



Synthesis, physical properties, and sensing behaviour of a novel naphthalenediimide derivative



Pei-Yang Gu^a, Zilong Wang^a, Guangfeng Liu^a, Lina Nie^a, Rakesh Ganguly^b, Yongxin Li^b, Qichun Zhang^{a, b, *}

^a School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

^b Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

ARTICLE INFO

Article history:

Received 2 March 2016

Received in revised form

2 April 2016

Accepted 9 April 2016

Available online 11 April 2016

Keywords:

Tetrabromonaphthalenediimide

Benzophenone imine

Synthesis

Sensor

Red emission

ABSTRACT

In our attempt to prepare compound 4,5,9,10-tetraamino-2,7-bis(2-octyldodecyl)benzo[*lmn*] [3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (**4NH₂NDI**) according to the reported procedure for constructing larger conjugated molecules, an unexpected by-product 2,8-bis(2-octyldodecyl)-5,5,11,11-tetraphenyl-5,6,11,12-tetrahydroimidazo[4',5':5,6]benzo[1,2,3,4-*lmn*]imidazo[4,5-*f*] [3,8]phenanthroline-1,3,7,9(2*H*,4*H*,8*H*,10*H*)-tetraone (**4NHNDI**) was obtained through the undesired hydrolysis of 4,5,9,10-tetrakis((diphenylmethylene)amino)-2,7-bis(2-octyldodecyl)benzo[*lmn*] [3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (**4NNDI**) when a drop of water was added in this reaction. The undesired hydrolysis was further confirmed by the direct hydrolysis of pure **4NNDI** in organic solvent with a drop of aqueous HCl solution. **4NHNDI** was fully characterized by NMR and mass spectroscopy and was further confirmed through a single crystal analysis. The absorption and emission wavelengths of **4NHNDI** were red-shifted ~ 20 and 30 nm with the increased polar of the solvents due to the dipole–dipole interactions between **4NHNDI** and the polarity solvents. Interestingly, **4NHNDI** can act as an efficient anion sensor for fluoride ion over a wide range of other anions (ClO₄⁻, Br⁻, BF₄⁻, I⁻, NO₃⁻, Cl⁻, PF₆⁻, AcO⁻, HSO₄⁻ and CN⁻) owing to the four N–H fragments in the main backbone. Surprisingly, **4NHNDI** didn't show any sensing behavior in aqueous solutions to all eleven anions including F⁻ anion, which might be due to the steric effects from long alkyl chains in aqueous solution. However, this phenomenon could allow us to recover the quenched spectrum induced by F⁻ anion through adding H₂O in pure THF solution.

© 2016 Elsevier Ltd. All rights reserved.

