



New two-photon absorption benzotriazole–coumarin dyads: the evidence of internal proton transfer in the excited state



Yulong Gong, Yao Lu, Zhenqiang Wang, Shengtao Zhang, Ziping Luo*, Hongru Li*, Fang Gao*

College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 40044, China

ARTICLE INFO

Article history:

Received 15 August 2014

Revised 14 November 2014

Accepted 17 November 2014

Available online 21 November 2014

Keywords:

Two-photon absorption

Organic dyads

H-bonding effect

Proton transfer

Excited state

ABSTRACT

New near-infrared two-photon absorption π -extended benzotriazole–coumarin dyads as target molecules were synthesized. The corresponding coumarin derivatives and esterified dyads were also prepared as the references. The experimental evidence of internal proton transfer in the excited state of the benzotriazole-based chromophores under one and near-infrared two-photon irradiation are firstly presented in this Letter.

© 2014 Elsevier Ltd. All rights reserved.

There is a long-staying scientific controversy on internal proton transfer in the excited state for *o*-hydroxy-phenyl-benzotriazole family, which contains typical intramolecular proton transfer groups. Unlike *o*-hydroxy-phenyl-benzothiazole and *o*-hydroxy-phenyl-benzoxazole,^{1,2} excited state intramolecular proton transfer (ESIPT) of *o*-hydroxy-phenyl-benzotriazole family is lack of the substantial experimental evidence. Due to more electron-deficiency in the heterocyclic ring of *o*-hydroxy-phenyl-benzotriazole comparing with *o*-hydroxy-phenyl-benzothiazole and *o*-hydroxy-phenyl-benzoxazole, the occurrence of internal proton transfer in the excited state of *o*-hydroxy-phenyl-benzotriazole family decreases.

So far, there have been different opinions on the occurrence of internal proton transfer in the excited state for this family.^{3–5} For instance, it was reported that intramolecular electron transfer led to the deactivation of the excited state for *o*-aryl-benzotriazoles,³ while internal proton transfer was regarded as the main decay pathway in the excited singlet state for 2-(2'-hydroxy-phenyl)-benzotriazole.^{4,5}

Two-photon absorption (TPA) chromophores opened a door for the application of near-IR laser,^{6–8} which demonstrated various superior physical advantages such as low energy, deep penetration, and negligible damage to normal biological tissues. A few 2-(2'-hydroxyphenyl)-benzoxazole-based dyes with TPA cross sections

were reported to exhibit ESIPT under near-IR laser excitation.⁹ Unfortunately, no characteristic proton transfer emission band was detected under near-IR laser irradiation to these benzoxazole-based dyes. To the best of our knowledge, there is no report on ESIPT of *o*-hydroxy-phenyl-benzotriazole-based organic chromophores under one-photon and near-IR laser irradiation.

