ChemComm

View Online / Journal Homepage / Table of Contents for this issue
Dynamic Article Links

Cite this: *Chem. Commun.*, 2012, **48**, 9720–9722

www.rsc.org/chemcomm

COMMUNICATION

New excited state intramolecular proton transfer (ESIPT) dyes based on naphthalimide and observation of long-lived triplet excited states†

Jie Ma,[ab] Jianzhang Zhao,*[a] Pei Yang,[a] Dandan Huang,[a] Caishun Zhang and Qiuting Li[a]

Received 19th July 2012, Accepted 9th August 2012
DOI: 10.1039/c2cc35210a

A new excited state intramolecular proton transfer chromophore of naphthalimide (NI) conjugated 2-(2-hydroxyphenyl) benzothiazole (HBT) was prepared which shows red shifted absorption and long-lived triplet excited states.

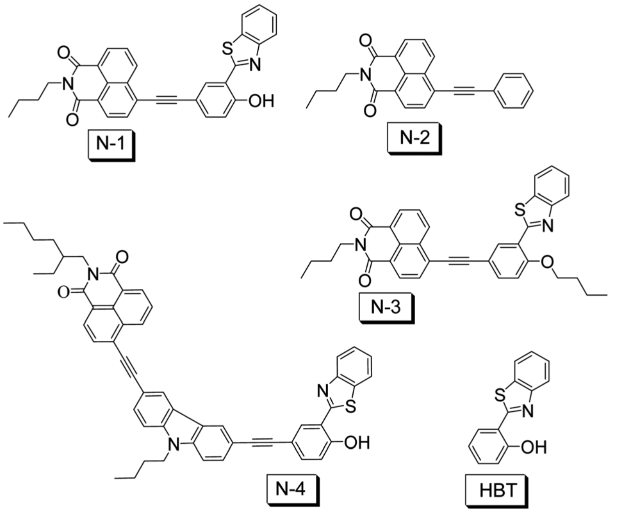
Excited state intramolecular proton transfer (ESIPT) dyes have attracted much attention due to the applications in luminescence materials,[1–7] molecular probes,[8–11] molecular logic gates,[12] biological imaging and labeling.[13–23] ESIPT dyes usually show large Stokes shifts and low fluorescence quantum yields, which are different from the ordinary fluorophores. Furthermore, the fluorescence of ESIPT dyes is usually due to the keto form, which is not responsible for the steady state UV-vis absorption.[1–5,24] The well-known ESIPT dyes are 2-(2-hydroxyphenyl) benzothiazole (**HBT**) and 2-(2-hydroxyphenyl) benzoxazole (HBO).[25] However, these dyes give weak absorption in the visible range, which is a disadvantage for the applications with visible light excitation. Derivatization of **HBT** and HBO was reported, such as with 7-hydroxy-1-indanone,[6] 2-phenylphenol,[17,20,26,27] 1,3-bis(imino)isoindole,[28] diphenyl-aminofluorene.[29] However, these derivatives usually show absorption in the UV range.[11]

A straightforward method to access red-shifted absorption/emission is to extend the π-conjugation of the chromophore.[30,31] To our surprise, the report of **HBT** and HBO derivatives with a large π-conjugation framework is rare.[29] ESIPT dyes with naphthalene units or electron acceptors on the benzothiazole part were prepared,[25,32] but the absorption is in the UV range.[25,32,33] Recently we reported **HBT** derivatives with boron-dipyrromethene (Bodipy) substituents, which gave much longer absorption/emission wavelength than **HBT** and HBO, but no ESIPT was found for the new derivatives.[34] Therefore, much room is left for revealing the elusive photophysics of ESIPT chromophores with a large π-conjugation framework.[24]

On the other hand, naphthalimide (NI) is a versatile chromophore and has been widely used in fluorescent molecular probes and molecular arrays.[35] But NI was never used for ESIPT. Herein we prepared new **HBT** derivatives with NI substituents (**N-1–N-4**, Scheme 1). The compounds show strong absorption of visible light. ESIPT was observed for **N-1**, which is different from the Bodipy-derived **HBT**.[34] Furthermore, a long-lived triplet excited state was also observed for the compounds. The present molecular structural motif may be useful for design of new luminescent ESIPT molecular probes or triplet photosensitizers.[24]

The starting material for the synthesis is 5-bromosalicylaldehyde (see ESI† for details). A C≡C linker was introduced with Pd(0) catalyzed Sonogashira coupling to ensure efficient electronic communication between the **HBT** and NI parts. **N-2** and **N-3** were prepared as controls to investigate the effect of a **HBT** unit and alkylation of the phenolic group on the photophysical properties. The π-conjugation of **N-4** is furthermore extended with a carbazole moiety, to access longer absorption wavelength. All the compounds were obtained in moderate to satisfactory yields.

