charge Redistribution in Imidazopyridines. *J. Phys. Chem.* **1995**, *99*, 76–80.
- (36) Douhal, A.; Amat-Guerri, F.; Acuña, A. U. Probing Nanocavities with Proton-Transfer Fluorescence. *Angew. Chem., Int. Ed.* **1997**, *36*, 1514–1516.
- (37) Mutai, T.; Tomoda, H.; Ohkawa, T.; Yabe, Y.; Araki, K. Switching of Polymorph-Dependent ESIPT Luminescence of an Imidazo[1,2-*a*]pyridine Derivative. *Angew. Chem., Int. Ed.* **2008**, *47*, 9522–9524.
- (38) Shigemitsu, Y.; Mutai, T.; Houjou, H.; Araki, K. Excited-State Intramolecular Proton Transfer (ESIPT) Emission of Hydroxyphenylimidazopyridine: Computational Study on Enhanced and Polymorph-Dependent Luminescence in the Solid State. *J. Phys. Chem. A* **2012**, *116*, 12041–12048.
- (39) Stasyuk, A. J.; Banasiewicz, M.; Cyrański, M. K.; Gryko, D. T. Imidazo[1,2-*a*]pyridines Susceptible to Excited State Intramolecular Proton Transfer: One-Pot Synthesis via an Ortoleva–King Reaction. *J. Org. Chem.* **2012**, *77*, 5552–5558.
- (40) Mutai, T.; Sawatani, H.; Shida, T.; Shono, H.; Araki, K. Tuning of Excited-State Intramolecular Proton Transfer (ESIPT) Fluorescence of Imidazo[1,2-*a*]pyridine in Rigid Matrices by Substitution Effect. *J. Org. Chem.* **2013**, *78*, 2482–2489.
- (41) Firmansyah, D.; Ciuciu, A. I.; Hugues, V.; Blanchard-Desce, M.; Flamigni, L.; Gryko, D. T. Bright, Fluorescent Dyes Based on Imidazo[1,2-*a*]pyridines Capable of Two-photon Absorption. *Chem. Asian J.* **2013**, *8*, 1279–1294.
- (42) Stasyuk, A. J.; Banasiewicz, M.; Ventura, B.; Cyrański, M. K.; Gryko, D. T. Benzo[*a*]imidazo[5,1,2-*cd*]indolizines – New Class of Molecules Displaying Excited State Intramolecular Proton Transfer. *New J. Chem.* **2013**, *38*, 189–197.
- (43) Jung, H. S.; Kim, H. J.; Vicens, J.; Kim, J. S. A New Fluorescent Chemosensor for F–based on Inhibition of Excited State Intramolecular Proton Transfer. *Tetrahedron Lett.* **2009**, *50*, 983–987.
- (44) Van Benthem, M. H.; Gillispie, G. D. Intramolecular Hydrogen Bonding. 4. Dual Fluorescence and Excited-State Proton Transfer in 1,5-Dihydroxyanthraquinone. *J. Phys. Chem.* **1984**, *88*, 2954–2960.
- (45) Smith, T. P.; Zaklika, K. A.; Thakur, K.; Barbara, P. F. Excited State Intramolecular Proton Transfer in 1-(Acylamino)-anthraquinones. *J. Am. Chem. Soc.* **1991**, *113*, 4035–4036.
- (46) Schmidtke, S. J.; Underwood, D. F.; Blank, D. A. Following the Solvent Directly during Ultrafast Excited State Proton Transfer. *J. Am. Chem. Soc.* **2004**, *126*, 8620–8621.
- (47) Chou, P.; McMorrow, D.; Aartsma, T. J.; Kasha, M. The Proton-transfer Laser. Gain Spectrum and Amplification of Spontaneous Emission of 3-Hydroxyflavone. *J. Phys. Chem.* **1984**, *88*, 4596–4599.
- (48) Acuna, A. U.; Amat, F.; Catalán, J.; Costela, A.; Figuera, J.; Munoz, J. M. Pulsed Liquid Lasers from Proton Transfer in the Excited State. *Chem. Phys. Lett.* **1986**, *132*, 576–569.
- (49) Sakai, K. I.; Tsuzuki, T.; Itoh, Y.; Ichikawa, M.; Taniguchi, Y. Using Proton-transfer Laser Dyes for Organic Laser Diodes. *Appl. Phys. Lett.* **2005**, *86*, 081103–081105.
- (50) Kim, S.; Park, S. Y. Photochemically Gated Protonation Effected by Intramolecular Hydrogen Bonding: Towards Stable Fluorescence Imaging in Polymer Films. *Adv. Mater.* **2003**, *15*, 1341–1344.
- (51) Kim, S.; Park, S. Y.; Tashida, I.; Kawai, H.; Nagamura, T. Amplified Spontaneous Emission from the Film of Poly(aryl ether) Dendrimer Encapsulating Excited-State Intramolecular Proton Transfer Dye. *J. Phys. Chem. B* **2002**, *106*, 9291–9294.
