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## Isomeric naphthalimides bearing pyran units: Insight into mutual relation between structure and photochromic properties



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### ABSTRACT

Two novel isomeric photochromic naphthopyrans (**1** and **2**) containing naphthalimide moieties were prepared and studied. In the compound **1**, O-atom of pyran cycle is at C-3 position of naphthalene ring, whereas, in compound **2**, O-atom of pyran cycle is at C-4 position. In the compound **2** due to *para*-position O-atom of pyran photochromic cycle is involved into the conjugated naphthalimide system. The variety in mutual position of pyran and naphthalimide units leads to remarkable difference in photochromic characteristics. Both compounds demonstrate the switching of the fluorescence by photoinduced conversion between the closed and open forms.

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### 1. Introduction

Nowadays, much attention has been paid to the design, synthesis and working operation of photochemical molecular devices. The development of a device concept to the molecular level is of interest from the fundamental point of view as well as for the growth of supramolecular chemistry, nanoscience and nanotechnology [1]. Molecular and supramolecular devices that show large changes in on–off states are intensively developed as they can be modulated by employing external stimuli such as ions, molecules, light, etc. [2]. The switchable states of the molecular-level devices refer to their luminescence, magnetic or electronic properties.

Luminescence is one of the most useful techniques to monitor the operation of molecular devices [3]. A part of this rapidly emerging field is the development of fluorescent sensors, non-destructive data storage, biological fluorescence labeling [4].

Photochromic molecules are able to perform binary states with different fluorescence characteristics [5]. Regulating fluorescence intensity is one of the most attractive uses for molecular photoswitches because of the high sensitivity, resolution, contrast and the fast response provided by fluorescence technology. The realization of the photocontrolled fluorophores requires the design and synthesis of the hybrid photochrome–fluorophore systems

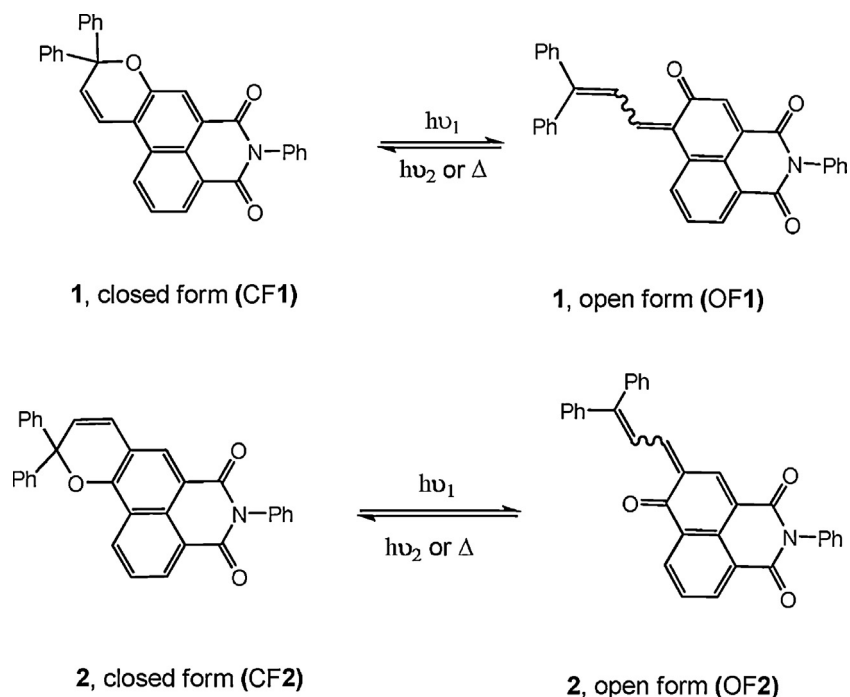
where the excited state communication between two chromophores has to be effective. A conventional approach to modulating the fluorescence relies on the integration of fluorescent dye and photochromic unit in one molecular skeleton.

Keeping these considerations in mind, we designed and synthesized 3H-naphtho[2,1-b]pyran (**1**) and 2H-naphtho[1,2-b]pyran (**2**) (Scheme 1) bearing naphthalimide units fused to pyran moieties. Naphthalenic acid imides (1,8-naphthalimides) with electron donating substituents attached to the naphthalene moiety are well-known fluorescent dyes high absorption coefficients and high fluorescent quantum yields in the visible region. Such compounds have been used in a large variety of areas, including coloration of polymers and optical brightening [6,7], laser active media [8], electroluminescent materials [9], optical chemosensors [10] and fluorescent markers in biology [11]. Naphthopyrans are known to exhibit excellent photochromic responses, good colorability, and rapid bleaching [12], and are explored in sensors [13], polymers [14], and organic gels [15].