The absorption of the compounds is red-shifted compared to **HBT** (Fig. 1). **N-1** gives absorption at 385 nm (ε = 34 000 M^{-1} cm^{-1}), in comparison **HBT** gives maximal absorption at 337 nm (ε = 20 100 M^{-1} cm^{-1}). Alkylation of –OH



Scheme 1 Molecular structures of **N-1**, **N-2**, **N-3** and **N-4**. The model compound **HBT** is also presented.

---

[a] *State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P. R. China. E-mail: zhaojzh@dlut.edu.cn, Web: http://finechem.dlut.edu.cn/photochem*
[b] *College of Chemistry and Chemical Engineering, Qiqihaer University, Qiqihaer 161006, Heilongjiang, P. R. China*

† Electronic supplementary information (ESI) available: Synthesis details, characterization data and more spectra. See DOI: 10.1039/c2cc35210a

Table 1 Photophysical properties of **N-1**, **N-2**, **N-3**, **N-4** and **HBT**[a]

	Solvents	λ_{abs}[b] (nm)	ε[c] (M^{-1} cm^{-1})	λ_{em}[d] (nm)	Φ_F[e]/ %	τ[f] (μs) Air	Ar
N-1	$PhCH_3$	405	30 400	545	12.8	31.0	63.0
	THF	384	35 300	592	9.2	—[g]	—[g]
	MeOH	396	32 500	—[g]	—[g]	124.5	118.2
N-2	$PhCH_3$	374	23 400	414	41.2	—[g]	—[g]
	THF	371	26 100	425	51.9	—[g]	—[g]
N-3	$PhCH_3$	386	17 200	440	54.4	—[h]	74.5
	THF	386	17 600	476	51.4	—[g]	—[g]
	MeOH	392	18 000	540	—[g]	—[h]	—[h]
N-4	$PhCH_3$	433	18 300	491	40.1	—[h]	—[h]
	THF	429	20 400	553	16.7	—[g]	—[g]
	MeOH	428	19 800	—[g]	—[g]	—[g]	—[g]
HBT	$PhCH_3$	337	20 100	514	0.5	10.9	18.6
	THF	335	21 200	363	—[h]	—[g]	—[g]
	MeOH	332	20 800	373	—[g]	9.7	10.9

[a] The excitation wavelength for **N-1**, **N-2**, **N-3**, **N-4** and **HBT** was 370 nm, 350 nm, 370 nm, 410 nm, 315 nm, respectively. 1.0 × 10^{-5} M, 20 °C. [b] Absorption wavelength. [c] Molar extinction coefficient. [d] Fluorescence emission wavelength. [e] Fluorescence quantum yields determined with Bodipy (Φ = 72% in THF) as the standard. [f] Lifetimes determined with the transient absorption spectroscopy. [g] Not determined. [h] The signal was too weak.

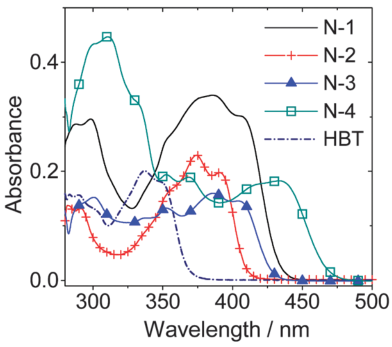


Fig. 1 UV-vis absorption of **N-1**, **N-2**, **N-3**, **N-4** and **HBT**. c = 1.0 × 10^{-5} M in toluene. 20 °C.