- (52) Catalán, J.; del Valle, J. C.; Claramunt, R. M.; Sanz, D.; Dotor, J. Photophysics of the 2-(2'-Hydroxyphenyl)perimidine: On the Fluorescence of the Enol Form. *J. Lumin.* **1996**, *68*, 165–170.
- (53) Parsapour, F.; Kelley, D. F. Torsional and Proton Transfer Dynamics in Substituted 3-Hydroxyflavones. *J. Phys. Chem.* **1996**, *100*, 2791–2798.
- (54) Sytnik, A.; Kasha, M. Excited-State Intramolecular Proton Transfer as a Fluorescence Probe for Protein Binding-site Static Polarity. *Proc. Natl. Acad. Sci. U. S. A.* **1994**, *91*, 8627–8630.
- (55) Kim, S.; Seo, J.; Jung, H. K.; Kim, J. J.; Park, S. Y. White Luminescence from Polymer Thin Films Containing Excited-State Intramolecular Proton-Transfer Dyes. *Adv. Mater.* **2005**, *17*, 2077–2082.
- (56) Park, S.; Kwon, J. E.; Kim, S. H.; Seo, J.; Chung, K.; Park, S.-Y.; Jang, D.-J.; Medina, B. M.; Gierschner, J.; Park, S.-Y. A White-Light-Emitting Molecule: Frustrated Energy Transfer between Constituent Emitting Centers. *J. Am. Chem. Soc.* **2009**, *131*, 14043–14049.
- (57) Martinez, M. L.; Cooper, W. C.; Chou, P.-T. A Novel Excited-state Intramolecular Proton Transfer Molecule, 10-Hydroxybenzo[*h*]quinoline. *Chem. Phys. Lett.* **1992**, *193*, 151–154.
- (58) Chou, P.-T.; Chen, Y.-C.; Yu, W.-S.; Chou, Y.-H.; Wei, C.-Y.; Cheng, Y.-M. Excited-State Intramolecular Proton Transfer in 10-Hydroxybenzo[*h*]quinoline. *J. Phys. Chem. A* **2001**, *105*, 1731–1740.
- (59) Chou, P.-T.; Wei, C. Y. Photophysics of 10-Hydroxybenzo[*h*]quinoline in Aqueous Solution. *J. Phys. Chem.* **1996**, *100*, 17059–17066.
- (60) Takeuchi, S.; Tahara, T. Coherent Nuclear Wavepacket Motions in Ultrafast Excited-State Intramolecular Proton Transfer: Sub-30-fs Resolved Pump–Probe Absorption Spectroscopy of 10-Hydroxybenzo[*h*]quinoline in Solution. *J. Phys. Chem. A* **2005**, *109*, 10199–10207.
- (61) Paul, B. K.; Guchhait, N. TD–DFT Investigation of the Potential Energy Surface for Excited-State Intramolecular Proton Transfer (ESIPT) Reaction of 10-hydroxybenzo[*h*]quinoline: Topological (AIM) and Population (NBO) Analysis of the Intramolecular Hydrogen Bonding Interaction. *J. Lumin.* **2011**, *131*, 1918–1926.
- (62) Higashi, M.; Saito, S. Direct Simulation of Excited-State Intramolecular Proton Transfer and Vibrational Coherence of 10-Hydroxybenzo[*h*]quinoline in Solution. *J. Phys. Chem. Lett.* **2011**, *2*, 2366–2371.
- (63) Chen, K.-Y.; Hsieh, C.-C.; Cheng, Y.-M.; Lai, C.-H.; Chou, P.-T. Extensive Spectral Tuning of the Proton Transfer Emission from 550 to 675 nm via a Rational Derivatization of 10-Hydroxybenzo[*h*]quinoline. *Chem. Commun* **2006**, 4395–4397.
- (64) Matsumiya, H.; Hoshino, H. Selective Determination of Beryllium(II) Ion at Picomole per Decimeter Cubed Levels by Kinetic Differentiation Mode Reversed-Phase High-Performance Liquid Chromatography with Fluorometric Detection Using 2-(2'-Hydroxyphenyl)-10-hydroxybenzo[*h*]quinoline as Precolumn Chelating Reagent. *Anal. Chem.* **2003**, *75*, 413–419.
- (65) Gryko, D. T.; Piechowska, J.; Gałczowski, M. Strongly Emitting Fluorophores Based on 1-Azaperylene Scaffold. *J. Org. Chem.* **2010**, *75*, 1297–1300.
- (66) Piechowska, J.; Gryko, D. T. Preparation of a Family of 10-Hydroxybenzo[*h*]quinoline Analogues via a Modified Sanford Reaction and Their Excited State Intramolecular Proton Transfer Properties. *J. Org. Chem.* **2011**, *76*, 10220–10228.
- (67) Piechowska, J.; Huttunen, K.; Wróbel, Z.; Lemmetyinen, H.; Tkachenko, N. V.; Gryko, D. T. Excited State Intramolecular Proton

