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A new class of N–H proton transfer molecules: wide tautomer emission tuning from 590 nm to 770 nm *via* a facile, single site amino derivatization in 10-aminobenzo[*h*]quinoline†

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Facile derivation of 10-aminobenzo[*h*]quinoline *via* replacing one of the N–H hydrogen atoms by various substituents generates a new series of excited-state intramolecular N–H proton-transfer molecules, for which the proton-transfer emission can be widely tuned from 590 nm to 770 nm simply by harnessing the electron-donating/withdrawing strength of the substituents.

The excited-state intramolecular proton transfer (ESIPT) reaction commonly incorporates transfer of a hydroxyl proton to the carbonyl oxygen (or pyridyl nitrogen) through a pre-existing hydrogen bonding configuration in the excited state.[1–3] The resulting proton-transfer tautomer reveals drastically different electron density distribution from its corresponding normal species. As a result, most of the ESIPT molecules show the $S_0 \rightarrow S_1$ transition band around near UV, while upon excitation, the occurrence of ESIPT gives rise to visible emissions with a large Stokes shift (peak-to-peak difference between absorption and emission) of >8000 cm^{-1}. Unlike the excited-state charge transfer or structural relaxation, in which the resulting large Stokes shifted emission is greatly perturbed by the environment such as polarity, viscosity/rigidity, *etc.*, the proton-transfer tautomer emission is virtually perturbation free except for external hydrogen bonding interferences.[3] In other words, the spectral profile of the tautomer emission in terms of peak wavelength and intensity is relatively insensitive to the external perturbation and is thus beneficial to a number of cutting-edge applications. One perspective is to apply an UV LED to excite a combination of ESIPT systems containing RGB colours without mutual interference such as reabsorption, energy transfer and electron transfer.[4–7] This may lead to white light generation in a more straightforward manner, and accordingly makes the wide tunability of the proton transfer emission highly desirable.

Recently, we have reported a series of amino-(NH–) type hydrogen bonding (H-bonding) compounds comprising 2-(2′-aminophenyl)-benzothiazole and its derivatives.[8] Upon derivation of the amino- or phenyl-moieties, we were able to tune both the normal and tautomer emissions throughout the visible range. This series of molecules have close-lying normal and tautomer excited states. In addition, the relatively weak intramolecular H-bond requires geometry adjustments prior to ESIPT, inducing a barrier. Therefore the ratiometric fluorescence for the normal *versus* tautomer emission is sensitive to the environmental perturbation. This, together with the rather weak emission due to the *cis–trans* isomerization, makes this class of 2-(2′-aminophenyl)benzothiazoles less potential in colour applications.

Bearing the above viewpoint in mind, we have thus screened through the –OH type of ESIPT molecules and strategically selected 10-hydroxybenzo[*h*]quinoline (HBQ) as a prototype.[9–11] Owing to the intrinsic six-membered ring hydrogen bond, HBQ serves as perhaps the most prominent ESIPT system that undergoes an ultrafast proton transfer free from the solvent perturbation.[12,13] Its great photostability and rigid fused rings lead to further derivations meaningful. Replacing the –OH by the –NHR group at the C(10) position of benzo[*h*]quinoline (see Scheme 1) we herein report on a new class of N–H proton transfer molecules, for which the tautomer emission can be widely tuned from 590 nm to 770 nm simply by a single site amino derivatization.

All the titled compounds are synthesized and characterized using ^{1}H/^{13}C NMR, IR and mass spectroscopies (see the ESI† for detailed synthesis and characterization). The parent compound **III** (10-aminobenzo[*h*]quinoline) was prepared with a high yield from 10-nitrobenzo[*h*]quinoline under iron/ammonium chloride reduction. As depicted in Scheme 1, starting from **III**, on the one hand, we were able to replace either one or two of the $-NH_2$ protons by electron-donating groups to give compounds **I**, **II**, **IX**

