



# Naphthalene diimide cocrystals: A facile approach to tune the optical properties



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## ABSTRACT

Core-substituted naphthalene diimides are attracting much interest because of their tunable optical properties, which are generally achieved by the elaborate introduction of electron-donating groups into electron-deficient core to form donor–acceptor compounds through the covalent bonds. Here we report that the optical properties of core-unsubstituted naphthalene diimides can be modulated by a facile cocrystal strategy. Based on the X-ray crystallographic and Hirshfeld surface analyses, the  $\pi$ – $\pi$  interactions have been demonstrated to be the most important factor that answers for the optical properties of naphthalene diimide cocrystals, while other interactions, such as hydrogen bonds and solvation effects, have little impact on their properties but influence  $\pi$  stacking. This insight is of considerable significance for the development of naphthalene diimide based materials in various directions.

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## 1. Introduction

Naphthalene diimides (NDIs) are an attractive class of electron-deficient organic dyes owing to their outstanding optical, electronic (n-type semiconducting), and light fastness properties [1], as well as potential applications in chemical sensing [2], photovoltaic [3], anion transport [4], and catalysis [5]. It is known that the core-unsubstituted NDIs are colorless and ultraviolet absorbing, and a common strategy to achieve a bathochromic shift of the absorption maximum is the incorporation of electron-donating groups into the NDI core to form donor–acceptor compounds, which can afford tunable charge transfer (CT) bands in the long-wavelength region [6]. However, such a covalent approach to modulate the optical properties is rather elaborate and often accompanied by decreased chemical stability [7], which limits their scope for applications.

Cocrystals are the crystalline molecular solids composed of at least two types of neutral chemical species [8]. Recently, cocrystal formation has received much attention as a means of modifying the optical properties of organic  $\pi$ -conjugated molecules in the solid state [9]. Theoretically, the optical properties of NDIs can also be

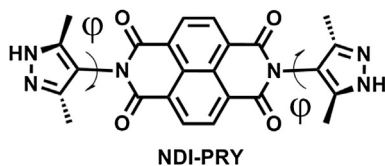
adjusted by such a cocrystal approach. For example, when the cocrystallization of core-unsubstituted NDIs with electron-rich molecules, donor–acceptor complexes can be formed and thus the tunable CT absorption properties are anticipated [10]. To our surprise, except for several fragmentary examples involved in the color changing of NDI crystals, there are no systematic studies on the detailed impact factors and regulation methods [11]. Herein, we focus on this foreseeable important but ignored strategy, and anticipate developing a facile method to fabricate multi-colored NDI materials.

From the viewpoint of convenience, organic solvents are ideal eutectoid compositions in the cocrystals. Considering most of core-unsubstituted NDIs can only be dissolved in non-protic polar solvents, e.g. dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF) and chloroform, which generally act as hydrogen bond acceptors during co-crystallization, we selected an available core-unsubstituted NDI, named NDI-PRY (Scheme 1) that was modified by two 3,5-dimethylpyrazole at two imide positions [12], as a proof-of-concept example, and anticipated it could co-crystallize with the above organic solvents *via* hydrogen bonding interactions. Moreover, in order to generate the donor–acceptor complexes, two electron-rich aromatic guest molecules, phenanthroline (Phen) and acenaphthene (Acen) were added into the crystallization solutions. As expected, five different colored NDI cocrystals, **1** (NDI-PYR), **2** (NDI-PYR·DMF), **3** (NDI-PYR·2DMF·2H<sub>2</sub>O), **4** (NDI-PYR·2Phen), **5** (NDI-PYR·Acen·H<sub>2</sub>O),

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Scheme 1. Chemical structure of NDI-PYR.

have been successfully prepared and their structural features have been studied by X-ray single crystal diffraction analyses. To explore the contributions of non-covalent interactions, particularly  $\pi$ – $\pi$  interactions, hydrogen bonds and solvation effects, towards optical properties, their Hirshfeld surfaces have also been calculated, and finally their structure–property relationships have been carefully discussed based on the above investigations.

## 2. Experimental

### 2.1. Materials and measurements

All chemicals and reagents were used as received without further purification. NMR spectra were performed with a Bruker Avance 400 MHz NMR spectrometer. Chemical shifts are given in parts per million (ppm) and referred to TMS as internal standard.  $^1\text{H}$  coupling constants  $J$  are given in Hertz (Hz). HRMS were recorded on the Exactive™ plus mass spectrometer from Thermo Fisher Scientific. The solid-state UV/Vis diffuse reflectance spectra (DRS) were recorded on a Lambda 900 UV–Vis spectrophotometer from Perkin–Elmer.