Transfer in Electron-Rich and Electron-Poor Derivatives of 10-Hydroxybenzo[h]quinoline. *J. Phys. Chem. A* **2012**, *116*, 12049–12055.

(68) Deperasińska, I.; Gryko, D. T.; Karpiuk, E.; Kozankiewicz, B.; Makarewicz, A.; Piechowska, J. 12-Hydroxy-1-azaperylene—Limiting Case of the ESIPT System: Enol–Keto Tautomerization in S_0 and S_1 States. *J. Phys. Chem. A* **2012**, *116*, 2109–2116.

(69) Foster, E. J.; Babuin, J.; Nguyen, N.; Williams, V. E. Synthesis of Unsymmetrical Dibenzoquinoline Discotic Mesogens. *Chem. Commun.* **2004**, 2052–2053.

(70) Foster, E. J.; Lavigneur, C.; Ke, Y.-C.; Williams, V. E. Self-assembly of Hydrogen-bonded Molecules: Discotic and Elliptical Mesogens. *J. Mater. Chem.* **2005**, *15*, 4062–4068.

(71) Foster, E. J.; Jones, R. B.; Lavigneur, C.; Williams, V. E. Structural Factors Controlling the Self-Assembly of Columnar Liquid Crystals. *J. Am. Chem. Soc.* **2006**, *128*, 8569–8574.

(72) Lavigneur, C.; Foster, E. J.; Williams, V. E. Modular Assembly of Elliptical Mesogens. *Liq. Cryst.* **2007**, *34*, 833–840.

(73) Lavigneur, C.; Foster, E. J.; Williams, V. E. Self-Assembly of Discotic Mesogens in Solution and in Liquid Crystalline Phases: Effects of Substituent Position and Hydrogen Bonding. *J. Am. Chem. Soc.* **2008**, *130*, 11791–11800.

(74) Voisin, E.; Foster, E. J.; Rakotomalala, M.; Williams, V. E. Effects of Symmetry on the Stability of Columnar Liquid Crystals. *Chem. Mater.* **2009**, *21*, 3251–3261.

(75) Lee, E.; Huang, Z.; Ryu, J.-H.; Lee, M. Rigid–Flexible Block Molecules Based on a Laterally Extended Aromatic Segment: Hierarchical Assembly into Single Fibers, Flat Ribbons, and Twisted Ribbons. *Chem.—Eur. J.* **2008**, *14*, 6957–6966.

(76) Hong, D.-J.; Jeong, H.; Lee, E.; Lee, J.-K.; Zin, W.-C.; Nguyen, T. D.; Glotzer, S. C.; Lee, M. Solid-State Scrolls from Hierarchical Self-Assembly of T-Shaped Rod–Coil Molecules. *Angew. Chem., Int. Ed.* **2009**, *48*, 1664–1668.

(77) Estrada, L. A.; Neckers, D. C. Synthesis and Photophysics of Dibenz[*a,c*]phenazine Derivatives. *Org. Lett.* **2011**, *13*, 3304–3307.

