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New V-shaped 2,4-di(hetero)arylpyrimidine push-pull systems: Synthesis, solvatochromism and sensitivity towards nitroaromatic compounds

Egor V. Verbitskiy[a,b,*], Ekaterina M. Dinastiya[a], Anna A. Baranova[b], Konstantin O. Khokhlov[b], Roman D. Chuvashov[b], Yuliya A. Yakovleva[b], Nadezhda I. Makarova[c], Elena V. Vetrova[c], Anatoly V. Metelitsa[c], Pavel A. Slepukhin[a,b], Gennady L. Rusinov[a,b], Oleg N. Chupakhin[a,b], Valery N. Charushin[a,b]

[a] *I. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, S. Kovalevskaya Str., 22, Ekaterinburg, 620990, Russia*
[b] *Ural Federal University, Mira St. 19, Ekaterinburg, 620002, Russia*
[c] *Institute of Physical and Organic Chemistry, Southern Federal University, Stachki Av., 194/2, Rostov on Don, 344090, Russia*

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ABSTRACT

Novel D–π–A–π–D type pyrimidine-based dyes, possessing (hetero)aryl electron-donating groups in 2,4-positions were synthesized, and their photophysical properties were investigated by using absorption and emission spectral analyses. All dyes proved to exhibit a strong emission solvatochromism with quantum yields up to 0.96, depending on their molecular structure and solvent polarity. The compounds have been established to undergo a reversible protonation, directed at nitrogen atoms of the pyrimidine ring, and these phenomena are associated with dramatic color changes. In addition, fluorophores **5a-d** show a high sensitive response for nitroaromatic traces in solutions or real-time detection of their vapors in air. These findings indicate that the compounds obtained can be regarded as excellent fluorophores for fluorescent material applications.

1. Introduction

During the last two decades, the family of fluorescent pyrimidine sensors of the D-π-A type (donor-π-acceptor), has demonstrated a growing interest due to their high sensitivity, selectivity and easy measurements [1]. Another fascinating advantage of such materials is that their electro-optical properties can be tuned effectively by judicious choice of electron-donating and electron-withdrawing substituents [1]. Particularly, pyrimidine fluorophores have been used as metal cation [2–4], polarity [5–9] and pH [9–12] sensors, and those structures with a larger absorption and emission wavelengths can also be applied in biological and medical studies [13,14]. Recently, the straightforward synthesis of the series of 4-(hetero)aryl (**I**), 4,5-di(hetero)aryl (**II**) and 4,5,6-tri(hetero)aryl (**III**) substituted pyrimidines by using the methodology of nucleophilic aromatic substitution (the $S_N{}^H$ protocol) [15] has been described, and these structures can be applied for effective detection of various nitroaromatic explosives (see Fig. 1) [16–21].

As a further extension of our research studies on the design of novel fluorophores for chemosensors, in this communication we wish to describe the synthesis of a new series of D-π-A- π-D pyrimidine-based compounds **5a-d** obtained through incorporation of appropriate electron-donative substituents into the pyrimidine ring *via* a 2,5-thienyl linkage, and systematic investigation of their photophysical properties, solvatochromism, structure-property relationships and applications, as fluorescent sensors for nitroaromatic explosives.

2. Experimental section

2.1. General information

All reagents and solvents were obtained from commercial sources and dried by using standard procedures before use. Nitroaromatic explosives, including 2,4-dinitroanisole (DNAN), picric acid (PA), styphnic acid (SA), 1,3,5-triethoxy-2,4,6-trinitrobenzene (TETNB), 2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT), 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) were of analytical grade and used directly without further purification. (Caution: All nitro-containing compounds used in the present study are high explosives and should be handled only in small analytical quantities). The solvents (1,4-dioxane and H_2O) for the microwave-assisted Suzuki cross-coupling reaction were deoxygenated by bubbling argon for 1 h.

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[*] Corresponding author. I. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, S. Kovalevskaya Str., 22, Ekaterinburg, 620990, Russia
E-mail address: verbitsky@ios.uran.ru (E.V. Verbitskiy).