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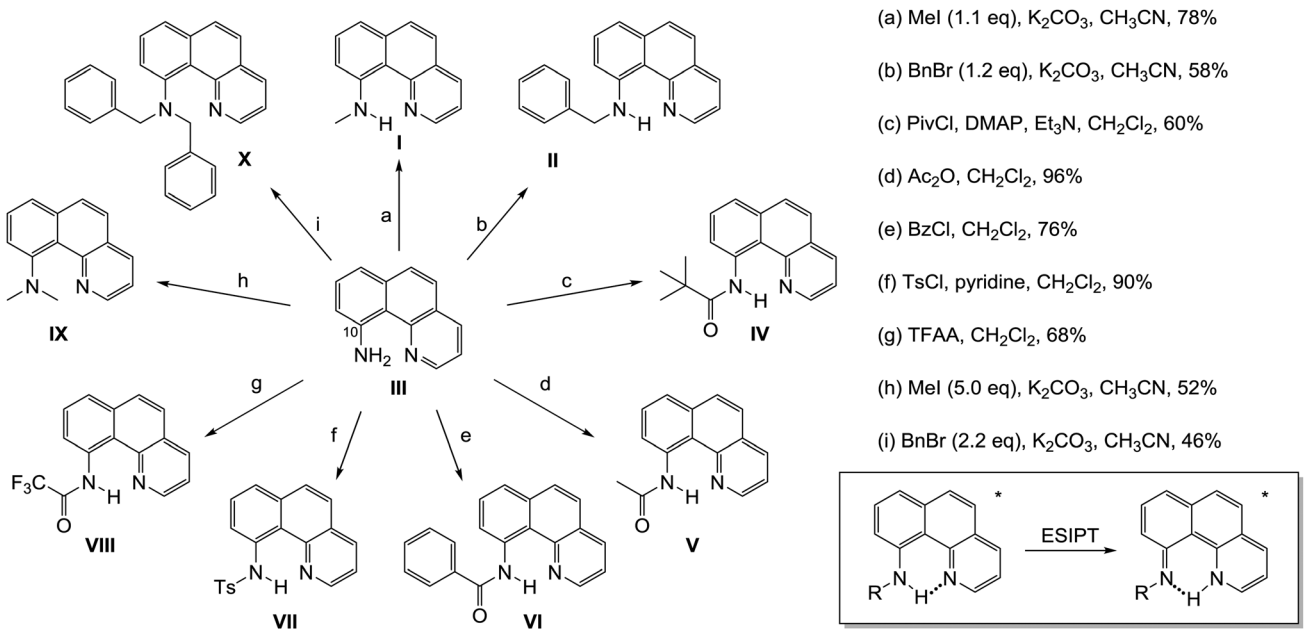


Scheme 1 The molecular structures and the syntheses of the titled compounds. Inset: The ESIPT process in the titled molecules.

and **X**. On the other hand, substitution of one of the $-NH_2$ protons by various electron-withdrawing groups forms compounds **IV–VIII**. The X-ray crystal structure of a representative compound **VI** is provided in Fig. S1 and the pertinent data are listed in Tables S1 and S2 (ESI†).

We first introduced electron-donating groups such as a benzyl or a methyl group to replace the amino hydrogen in **III**. Upon adding 1.1–1.2 equivalents of iodomethane or benzyl bromide with respect to **III** into the reaction, we were able to obtain the mono *N*-substituted compounds **I** & **II** with good yields (78% & 58%), accompanied by the isolation of a small amount (<5%) of the doubly *N*-substituted compounds. When the quantity of iodomethane or benzyl bromide was increased to exceed two folds with respect to **III**, the doubly *N*-substituted compounds could be readily synthesized.

To increase the acidity of the N(R)–H proton, various electron-withdrawing groups, R, with different strength (pivaloyl, acetyl, benzoyl, tosyl and trifluoroacetyl) could also be introduced onto the amino nitrogen. Prototype **III** was easily transformed into a series of amide compounds **IV**, **V**, **VI** and **VIII** through acyl substitution reactions by reacting with pivaloyl chloride, acetic anhydride, benzoyl chloride and trifluoroacetic anhydride, respectively. The sulfonamide compound **VII** was prepared by reacting **III** with toluenesulfonyl chloride. In these reactions we could obtain only the mono *N*-substituted compounds. The introduction of the first electron-withdrawing substituent onto the amino group may lower the nucleophilicity of N (of the resulting amide) and consequently prevents the second substitution.