### 2.2. Synthesis

#### 2.2.1. Synthesis of NDI-PYR

According to the procedure reported in the literature [12], under the argon, a mixture of 1,4,5,8-naphthalenetetracarboxylic dianhydride (0.86 g, 3.2 mmol), 4-amino-3,5-di-methyl-pyrazole (0.75 g, 6.8 mmol), and anhydrous DMF (50 mL) were added to a three-necked flask and then heated in 150 °C for 8 h. After being cooled to room temperature, the dark brown DMF solution was poured into stirring diethyl ether (150 mL). The precipitated yellow solid was separated by filtration and re-crystallized from DMF/diethyl ether (10 mL/20 mL). The product was filtered and dried at 70 °C to afford 1.2 g (82%) of light yellow powder.  $^1\text{H}$  NMR (400 MHz; DMSO- $d_6$ , 298 K):  $\delta$  = 2.03 (s, 12H, pyrazole-CH<sub>3</sub>), 8.76 (s, 4H, naph-CH), 12.50 (s, 2H, pyrazole-NH).  $^{13}\text{C}$  NMR (100 MHz; DMSO- $d_6$ , 298 K):  $\delta$  = 31.25, 36.25, 112.29, 127.23, 127.34, 131.32, 162.77. HRMS (ESI): calculated for [M]<sup>−</sup>, 454.1390, found, 454.1386.

#### 2.2.2. Synthesis of crystals 1–3

Single crystals of 1–3 suitable for X-ray diffraction analyses were obtained by dissolving NDI-PYR in DMSO, DMF/diethyl ether (10:20) mixture solvent and DMF, respectively, followed by slow evaporation of the solvents.

#### 2.2.3. Synthesis of crystal 4 and 5

Single crystals of 4 and 5 suitable for X-ray diffraction analyses were obtained by dissolving a mixture of NDI-PYR and Phen (or Acen) (molar ratios are around 1:2) in DMF and then heating at 90 °C for one day, followed by cooling to room temperature.

### 2.3. X-ray crystallography study

Crystal data for cocrystals 1–4 were collected on a Rigaku Saturn 724 CCD diffractometer with Mo  $K\alpha$  radiation ( $\lambda$  = 0.71073 Å) at

173 K at 173 K, while 5 was collected using a SuperNova Atlas diffractometer equipped with Cu  $K\alpha$  radiation ( $\lambda$  = 1.54184 Å) at 293 K. The structures were solved by the direct method and different Fourier syntheses. All calculations were performed by full-matrix least-squares methods on  $F^2$  by using the SHELX-97 program [13], all non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were fixed at calculated positions and refined by a riding mode. Crystal data and the structure refinements are summarized in Table 1. In addition, crystallographic data have been deposited in the Cambridge Crystallographic Data Center as supplementary publication number CCDC 999709-999713, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### 2.4. Hirshfeld surface analysis

Molecular Hirshfeld surfaces [14] were constructed on the basis of the electron distribution calculated as the sum of spherical atom electron densities [15]. For a given crystal structure and a set of spherical atomic densities, the Hirshfeld surface is unique [16]. The normalized contact distance ( $d_{\text{norm}}$ ) based on both  $d_e$  and  $d_i$ , and the vdW radii of each atom, as given by eqn (1) enables identification of the regions of particular importance to intermolecular interactions. The combination of  $d_e$  and  $d_i$  in the form of a 2D fingerprint plot [17] provides a summary of intermolecular contacts in each crystal. The Hirshfeld surfaces mapped with  $d_{\text{norm}}$  and 2D fingerprint plots were generated using Crystal Explorer 2.1 [18]. Graphical plots of the molecular Hirshfeld surfaces mapped with  $d_{\text{norm}}$  used a red–white–blue color scheme, where red highlights shorter contacts, white represents the contact around vdW separation and blue is for longer contacts. Additionally, two further colored plots representing shape index and curvedness based on local curvatures are also presented [19].

$$d_{\text{norm}} = \frac{d_i - r_i^{\text{vdW}}}{r_i^{\text{vdW}}} + \frac{d_e - r_e^{\text{vdW}}}{r_e^{\text{vdW}}} \quad (1)$$

## 3. Results and discussions

### 3.1. Synthesis

NDI-PYR was synthesized in one step from the starting material naphthalene tetracarboxylic dianhydride and 4-amino-3,5-di-methyl-pyrazole in a high yield of 82% [12]. Single crystals of 1–3 were obtained by dissolving NDI-PYR in the commercially available DMSO, DMF/diethyl ether (10:20) mixture solvent and DMF, respectively, and then followed by slow evaporation of the solvents. However, the crystals 4 and 5 were afforded by heating a mixture NDI-PYR and phenanthroline (or acenaphthene) in pure DMF at 90 °C for 24 h and then cooling to room temperature. Interestingly, no cocrystals have been obtained when replacing the phenanthroline by other aromatic molecules, such as benzene, toluene, naphthalene, anthracene, phenanthrene, biphenyl, 2-(2-pyridyl)pyridine and 4-(4-pyridyl)pyridine.

### 3.2. Single-crystal structural descriptions

#### 3.2.1. Crystal structure of 1

The X-ray single crystal diffraction analysis reveals that crystal 1 is pure NDI-PYR that has been crystallized in a monoclinic space group  $P2_1/c$ . The dihedral angle between NDI core and pyrazole group is 75.63°. The adjacent NDI-PYR molecules are connected each other through intermolecular hydrogen bonds between H

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