

# Novel chromophores of cyanopyridine series with strong solvatochromism and near-infrared solid-state fluorescence

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## ABSTRACT

A series of novel pyridine derivatives containing tetracyanobutadiene moiety (4-CN-TCPy) were obtained in good yields by the reaction of 2-chlorosubstituted pyridine-3,4-dicarbonitriles with malononitrile using Cs<sub>2</sub>CO<sub>3</sub> as a catalyst. The resulting 4-CN-TCPy are stable intensively colored substances possessing a solid-state emission in the red and near-infrared region. Solutions thereof are characterized with a strong solvatochromic effect as well as weak blue fluorescence.

## 1. Introduction

The study of methods for the synthesis of novel organic chromophores, in particular cyano-containing ones, as well as the study of their physicochemical properties, is an intensively developing field of modern science [1–27]. Conjugated small molecules are functional  $\pi$ -electron systems forming the molecular basis of the modern organic optoelectronics and solar energy conversion. For instance, cyano-substituted chromophores find applications in organic electro-optic materials [1–4], non-linear optic (NLO) materials [5–11], organic light-emitting diodes (OLEDs) [12–15], dye-sensitized solar cells (DSSCs) [16–21], organic field effect transistors (OFETs) [22–24] or chemosensor arrays in analytics [25–27].

Among the organic chromophores a special place is occupied by nitriles. This is due to the fact that the cyano group is very polar, compact, flat and possesses a strong electron withdrawing effect. The most well-known representatives of compounds containing several cyano groups are acyclic tricyanobutadienes (TCB) [9,10], 2-dicyanomethylene-3-cyano-2,5-dihydrofurans (TCF) [1,5–7,11,20] and 3-cyano-5-dicyanomethylene-pyrrolidines (TCP) [4,8,19,28,29] (Fig. 1). They are known to exhibit fluorescent, nonlinear optical properties, and can be used as components of information storage devices as well as components of active layer in the dye-sensitized solar cells (DSSC) [7].

At the same time, there is almost no information in the literature about such properties and an application of the recently synthesized 2-(3-cyanopyridin-2(1*H*)-ylidene)malononitriles (tricyanopyridines,

TCPy) [30], except of 4-Ar-TCPy derivatives [31]. In our opinion, the structure TCPy has a number of advantages over well-studied TCB, TCF and TCP. Since the presence of three different substituents makes it possible to significantly vary the conjugated system by the addition of donor or acceptor groups (Fig. 1). It offers an abundant library of compounds with well-adjustable molecular properties.

There are only a few methods for the synthesis of TCPy derivatives [30–32], and because of this their application is very limited. Previously, we reported that tricyanopyridines can be obtained on the basis of the dimer malononitrile and carbonyl compounds [30–32] and we noted that the products exhibit fluorescent properties [31]. Continuing our investigations, we set a purpose to obtain a stronger acceptor moiety, in this work we describe for the first time a method for the synthesis of pyridines containing a tetracyanobutadiene fragment. Moreover, it is known that the introduction of the cyano group at the fourth position of the pyridine ring affects significantly on the fluorescent properties of the compounds. In particular, for the 4-CN-TCPy analogues having an oxo group in place of the malononitrile fragment a high quantum yield of fluorescence was shown in comparison with analogues without cyano groups [33,34].

## 2. Experimental section

### 2.1. Materials and apparatus

The progress of reactions and the purity of the products were

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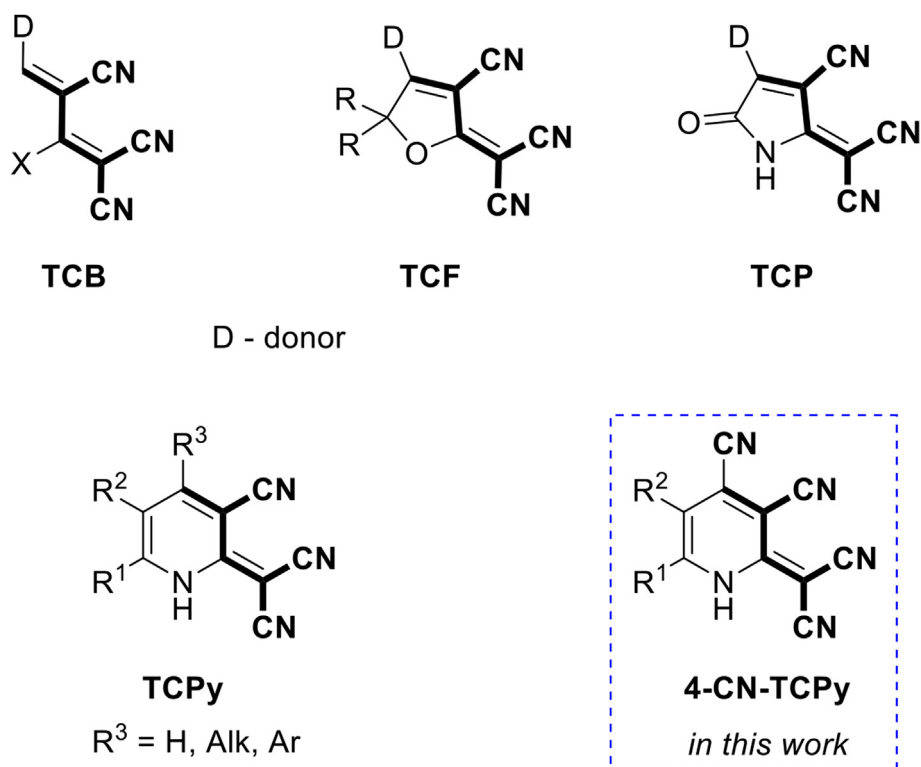