From conventional wisdom, we do not anticipate the parent molecule, compound **III**, with only a primary amino group to be the potential ESIPT system. This viewpoint is based on the fact that the protons in $-NH_2$ have much weaker acidity than that in –OH. Therefore, unless one of the $-NH_2$ protons is replaced by an electron withdrawing group to increase the N–H acidity, ESIPT is generally considered to be prohibited. In fact, to our knowledge, none of the primary amino ($-NH_2$) hydrogen bonding systems has ever been reported so far to proceed with ESIPT.[8,14] To our surprise, however, compound **III** exhibits a remarkable proton transfer phenomenon in the excited state. As shown in Fig. 1 and Table 1, compound **III** in cyclohexane shows the lowest lying absorption band maximum at around 400 nm. Upon excitation, an exceedingly long wavelength emission maximized at 740 nm is resolved. The Stokes shift was calculated to be as large as 11 500 cm^{-1}. The corresponding excitation spectrum is identical to the absorption spectrum (see Fig. S2, ESI†), eliminating any artefact caused by a trace of impurity. The result thus unambiguously concludes the occurrence of ESIPT for compound **III**, which demonstrates for the first time that the primary amino ($-NH_2$) H-bonded system is able to execute ESIPT. The acidity of the amino proton was generally considered to be too weak to provide the driving force for ESIPT. The ability of ESIPT for **III** may plausibly be relevant to the strong six-membered ring hydrogen bonding formation that is constrained in a fused, rigid benzo[*h*]quinoline moiety (see Scheme 1). The resulting shorter hydrogen bonding distance thus acts as the driving force for efficient ESIPT (*vide infra*).

One great advantage of the $-NH_2$ H-bonded system over that of the –OH class lies in the fact that one of the $-NH_2$ protons can be chemically modified by an R group to systematically tuning the N(R)–H proton acidity. We then demonstrate that the tautomer emission can be widely tuned by simply altering the electronic properties of the R group, which are otherwise inaccessible in –OH ESIPT systems that have been ubiquitously adopted in both fundamental and application approaches.

Firstly we began with the substitution of the N–H proton by an electron donating methyl or benzyl group (relative to H),

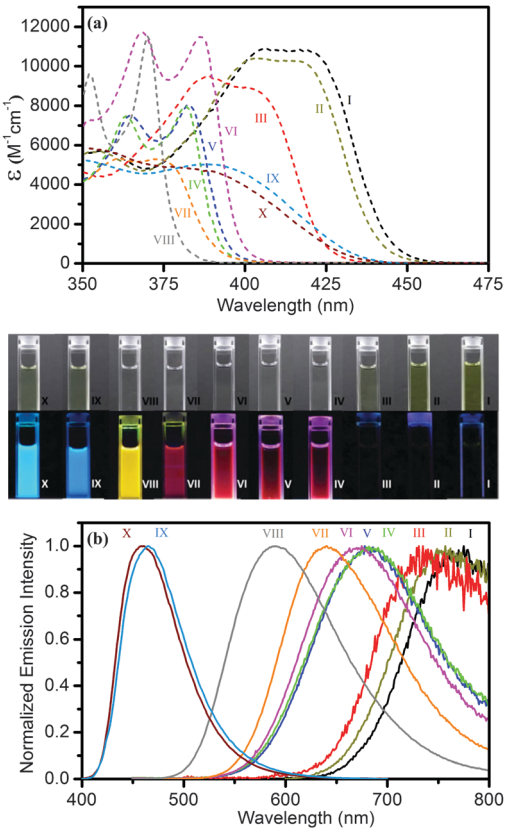


Fig. 1 (a) Absorption and (b) normalized emission spectra of the titled compounds in cyclohexane at room temperature. The concentrations are 8.8×10^{-6}–2.2×10^{-5} M for the emission spectra measurements. Photos in the middle: the photos of the titled compounds in cyclohexane under room light and the emission hue under 365 nm UV irradiation.