Recently, naphthalimide units have been incorporated into photochromic spirooxazine, diarylethene systems, especially realizing a significantly long lifetime in the open merocyanine (MC) forms [16]. Two photochromic naphthopyrans containing naphthalimide moieties were studied in solution under flash photolysis conditions, exhibiting predominant thermal reversibility in color-fading and fluorescence switch [17].

The goals of the present investigations are to analyze (i) how the mutual positions of pyran and naphthalimide units in

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**Scheme 1.** Structures of closed and open forms of compounds **1** and **2**.

photochromic fluorophore influences on the optical characteristics of closed and open forms (CF and OF respectively); (ii) how the existence of naphthalimide unit with strong electron-withdrawing imide group can somehow change the ratio of *transoid-trans* (TT) and *transoid-cis* (TC), thus facilitating the thermal back to closed form with a preferable color bleaching rate and thermal reversibility; and (iii) how the fluorescence of naphthalimide unit can be switched on–off by photochromic conversion.

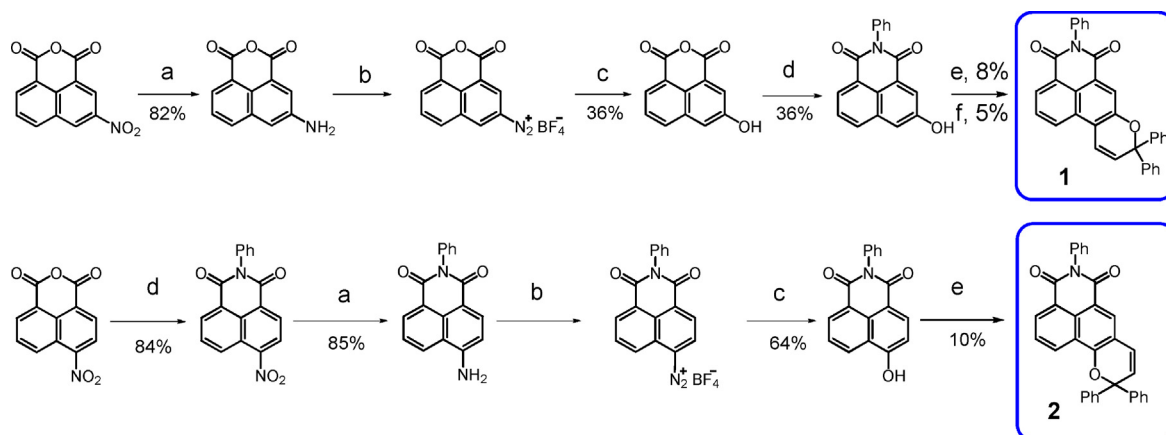
## 2. Material and methods

Synthesis of 4- and 3-hydroxy-1,8-naphthalimides (Scheme 2) was carried out according to earlier reports [18–22]. The following procedures describe the experimental details of preparation of target compounds **1** and **2**.

### 2.1. 5,10,10-Triphenylbenzo[de]pyrano[2,3-f]isoquinoline-4,6 (5*H*,10*H*)-dione (**1**)

**Method 1.** The procedure was adopted from literature [18]. 3-Hydroxy-1,8-naphthalimide (1.00 g, 3.5 mmol) and 0.70 g (3.5 mmol) of 1,1-diphenylprop-2-yn-1-ol while heating to 50–55 °C were dissolved in 60 ml of toluene, and 0.06 g (0.35 mmol) of *p*-toluenesulfonic acid was added. The reaction mixture was stirred at 50–60 °C for 1 h and then at 70–80 °C for 3–4 h. The solvent was evaporated. After the column chromatography (eluent PhH–EtOH, *v/v* = 10/1) 0.13 g of naphthopyran **1** was obtained as a yellow powder (yield was 8%).

**Method 2.** The procedure was adopted from literature [19]. 4-Hydroxy-1,8-naphthalimide (1.0 g, 3.5 mmol) and 0.8 g (3.5 mmol) of  $\beta$ -phenylcinnamaldehyde were dissolved in 60 ml of toluene, and a solution of 1.2 g (5.2 mmol) of titanium(IV) tetraethoxide in



**Scheme 2.** Synthetic routes to the naphthopyrans **1** and **2**. Reagents and conditions: (a)  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , HCl, AcOH or EtOH, 80 °C; (b) (1)  $\text{H}_2\text{SO}_4$ ,  $\text{NaNO}_2$ ,  $\text{H}_2\text{O}$ , 0–5 °C; (2)  $\text{HBF}_4$ ; (c)  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ , 100 °C; (d)  $\text{PhNH}_2$ , AcOH, 120 °C; (e) 1,1-diphenylprop-2-yn-1-ol, TsOH, MeCN, 25–50 °C; (f) 3,3-diphenyl-acrylaldehyde,  $\text{Ti}(\text{OEt})_4$ ,  $\text{PhCH}_3$ , 100 °C.

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