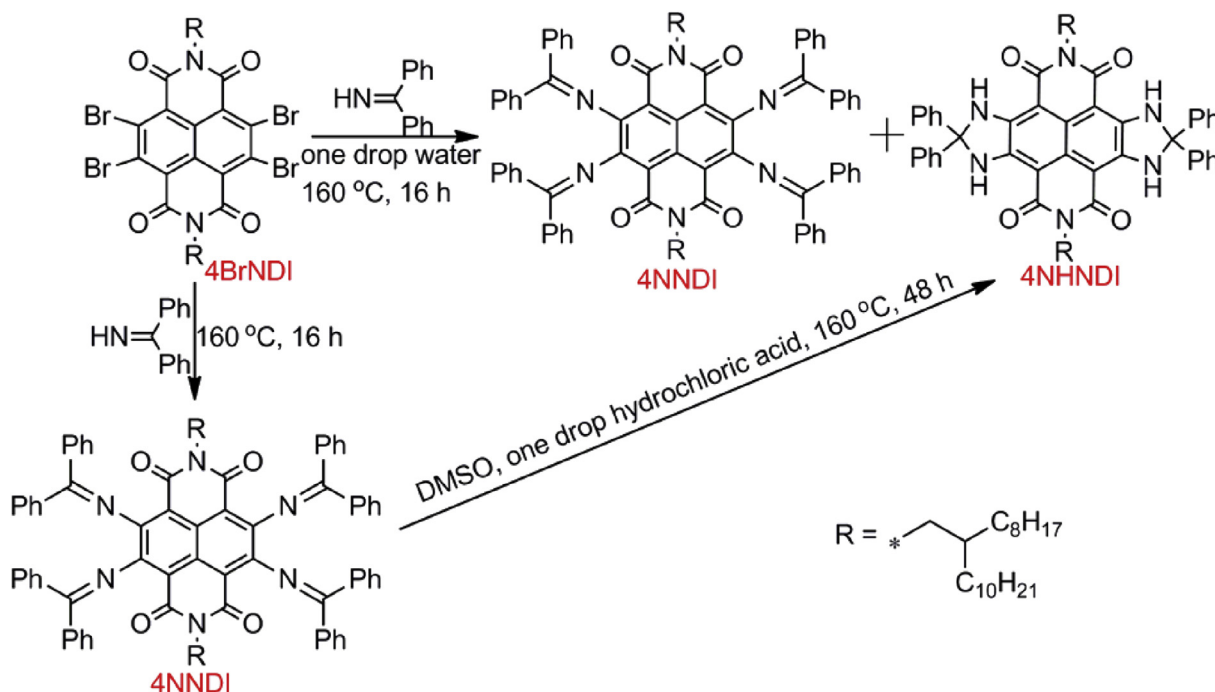
1. Introduction

In recent years, naphthalenediimide (**NDI**) and its derivatives have received the increasing attention due to their interesting electro-optical properties [1–5], high chemical and thermal stability [6–9], and wide applications in organic electronic devices [10–15], supramolecular self-assembly [16–21], and chemosensors [22–28]. Generally, the backbone of **NDIs** can be functionalized along two directions: the *peri* position (1, 4, 5, 8) and the *lateral* position (2, 3, 6, 7). In the past decades, most functionalization was conducted along the *peri* position of **NDIs** due to the synthetic convenience and the tuneable optical properties of as-prepared

products [29–33]. In contrast, the functionalization along the *lateral* position of **NDIs** didn't receive too much effort. Until recently, the synthesis of 2,6-dibromo-, 3,6-dibromo-, and 2,3,6,7-tetrabromo-1,4,5,8-naphthalenediimides become more efficient [34–40]. Since then, various core-substituted **NDIs** have been reported as novel functional π -systems with unique optical and electrical properties. Very recently, a tetraamino core-substituted **NDI** derivative 4,5,9,10-tetraamino-2,7-bis(2-octyldodecyl)benzo[*lmn*] [3,8]phenanthroline-1,3,6,8 (2*H*,7*H*)-tetraone (**4NH₂NDI**, Chart 1) has been developed as a promising p-type semiconductor and has been employed as an important building block to construct larger conjugated molecules [41]. In our attempt to prepare some **4NH₂NDI** according to the reported procedure, an unexpected by-product 2,8-bis(2-octyldodecyl)-5,5,11,11-tetraphenyl-5,6,11,12-tetrahydroimidazo[4',5':5,6]benzo[1,2,3,4-*lmn*]imidazo[4,5-*f*] [3,8]phenanthroline-1,3,7,9(2*H*,4*H*,8*H*,10*H*)-tetraone (**4NHNDI**) was obtained through the undesired hydrolysis of 4,5,9,10-

* Corresponding author. School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore.

E-mail address: qc Zhang@ntu.edu.sg (Q. Zhang).



Scheme 1. The synthesis route to **4NHNDI**.

tetrakis((diphenylmethylene)amino)-2,7-bis(2-octyldodecyl)benzo[*lmn*] [3,8] phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (**4NNDI**) when a drop of water was added in this reaction (Scheme 1). The undesired hydrolysis was further confirmed by the direct hydrolysis of pure **4NNDI** in organic solvent with a drop of aqueous HCl solution. The as-prepared by-product **4NHNDI** was further investigated as a chemosensor for fluoride ion due to two reasons: (1) Like other tetraalkylamino-substituted **NDI** derivatives [42,43], **4NHNDI** has a strong red emission; (2) **4NHNDI** contains four N–H groups, which could have a strong interaction with fluoride ion through H-bonding, leading to the changes of the absorption and emission of **4NH₂NDI** [44–51]. The UV/Vis and fluorescent characteristics of **4NHNDI** dramatically changed with the addition of fluoride ion in DMF solution.