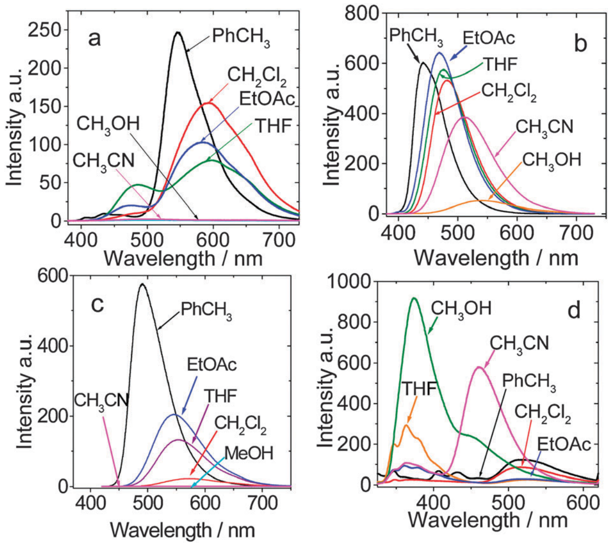


Fig. 2 (a) Fluorescence emission spectra of **N-1** (λ_{ex} = 370 nm). (b) **N-3** (λ_{ex} = 370 nm). (c) **N-4** (λ_{ex} = 410 nm). (d) **HBT** (λ_{ex} = 315 nm) in different solutions. c = 1.0 × 10^{-5} M. 20 °C.

reduces the absorption intensity, but not the wavelength (**N-1** and **N-3**). **N-2** gives slightly blue-shifted absorption *vs.* **N-1** and **N-3**. **N-4** gives absorption at 433 nm (ε = 18 300 M^{-1} cm^{-1}) (Table 1). The absorption of these compounds in the visible region is mainly attributed to the NI parts. Very few ESIPT dyes give absorption in the visible range.[4] Previously a **HBT** derivative with a diphenylaminofluorene substituent was reported to show similar absorption.[29] Recently we reported Bodipy-grafted **HBT** with strong absorption in the visible range, but the compounds did not show any ESIPT effect.[34]

N-1 gives strong emission in toluene (Φ_F = 12.8%). The emission intensity is reduced in polar solvents, such as CH_2Cl_2 and THF (Fig. 2a). Interestingly, dual emission was observed for **N-1** in THF and ethyl acetate, which is characteristic of ESIPT. The enol form gives emission at shorter wavelength and the keto form gives emission at longer wavelength.[32] The emission of **N-1** is completely quenched in methanol, due to the significant intramolecular charge transfer character (ICT). This result is similar to a HBO derivative with an ICT effect.[32] Different from **N-1**, the quenching of **N-3** fluorescence in polar solvents is not significant, and no dual emission was observed. This is reasonable since ESIPT is completely prohibited in **N-3** by alkylation of –OH (Fig. 2b). Similarly, the emission of **N-4** indicated the absence of ESIPT, which is supported by the lack of transient absorption (Fig. 2c). Dual emission was observed for **HBT** in THF, acetonitrile, which is an indication of ESIPT (Fig. 2d). The calculated free energy changes for the support that **N-1** is more likely to undergo ESIPT (Fig. S27, ESI†).[34]

The nanosecond time-resolved transient difference absorption spectra of **N-1** were studied (Fig. 3a). Upon pulsed laser excitation, bleaching at 380 nm was observed. Furthermore, transient absorption (TA) at 328 nm and in the 400–750 nm range was observed. The lifetime of the transient was determined to be 63.0 μs.

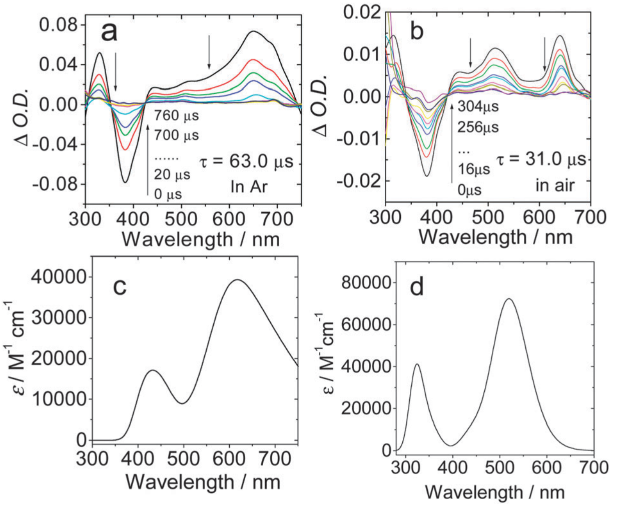


Fig. 3 Nanosecond time-resolved transient difference absorption spectra of **N-1**. (a) In deaerated benzene and (b) in aerated benzene, after pulsed laser excitation (λ_{ex} = 355 nm). c = 2.0 × 10^{-5} M. 20 °C. DFT calculated absorption spectra of (c) the triplet state of **N-1** and (d) the *Z*-keto form of **N-1**. Calculated by TDDFT at the B3LYP/6-31G(d) using Gaussian 09W.