Fig. 1. Cyano-substituted chromophores containing butadiene-1,1,3-tricarbonitrile moiety.

monitored by TLC on Sorbfil plates (spots were visualized under UV light, by treatment with iodine vapor or by heating). The IR spectra were recorded on an FSM-1202 spectrometer with Fourier transform from samples dispersed in mineral oil. The NMR spectra were measured in DMSO-*d*<sub>6</sub> on a Bruker DRX-500 spectrometer using TMS as an internal reference. The elemental compositions were determined on a CHN analyzer vario Micro cube. The mass spectra (EI, 70 eV) were obtained on a Finnigan MAT INCOS-50 spectrometer. The UV spectra were recorded on an SF-2000 spectrophotometer. Melting points were determined on the device OptiMelt MPA-100. Fluorescence spectra were recorded on a Fluorat<sup>®</sup>-02-Panorama spectrofluorimeter. Solid-state emission was registered in powders at room temperature on the Cary Eclipse fluorescence spectrophotometer.

The XRD data of **3m** and **5** were collected by using STOE diffractometer Pilatus100 K detector, focusing mirror collimation Cu K $\alpha$  (1.54086 Å) radiation, rotation method mode. STOE X-AREA software was used for cells refinement and data reduction. Data collection and image processing was performed with X-Area 1.67 (STOE & Cie GmbH, Darmstadt, Germany, 2013). Intensity data were scaled with LANA (part of X-Area) in order to minimize differences of intensities of symmetry-equivalent reflections (multi-scan method). The structures were solved and refined with SHELX program [35]. The non-hydrogen atoms were refined by using the anisotropic full matrix least-square procedure. Hydrogen atoms were placed in the calculated positions and allowed to ride on their parent atoms. The final R 0.043/0.039 against 1886/1882 F<sub>2</sub> > 2 $\sigma$ (F<sub>2</sub>) for compound **3m** and compound **5** crystals respectively.

Molecular geometry calculations were performed with the SHELX program, and the molecular graphics were prepared by using DIAMOND software.

These data 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) (**3m** – CCDC 1813743; **5** – CCDC 1813744).

## 2.2. General procedure for the preparation of dyes

The syntheses of compounds **1** and **2** were described previously. Starting 4-oxoalkane-1,1,2,2-tetracyanonitriles **1** were prepared according to the known procedure for interaction of tetracyanoethylene (TCNE) and carbonyl compounds [36–38]. 2-Chloropyridine-3,4-dicarbonitriles **2a-h** were obtained from corresponding 4-oxoalkane-1,1,2,2-tetracyanonitriles **1** and hydrogen chloride [38–40].

Synthesis of TCPy **3a-3m**: 0.70 g (10.61 mmol) of malononitrile was dissolved in 10 ml of DMF, then 3 g (9.2 mmol) of cesium carbonate and 7 mmol of the appropriate chloropyridine **2** were added. The reaction mixture was stirred at room temperature for 20 h. Then the mixture was diluted up to 100 ml with water and acidified with 15% aqueous HCl (till pH = 1) and then stirring was continued for 1 h. Further precipitate crystals were filtered off, washed with water (30 ml) and propan-2-ol (20 ml). The precipitate was dried in a vacuum desiccator.

### 2.2.1. 2-(Dicyanomethylene)-6-methyl-1,2-dihydropyridine-3,4-dicarbonitrile (**3a**)

Red solid. Yield: 78%. mp 249–251 °C (dec.). IR (KBr): 2211, 2201 (C $\equiv$ N), 1568, 1531 cm<sup>-1</sup>. <sup>1</sup>H NMR (500.13 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 2.32 (s, 3H, CH<sub>3</sub>), 6.55 (br. s, > 1H, NH + H<sub>2</sub>O), 6.90 (s, 1H, CH Pyr). <sup>13</sup>C NMR (125.76 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 23.96 (CH<sub>3</sub>), 41.96 (C(CN)<sub>2</sub>), 91.70 ( $\beta$ -Pyr), 114.67 (CN), 114.80 (CN), 115.26 (CN), 120.26, 125.31, 159.63, 161.74. MS *m/z* (%): 207 ([M<sup>+</sup>], 34). Anal. Calcd for C<sub>11</sub>H<sub>5</sub>N<sub>5</sub>: C, 63.77; H, 2.43; N, 33.80. Found: C, 63.71; H, 3.22; N, 31.73.

### 2.2.2. 2-(Dicyanomethylene)-5,6-dimethyl-1,2-dihydropyridine-3,4-dicarbonitrile (**3b**)

Dark red solid. Yield: 82%. mp 240–241 °C (dec.). IR (KBr): 2211, 2198 (C $\equiv$ N), 1577, 1532 cm<sup>-1</sup>. <sup>1</sup>H NMR (500.13 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 2.24 (s, 3H, CH<sub>3</sub>), 2.35 (s, 3H, CH<sub>3</sub>), 10.35 (br. s, > 1H, NH + H<sub>2</sub>O). <sup>13</sup>C NMR (125.76 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 16.22 (CH<sub>3</sub>), 22.97 (CH<sub>3</sub>), 40.20 (C(CN)<sub>2</sub>), 91.38 ( $\beta$ -Pyr), 114.75 (CN), 115.17 (CN), 120.90 (2CN), 122.90, 124.44, 157.66, 161.36. MS *m/z* (%): 221 ([M<sup>+</sup>], 11).

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