2. Results and discussion

2.1. Synthesis and structure of **4NHNDI**

The synthetic procedure for **4NHNDI** is described in Scheme 1. 4,5,9,10-tetrabromo-2,7-bis(2-octyldodecyl)benzo[*lmn*] [3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (**4BrNDI**) was synthesized according to the reported procedure [52–57]. **4BrNDI** could further react with benzophenone imine to form **4NNDI** as indicated in the previous literature. However, when the reaction system has a trace amount of water or was added a drop of water purposely, an unexpected byproduct **4NHNDI** was obtained through the undesired hydrolysis of **4NNDI** (Scheme 1). Note that **4NHNDI** can be prepared by direct hydrolysis of pure **4NNDI** in organic solvent with a drop of aqueous acid (HCl). Interestingly, more water in original reaction or direct hydrolysis of pure **4NNDI** didn't increase the yield of byproduct **4NHNDI**. The as-prepared **4NHNDI** was confirmed by NMR and mass spectroscopy (Supporting information). Strong effort has been made to grow a suitable crystal for single-crystal analysis for further confirming the structure of **4NHNDI**. Although **4NHNDI** could form crystals by diffusing ethanol into a chloroform solution, unfortunately, the disorder of long alkyl chains in

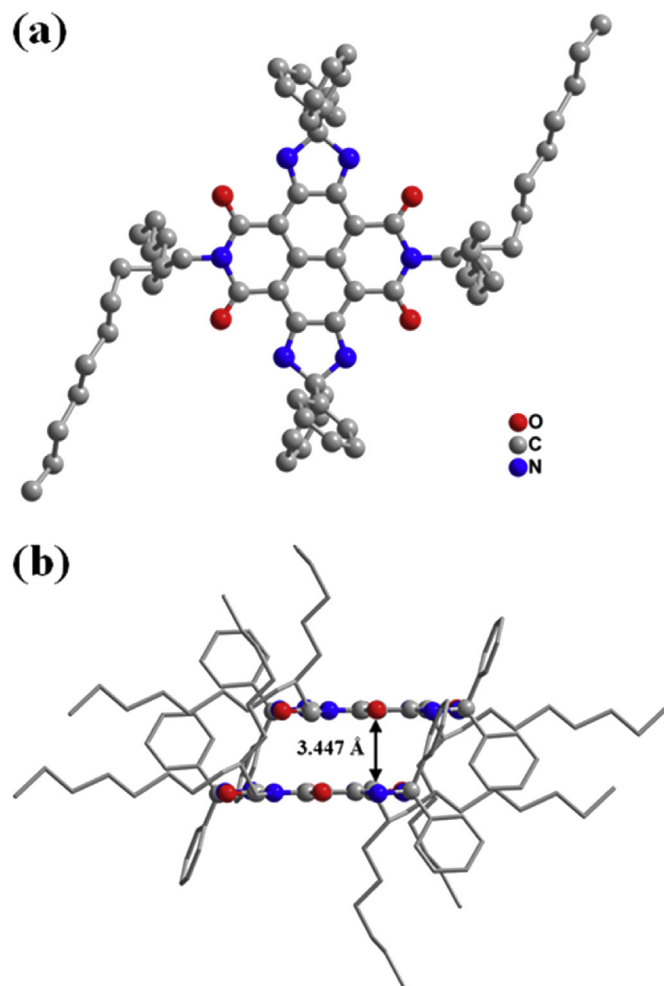


Fig. 1. (a) Single crystal structure of **4NHNDI**. (b) Interlayer distances between the neighboring molecules.

Download English Version:

<https://daneshyari.com/en/article/175294>

Download Persian Version:

<https://daneshyari.com/article/175294>

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