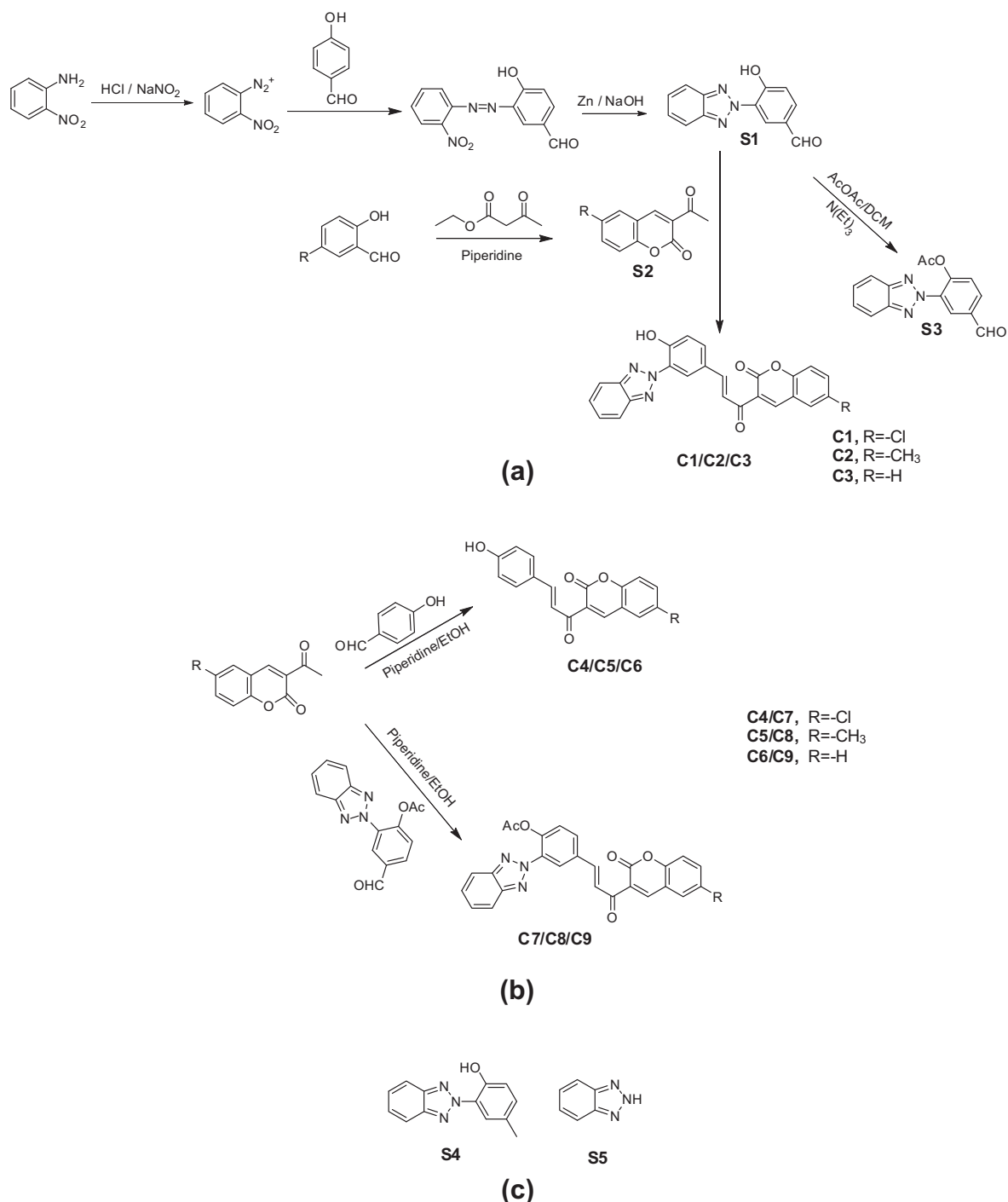
Extended organic chromophores with ESIPT possess more application potentials.^{10,11} In particular, π -extended organic chromophores with ESIPT can be utilized as TPA dyes by near-IR femtosecond laser. Several groups developed enlarged organic molecules containing proton transfer segments through the chemical covalent bond.^{12–14} However, the insertion of π -conjugation units was reported to inhibit intramolecular proton transfer in the excited state for an organic chromophore.¹² Therefore, the development of new π -extended *o*-hydroxy-phenyl-benzotriazole-based organic chromophores with internal proton transfer in the excited state is still a great challenge.

In this Letter, coumarin is used as the π -unit to construct new benzotriazole–coumarin dyads, where the electron-accepting α,β -unsaturated carbonyl group acts as the π -linker to increase the activity of the phenolic hydroxy group. Herein, we describe our studies on the internal proton transfer of 2-(2'-hydroxy-phenyl)-benzotriazole–coumarin dyads in the excited state under both one-photon and near-IR two-photon irradiation, respectively.

Several target benzotriazole–coumarin dyads (**C1–C3**) were designed and synthesized as shown in **Scheme 1**. The corresponding coumarins (**C4–C6**) and *O*-acetyl dyads (**C7–C9**) were also prepared

* Corresponding authors. Tel./fax: +86 23 65102531.

E-mail addresses: zpluo@126.com (Z. Luo), hongruli1972@gmail.com (H. Li), fanggao1971@gmail.com (F. Gao).



Scheme 1. Chemical structures of the molecules studied in this work.

for reference. The detailed procedures for the target and reference molecules are described in [Supplementary material](#).

As shown in ¹H NMR (Fig. 1), the chemical shift of OH in **C1** moves to downfield comparing with those of **C4** and phenol in D⁶-DMSO (**C1**, 11.23 ppm, **C4**, 10.20 ppm, phenol, 9.35 ppm). It is also noticed that ¹H NMR chemical shift of OH in the equal molar mixture of **C4**/1,2,3-benzotriazole (**S5**) is almost the same as that of **C4** (Fig. S1, [Supplementary material](#)). In addition, ¹H NMR chemical shift of OH in the equal molar mixture of **C7**/phenol is almost the same as that of phenol (Fig. S1).

Compounds **C2** and **C3** exhibit similar ¹H NMR nature as **C1**. ¹H NMR chemical shift of OH in **C2** or **C3** situates at downfield comparing with those of **C5** or **C6** in D⁶-DMSO. ¹H NMR chemical shift of OH in the equal molar mixture of **C5**/1,2,3-benzotriazole or **C6**/1,2,3-benzotriazole is almost identical to that of **C5** or **C6**, respectively. Furthermore, ¹H NMR chemical shift of OH in the equal molar mixture of **C8**/phenol or **C9**/phenol is similar to that of phenol, respectively.

The above results also show that there is no strong interaction between OH and C=N groups in the ground state as they are contained in different molecules respectively. The fact that ¹H

Download English Version:

<https://daneshyari.com/en/article/5262630>

Download Persian Version:

<https://daneshyari.com/article/5262630>

[Daneshyari.com](https://daneshyari.com)