forming compounds **I** and **II**. In an opposite synthetic strategy, we then substitute one of the $-NH_2$ hydrogen atoms by electron-withdrawing groups, yielding compounds **IV–VIII**. In this approach we intentionally enhance the acidity of the N–H proton by increasing the electron withdrawing ability of the R group. As a result, the downfield shift of the N–H proton (in $CDCl_3$) for **I–VIII** is in the order of **I** ($\delta \sim 10.72$ ppm) < **II** ($\delta \sim 11.55$ ppm) < **IV** ($\delta \sim 14.91$ ppm) ~ **V** ($\delta \sim 14.83$ ppm) < **VI** ($\delta \sim 15.67$ ppm) ~ **VII** ($\delta \sim 15.28$ ppm) < **VIII** ($\delta \sim 16.68$ ppm). Note that we only compare the mono-substituted compounds and exclude compound **III** ($-NH_2$) for its distinct chemical environment. For the same class of H-bonded molecules, the intramolecular H-bonding strength can empirically correlate with the corresponding proton shift, with larger downfield shift leading to stronger H-bonds. Since **I–VIII** possess the same proton acceptor, *i.e.*, the benzo[*h*]-quinoline nitrogen, the stronger H-bond thus infers the increase of the proton donating strength, *i.e.*, the increase of the N(R)–H acidity from **I** to **VIII**.

Experimentally, as shown in Fig. 1b, ESIPT takes place for all titled 10-aminobenzo[*h*]quinoline derivatives. This is evidenced by the appearance of a unique, large Stokes shifted (>8000 cm^{-1}) tautomer emission for **I–VIII**. Again, to our surprise, despite the N–H acidity of **I** and **II** being weaker than that of **III**, a pronounced tautomer emission maximized at 770 nm (**I**) and 750 nm (**II**) was observed. Also, none of the normal emission, which is expected to be in the range of <500 nm, could be resolved, concluding the occurrence of the fast and highly exergonic type of ESIPT for **I–VIII** (*vide infra*).

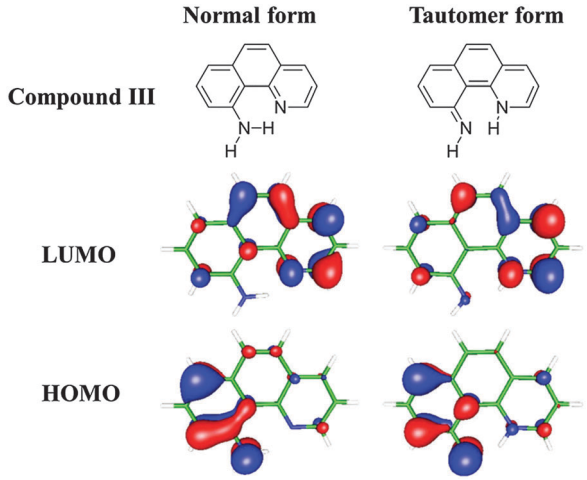
Moreover, remarkably, the tautomer emission peak is strongly dependent on the electronic properties of the N–R group, being blue shifted as R increases the electron withdrawing ability (*i.e.*, the greater acidity and hence the H-bond strength). Theoretically, this can be rationalized by the ESIPT reaction product, *i.e.*, a proton transfer tautomer for which the lowest lying excited state inherits a HOMO → LUMO charge transfer character from the imino (HOMO) to the quinoline (LUMO) moiety (see Scheme 2). Thus, adding an electron withdrawing substituent R at the amino site results in the lowering of HOMO energy, hence the increase of the energy gap of the imino-tautomer emission. As a result, depending on the electron withdrawing/donating strength a wide and tuneable range of the proton-transfer tautomer emission is achieved from 590 nm (in **VIII**) to 770 nm (in **I**) (see Fig. 1b) *via* a facile, single amino derivatization in 10-aminobenzo[*h*]quinoline. To show the clear contrast, the emission of double *N*-substitution of **I** and **II**, forming **IX** and **X**, respectively (see Scheme 1), is also depicted in Fig. 1b. Due to the lack of the N–H proton, **IX** and **X** exhibit normal emission maximized at 467 and 458 nm, respectively.