Interestingly, the transient was not completely quenched in *aerated* solution (Fig. 3b), thus the long-lived transient observed in *aerated* solution can be attributed to the keto form (*i.e.* the product of ESIPT).[25] We propose that the triplet state feature is more significant for the TA measured in deaerated solution (Fig. 3a), whereas the keto-form based absorption is dominant in the TA spectra measured in aerated solution (Fig. 3b). This postulation is supported by the DFT calculations on the TA spectra (Fig. 3c and d). The TA of the previously reported Bodipy-conjugated **HBT** was completely quenched in aerated solution, which indicated the triplet feature of the transients, and the absence of ESIPT.[34]

The TA of **N-1** in methanol was also studied. We found a long-lived transient species (τ = 118.2 μs), which was not quenched in aerated solution (see ESI†, Fig. S20 and S21), thus the transient was attributed to the keto form of **N-1**,[25] *i.e.* the product of the ESIPT of **N-1**. Similarly **HBT** was studied with the TA spectra. ESIPT was confirmed in both benzene and methanol solution (see ESI†, Fig. S22–S25).

For **N-3**, transient with τ_T of 74.5 μs was observed in deaerated solution, which was quenched in aerated solution (see ESI†, Fig. S26). Therefore the transient of **N-3** is due to the triplet excited state. This observation is in agreement with the results of the emission of **N-3**, as well as the molecular structure of **N-3** (–OH group is alkylated). For **N-4**, no transient was observed, indicating the absence of ESIPT.

In summary, naphthalimide conjugated-2-(2-hydroxyphenyl) benzothiazole (**HBT**) compounds were prepared as a new excited state intramolecular proton transfer (ESIPT) chromophore. These compounds have a larger π-conjugation framework and show strong red-shifted absorption *vs.* **HBT**. ESIPT was observed for the new compound. This result is in contrast to the previously reported Bodipy-conjugated **HBT** derivatives (for which no ESIPT was observed) and demonstrated the elusive properties of the **HBT** derivatives with a large π-conjugation framework, *e.g.* the unpredictable ESIPT property of these derivatives. Furthermore, a long-lived triplet excited state was populated upon photooxidation of the compounds. The new ESIPT chromophore can be used in luminescent molecular probes, and will inspire more investigations into this fascinating area.

We thank the NSFC (20972024 and 21073028), Royal Society (UK) and NSFC (China-UK Cost-Share program-21011130154) for financial support.