(78) Zhu, Y.; Gibbons, K. M.; Kulkarni, A. P.; Jenekhe, S. A. Polyfluorenes Containing Dibenz[*a,c*]phenazine Segments: Synthesis and Efficient Blue Electroluminescence from Intramolecular Charge Transfer States. *Macromolecules* **2007**, *40*, 804–813.

(79) Gautrot, J. E.; Hodge, P. Poly(dibenzo[*a,c*]phenazine-2,7-diyl)s – Synthesis and Characterisation of a New Family of Electron-Accepting Conjugated Polymers. *Polymer* **2007**, *48*, 7065–7077.

(80) Dubey, R. K.; Kumpulainen, T.; Efimov, A.; Tkachenko, N. V.; Lemmetyinen, H. Close Proximity Dibenz[*a,c*]phenazine–Fullerene Dyad: Synthesis and Photoinduced Singlet Energy Transfer. *Eur. J. Org. Chem.* **2010**, 3428–3436.

(81) Carlier, L.; Baron, M.; Chamayou, A.; Couarraze, G. Use of Co-Grinding as a Solvent-free Solid State Method to Synthesize Dibenzophenazines. *Tetrahedron Lett.* **2011**, *52*, 4686–4689.

(82) Carlier, L.; Baron, M.; Chamayou, A.; Couarraze, G. Greener Pharmacy Using Solvent-Free Synthesis: Investigation of the Mechanism in the Case of Dibenzophenazine. *Powder Technol.* **2013**, *240*, 41–47.

(83) Dick, A. R.; Hull, K. L.; Sanford, M. S. A Highly Selective Catalytic Method for the Oxidative Functionalization of C–H Bonds. *J. Am. Chem. Soc.* **2004**, *126*, 2300–2301.

(84) Desai, L. V.; Stowers, K. J.; Sanford, M. S. Insights into Directing Group Ability in Palladium-Catalyzed C–H Bond Functionalization. *J. Am. Chem. Soc.* **2008**, *130*, 13285–13293.

(85) Stowers, K. J.; Sanford, M. S. Mechanistic Comparison between Pd-Catalyzed Ligand-Directed C–H Chlorination and C–H Acetoxylation. *Org. Lett.* **2009**, *11*, 4584–4587.

(86) Dick, A. R.; Kampf, J. W.; Sanford, M. S. Unusually Stable Palladium(IV) Complexes: Detailed Mechanistic Investigation of C–O Bond-Forming Reductive Elimination. *J. Am. Chem. Soc.* **2005**, *127*, 12790–12791.

(87) Fu, Y.; Li, Z.; Liang, S.; Guo, Q.-X.; Liu, L. Mechanism for Carbon–Oxygen Bond-Forming Reductive Elimination from Palladium(IV) Complexes. *Organometallics* **2008**, *27*, 3736–3741.

(88) Racowski, J. M.; Dick, A. R.; Sanford, M. S. Detailed Study of C–O and C–C Bond-Forming Reductive Elimination from Stable $C_2N_2O_2$ -Ligated Palladium(IV) Complexes. *J. Am. Chem. Soc.* **2009**, *131*, 10974–10983.

(89) Lyons, T. W.; Sanford, M. S. Palladium-Catalyzed Ligand-Directed C–H Functionalization Reactions. *Chem. Rev.* **2010**, *110*, 1147–1169.

(90) Powers, D. C.; Ritter, T. Bimetallic Pd(III) complexes in palladium-catalyzed carbon–heteroatom bond formation. *Nat. Chem.* **2009**, *1*, 302–309.

(91) Bian, Y.-J.; Xiang, C.-B.; Chen, Z.-M.; Huang, Z.-Z. Copper-Catalyzed Domino Oxidation-Acyloxylation Reaction of 2-Arylpyridines with Aldehydes or Methylarenes. *Synlett* **2011**, 2407–2409.

(92) Pedersen, D. S.; Rosenbohm, C. Dry Column Vacuum Chromatography. *Synthesis* **2001**, 2431–2434.

(93) Amashukeli, X.; Winkler, J. R.; Gray, H. B.; Gruhn, N. E.; Lichtenberger, D. L. Electron-Transfer Reorganization Energies of Isolated Organic Molecules. *J. Phys. Chem. A* **2002**, *106*, 7593–7598.