The tautomer emission yield reveals a decreasing trend upon lowering the emission gap. We then compared their emission intensity by assessing the quantum yield (Φ_{em}) of the tautomer emission. This approach becomes possible by

Table 1 Photophysical data for the titled compounds

#	λ_{abs}/nm (ε/M^{-1} cm^{-1})	λ_{em}/nm	Φ_{em}	τ_{obs}	k_{nr} ($\times 10^{10}$ s^{-1})	ΔE^* (kcal mol^{-1})
I	419 (10 907)	770	5.09×10^{-5}	[a]		−2.07
II	415 (10 444)	750	9.74×10^{-4}	[a]		−3.47
III	401 (8920)	740	1.19×10^{-3}	17.1 ps	5.84	−3.31
IV	383 (8020)	684	2.92×10^{-3}	61.4 ps	1.63	−5.43
V	382 (7980)	682	3.46×10^{-3}	59.5 ps	1.67	−5.84
VI	385 (11 100)	670	6.61×10^{-3}	95.7 ps	1.03	−7.15
VII	372 (5720)	640	1.98×10^{-2}	247 ps	0.39	[b]
VIII	370 (11 700)	590	0.11	1.08 ns	0.08	[b]
IX	390 (5016)	467	0.07	1.28 ns		
X	386 (4760)	458	0.07	1.33 ns		

[a] Emission too weak to be monitored using a fluorescence upconversion technique. [b] The energy difference between excited normal and tautomer states, ΔE^*, could not be calculated due to the failure of locating energy minimum of the excited normal state (see the text for details).



Scheme 2 The calculated HOMO and LUMO of normal and tautomer forms of **III**.

assuming that the reaction thermodynamics is highly exergonic and the efficiency of ESIPT is unity. The latter is implied by the lack of resolving any normal emission in a steady-state manner. The former is supported by the computational approach (see the ESI† for a detailed methodology). The resulting ΔE^* (computed energy differences between the normal and tautomer form species in the lowest excited state) shown in Table 1 (and details in Table S3, ESI†) indicates that thermodynamics of ESIPT for compounds **I–VI** are exergonic by at least 2 kcal mol^{-1}. It is worthy of note that ΔE^* cannot be obtained for **VII** and **VIII** because the minimum energy of the excited-state normal form was unable to be located, implying more exergonic ESIPT thermodynamics.

The nearly unitary ESIPT efficiency implies a fast rate of ESIPT, which can be probed by early reaction dynamics *via* a femtosecond fluorescence upconversion technique. Using **III**, **VII** and **VIII** as the prototypes, we applied 370 nm femtosecond pulse (~150 fs) excitation and then monitoring at 680, 640 and 600 nm tautomer emission. The results clearly showed the system response limited (~150 fs) rise time of the tautomer emission (see Fig. S3, ESI†), supporting the ultrafast rate of ESIPT. Furthermore, the tautomer population decay for **III–VIII** was resolved and pertinent data (τ_{obs}) are listed in Table 1. With QY and population decay rate k_{obs} provided (Table 1), the radiative decay rate constant k_r and nonradiative decay rate constant k_{nr} can thus be deduced from the relationship $k_r = k_{obs} \times \Phi_{em}$ and $k_{nr} = k_{obs} - k_r$, respectively. The k_{nr} value listed in Table 1 clearly shows a decreasing trend, which is in the order **III** > **IV** ~ **V** > **VI** > **VII** > **VIII**. For the deactivation process between two states (generally S_1 and S_0 states) with low energy gap and in the absence of a zero-order surface crossing, an empirical energy gap law[15] specifies that the rate constant for the radiationless deactivation k_{nr} (generally denotes the internal conversion process) can be assessed by $k_{nr} \sim \nu e^{-\alpha \Delta E}$ where α is a proportionality constant and ΔE denotes the emission energy gap, respectively. As ΔE decreases k_{nr} increases in an exponential manner, which also correlates well with the decrease of the tautomer emission yield (Φ_{em}) from 0.11 in **VIII** (590 nm) to 5.09×10^{-5} in **I** (770 nm). For the new ESIPT systems **I–VIII**, the great shift of the tautomer emission to the near IR region thus clearly witnesses the energy gap law.