Notes and references

1 W. E. Brewer, M. L. Martinez and P. Chou, *J. Phys. Chem.*, 1990, **94**, 1915.
2 T. Mutai, H. Tomoda, T. Ohkawa, Y. Yabe and K. Araki, *Angew. Chem., Int. Ed.*, 2008, **47**, 9522.
3 S. Park, J. Seo, S. H. Kim and S. Y. Park, *Adv. Funct. Mater.*, 2008, **18**, 726.
4 J. E. Kwon and S. Y. Park, *Adv. Mater.*, 2011, **23**, 3615.
5 S. Park, J. E. Kwon, S. H. Kim, J. Seo, K. Chung, S. Y. Park, D. J. Jang, B. M. Medina, J. Gierschner and S. Y. Park, *J. Am. Chem. Soc.*, 2009, **131**, 14043.
6 K. C. Tang, M. J. Chang, T. Y. Lin, H. A. Pan, T. C. Fang, K. Y. Chen, W. Y. Hung, Y. H. Hsu and P. T. Chou, *J. Am. Chem. Soc.*, 2011, **133**, 17738.
7 S. Park, J. E. Kwon and S. Y. Park, *Phys. Chem. Chem. Phys.*, 2012, **14**, 8878.
8 B. Liu, H. Wang, T. Wang, Y. Bao, F. Du, J. Tian, Q. Li and R. Bai, *Chem. Commun.*, 2012, **48**, 2867.
9 J. S. Wu, W. M. Liu, J. C. Ge, H. Y. Zhang and P. F. Wang, *Chem. Soc. Rev.*, 2011, **40**, 3483.
10 Y. Abraham, H. Salman, K. Suwinska and Y. Eichen, *Chem. Commun.*, 2011, **47**, 6087.
11 (*a*) Y. Xu and Y. Pang, *Dalton Trans.*, 2011, **40**, 1503; (*b*) Y. Xu and Y. Pang, *Chem. Commun.*, 2010, **46**, 4070.
12 V. Luxami and S. Kumar, *New J. Chem.*, 2008, **32**, 2074.
13 T. Kim, H. J. Kang, G. Han, S. J. Chung and Y. Kim, *Chem. Commun.*, 2009, 5895.
14 A. J. Stasyuk, M. Banasiewicz, M. K. Cyrański and D. T. Gryko, *J. Org. Chem.*, 2012, **77**, 5552.
15 C. H. Kim and T. Joo, *Phys. Chem. Chem. Phys.*, 2009, **11**, 10266.
16 A. Brenlla, M. Veiga, M. Mosquera and F. Rodríguez-Prieto, *Photochem. Photobiol. Sci.*, 2011, **10**, 1622.
17 M. Lukeman and P. Wan, *Chem. Commun.*, 2001, 1004.
18 K.-I. Sakai, S. Takahashi, A. Kobayashi, T. Akutagawa, T. Nakamura, M. Dosen, M. Katoc and U. Nagashima, *Dalton Trans.*, 2010, **39**, 1989.
19 Y. Qian, S. Li, Q. Wang, X. Sheng, S. Wu, S. Wang, J. Li and G. Yang, *Soft Matter*, 2012, **8**, 757.
20 Y.-H. Wang and P. Wan, *Photochem. Photobiol. Sci.*, 2011, **10**, 1934 .
21 B. K. Paul, D. Ray and N. Guchhait, *Phys. Chem. Chem. Phys.*, 2012, **14**, 8892.
22 M. Sliwa, N. Mouton, C. Ruckebusch, L. Poisson, A. Idrissi, S. Aloïse, L. Potier, J. Dubois, O. Poizat and G. Buntinx, *Photochem. Photobiol. Sci.*, 2010, **9**, 661.
23 G.-J. Zhao and K.-L. Han, *Acc. Chem. Res.*, 2012, **45**, 404.
24 (*a*) J. Zhao, S. Ji, Y. Chen, H. Guo and P. Yang, *Phys. Chem. Chem. Phys.*, 2012, **14**, 8803; (*b*) C.-C. Hsieh, C.-M. Jing and P.-T. Chou, *Acc. Chem. Res.*, 2010, **43**, 1364.
25 M. Ikegami and T. J. Arai, *J. Chem. Soc., Perkin Trans. 2*, 2002, 1296.
26 M. Lukeman and P. Wan, *J. Am. Chem. Soc.*, 2002, **124**, 9458.
27 M. Lukeman and P. Wan, *J. Am. Chem. Soc.*, 2003, **125**, 1164.
28 K. Hanson, N. Patel, M. T. Whited, P. I. Djurovich and M. E. Thompson, *Org. Lett.*, 2011, **13**, 1598.
29 A. R. Morales, K. J. Schafer-Hales, C. O. Yanez, M. V. Bondar, O. V. Przhonska, A. I. Marcus and K. D. Belfield, *ChemPhysChem*, 2009, **10**, 2073.
30 G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem., Int. Ed.*, 2008, **47**, 1184.
31 R. Ziessel and A. Harriman, *Chem. Commun.*, 2011, **47**, 611.
32 J. Seo, S. Kim and S. Y. Park, *J. Am. Chem. Soc.*, 2004, **126**, 11154.
33 C. R. Baiz, S. J. Ledford, K. J. Kubarych and B. D. Dunietz, *J. Phys. Chem. A*, 2009, **113**, 4862.
34 P. Yang, J. Zhao, W. Wu, X. Yu and Y. Liu, *J. Org. Chem.*, 2012, **77**, 6166.
35 (*a*) C. Thalacker, C. Roeger and F. Würthner, *J. Org. Chem.*, 2006, **71**, 8098; (*b*) X. Lu, W. Zhu, Y. Xie, X. Li, Y. Gao, F. Li and H. Tian, *Chem.–Eur. J.*, 2010, **16**, 8355; (*c*) S. Guo, W. Wu, H. Guo and J. Zhao, *J. Org. Chem.*, 2012, **77**, 3933; (*d*) W. Zhu, M. Dai, Y. Xu and X. Qian, *Bioorg. Med. Chem.*, 2008, **16**, 3255.