(94) Niemi, M.; Tkachenko, N. V.; Efimov, A.; Lehtivuori, H.; Ohkubo, K.; Fukuzumi, S.; Lemmetyinen, H. Exciplex Mediated Photoinduced Electron Transfer Reactions of Phthalocyanine–Fullerene Dyads. *J. Phys. Chem. A* **2008**, *112*, 6884–6892.

(95) Itoho, K.; Kosugi, Y. On the products of Ullmann–Ankersmit reaction and Horner–Dehnert reaction. *Daiichi Yakka Daigaku Kenkyu Nenpo* **1993**, *24*, 19–21.

(96) Dobrinevskii, S. F.; Karypov, A. V.; Maier, G. V.; Tikhomirov, S. A.; Tolstorozhev, G. B. Mechanism of Formation of Nonsteady-State Absorption Spectra from Excited States of Phenazines on the Picosecond Time Scale. *J. Appl. Spectrosc.* **1991**, *55*, 89–94.

(97) Domcke, W.; Sobolewski, A. L.; Woywod, C. Internal Conversion Funnel in Benzene and Pyrazine: Adiabatic and Diabatic Representation. *Chem. Phys. Lett.* **1993**, *203*, 220–226.

(98) Kim, S.; Seo, J.; Park, S. Y. Torsion-Induced Fluorescence Quenching in Excited-state Intramolecular Proton Transfer (ESIPT) Dyes. *J. Photochem. Photobiol. A: Chem* **2007**, *191*, 19–24.

(99) Idelson, E. M. U.S. Patent 3,920,667, 1975; *Chem. Abstr.* **1976**, *84*, 84.

(100) Wolfbeis, O. S. Probes, Sensors, and Labels: Why is Real Progress so Slow? *Angew. Chem., Int. Ed.* **2013**, *52*, 9864–9865.

(101) Xu, Y.; Pang, Y. Zinc Binding-induced Near-IR Emission from Excited-state Intramolecular Proton Transfer of a Bis(benzoxazole) Derivative. *Chem. Commun.* **2010**, *46*, 4070–4072.

(102) Kumar, M.; Kumar, N.; Bhalla, V. Highly Selective Fluorescent Probe for Detection and Visualization of Palladium Ions in Aqueous Media. *RSC Adv.* **2013**, *3*, 1097–1102.

(103) Seo, J.; Kim, S.; Park, S. Y. Strong Solvatochromic Fluorescence from the Intramolecular Charge-Transfer State Created by Excited-State Intramolecular Proton Transfer. *J. Am. Chem. Soc.* **2004**, *126*, 11154–11155.

(104) Yang, P.; Zhao, J.; Wu, W.; Yu, X.; Liu, Y. Accessing the Long-Lived Triplet Excited States in Bodipy-Conjugated 2-(2-Hydroxyphenyl) Benzothiazole/Benzoxazoles and Applications as Organic Triplet Photosensitizers for Photooxidations. *J. Org. Chem.* **2012**, *77*, 6166–6178.

(105) Zhao, J.; Ji, S.; Chen, Y.; Guo, H.; Yang, P. Excited State Intramolecular Proton Transfer (ESIPT): from Principal Photophysics to the Development of New Chromophores and Applications in Fluorescent Molecular Probes and Luminescent Materials. *Phys. Chem. Chem. Phys.* **2012**, *14*, 8803–8817.

(106) Ma, J.; Zhao, J.; Yang, P.; Huang, D.; Zhang, C.; Li, Q. New Excited State Intramolecular Proton Transfer (ESIPT) Dyes Based on Naphthalimide and Observation of Long-lived Triplet Excited States. *Chem. Commun.* **2012**, *48*, 9720–9722.

(107) Zhou, J.; Liu, H.; Jin, B.; Liu, X.; Fu, H.; Shangguan, D.; Guanidine, A. Derivative of Naphthalimide with Excited-state Deprotonation Coupled Intramolecular Charge Transfer Properties and Its Application. *J. Mater. Chem. C* **2013**, *1*, 4427–4436.

(108) Nagaoka, S.-i.; Nagashima, U.; Ohta, N.; Fujita, M.; Takemura, T. Electronic-state Dependence of Intramolecular Proton Transfer of o-Hydroxybenzaldehyde. *J. Phys. Chem.* **1988**, *92*, 166–171.

(109) Nagaoka, S.-i.; Teramae, H.; Nagashima, U. Computational Study of Excited-State Intramolecular-Proton-Transfer of o-Hydroxybenzaldehyde and Its Derivatives. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 570–573.