10-Aminobenzo[*h*]quinoline (compound **III**) forms a geometry favorable, strong six-membered ring $NH_2 \cdots N$ intramolecular hydrogen bond, from which we report for the first time the occurrence of ESIPT in the primary amino-($-NH_2$) H-bonded system. Otherwise, the N–H H-bonded systems require secondary NRH derivation, in which R has to be the electron withdrawing group, to boost ESIPT. We are thus able to replace one of the amino protons in **III** by various R groups spanning from electron donating to withdrawing group, forming **I–VIII**. Compounds **I–VII** all exhibit $S_0 \rightarrow S_1$ absorption at around 400 nm, while ESIPT apparently takes place, resulting in a large Stokes-shifted tautomer emission, for which the peak wavelength can be widely tuned from 590 nm to 770 nm. The results also unveil a correlation that the stronger the electron withdrawing R group is, the bluer the shift of the emission. This has been rationalized by the decrease of HOMO energy of the tautomer due to the electron withdrawing properties of the –NR group, enlarging the energy gap. The intensity of the emission also correlates with the peak wavelength, with reduction of the emission quantum yield upon increasing the emission to the near infrared, which is well explained by the operation of the energy gap law. In summary, a new class of N–H proton transfer dyes has been generated, for which the tautomer emission spans from yellow to the near infrared region *via* a facile and single site derivation of 10-aminobenzo[*h*]quinoline. The result should attract a broad spectrum of interest in the fields of proton transfer research and functional organic materials for optoelectronics.

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References

1 P.-T. Chou, *J. Chin. Chem. Soc.*, 2001, **48**, 651–682.
2 J. E. Kwon and S. Y. Park, *Adv. Mater.*, 2011, **23**, 3615–3642.
3 A. P. Demchenko, K.-C. Tang and P.-T. Chou, *Chem. Soc. Rev.*, 2013, **42**, 1379–1408.
4 S. Kim, J. Seo, H. K. Jung, J. J. Kim and S. Y. Park, *Adv. Mater.*, 2005, **17**, 2077–2082.
5 T. Mutai, H. Tomoda, T. Ohkawa, Y. Yabe and K. Araki, *Angew. Chem., Int. Ed.*, 2008, **47**, 9522–9524.
6 H. Shono, T. Ohkawa, H. Tomoda, T. Mutai and K. Araki, *ACS Appl. Mater. Interfaces*, 2011, **3**, 654–657.
7 T. Mutai, H. Shono, Y. Shigemitsu and K. Araki, *CrystEngComm*, 2014, **16**, 3890–3895.
8 H.-W. Tseng, J.-Q. Liu, Y.-A. Chen, C.-M. Chao, K.-M. Liu, C.-L. Chen, T.-C. Lin, C.-H. Hung, Y.-L. Chou, T.-C. Lin, T.-L. Wang and P.-T. Chou, *J. Phys. Chem. Lett.*, 2015, **6**, 1477–1486.
9 M. L. Martinez, W. C. Cooper and P.-T. Chou, *Chem. Phys. Lett.*, 1992, **193**, 151–154.
10 P.-T. Chou and C.-Y. Wei, *J. Phys. Chem.*, 1996, **100**, 17059–17066.
11 K.-Y. Chen, C.-C. Hsieh, Y.-M. Cheng, C.-H. Lai and P.-T. Chou, *Chem. Commun.*, 2006, 4395–4397, DOI: 10.1039/B610274c.
12 P.-T. Chou, Y.-C. Chen, W.-S. Yu, Y.-H. Chou, C.-Y. Wei and Y.-M. Cheng, *J. Phys. Chem. A*, 2001, **105**, 1731–1740.
13 S. Takeuchi and T. Tahara, *J. Phys. Chem. A*, 2005, **109**, 10199–10207.
14 T. P. Smith, K. A. Zaklika, K. Thakur and P. F. Barbara, *J. Am. Chem. Soc.*, 1991, **113**, 4035–4036.
15 W. Siebrand, *J. Chem. Phys.*, 1967, **47**, 2411–2422.