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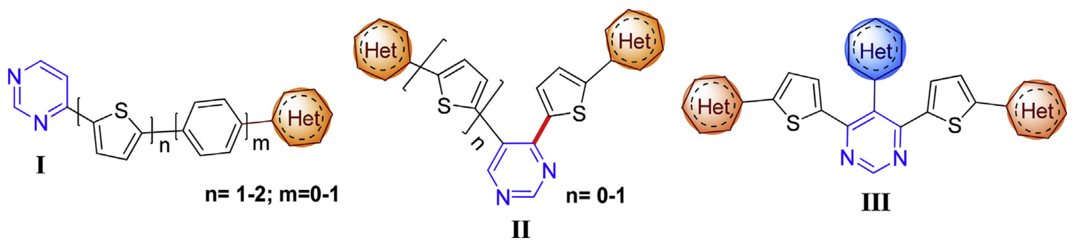

Fig. 1. Structures of push-pull pyrimidine-based fluorophores **I-III**.

^{1}H and ^{13}C NMR spectra were recorded on an AVANCE-500 instrument using Me4Si as an internal standard. Elemental analysis was carried on a Eurovector EA 3000 automated analyzer. High resolution mass spectrometry was performed using a Bruker maXis Impact HD spectrometer. Melting points were determined on Boetius combined heating stages and were not corrected.

Flash-column chromatography was carried out using Alfa Aesar silica gel 0.040–0.063 mm (230e400 mesh), eluting with ethyl acetate-hexane. The progress of reactions and the purity of compounds were checked by TLC on Sorbfil plates (Russia), in which the spots were visualized with UV light (λ 254 or 365 nm).

The XRD analysis of the single crystal of **5a** was carried out using an "Xcalibur 3" diffractometer on standard procedure (MoK-irradiation, graphite monochromator, ω-scans with 1° step, $T = 295(2)$ K). The empirical absorption correction was applied. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization in anisotropic approximation for non-hydrogen atoms. The H-atoms were refined in isotropic approximation in the "rider" model. Deposition number CCDC 1846582 for **5a** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

Microwave experiments were carried out in a Discover unimodal microwave system (CEM, USA) with a working frequency of 2.45 GHz and the power of microwave radiation ranged from 0 to 300 W. The reactions were carried out in a 10 mL reaction tube with the hermetic Teflon cork. The temperature of the reaction was monitored using an inserted IR sensor by the external surface of the reaction vessel.

UV/vis spectra were recorded for a 2×10^{-5} M solutions with Varian Cary 100 spectrophotometer. Photoluminescent spectra were recorded for a $(1.0–3.0) \times 10^{-6}$ M solutions on a Varian Cary Eclipse fluorescence spectrophotometer. UV/vis and fluorescence spectra were recorded using standard 1 cm quartz cells at room temperature. The Φ_F values were calculated using a well known procedure with quinine sulfate in 0.1 M H_2SO_4 [22]. Stokes shifts were calculated considering the lowest energetic absorption band.

The fluorescence quenching studies were carried out on a Hitachi F-7000 fluorescence spectrophotometer at room temperature in acetonitrile. For each analyte, the typical test procedure was as follows: 2.5 mL of acetonitrile solution of one of the fluorophores (5.0×10^{-7} mol/L) was drawn and placed in a quartz cell of the standard size. Without analyte the fluorescence spectrum of pure fluorophore was first recorded. Subsequently, different amounts of analyte were added respectively in the cell. Each time after full mixing the analyte with fluophore, the fluorescence spectrum was registered. The plots of I_0/I values of the quenching systems as functions of quencher concentrations ([Q]) were well described by the Stern–Volmer equation, $I_0/I = 1 + K_{sv}[Q]$, where I_0 and I are fluorescence intensities without and in the presence of analyte. The detection limits were calculated by use literature procedure (see details in *Supporting Information*). To investigate detection of nitroaromatic explosives in vapor phase the original device « Zaslon-M» (see Fig. S1 in *Supporting Information*) has been used.

This device was produced by company « EnergoSpetsKomplektServis» (Moscow region, Mytischi, Russia). The instrument is based on registration of excited steady-state luminescence quenching. Sensors for this device were obtained by application of a dye solution on the cellulose matrix. Reduction of the luminescence intensity of the sensor takes place due to an interaction with explosive vapors contained in the air. The decrease rate of the luminescence intensity indicates at the concentration of vapors. To study luminescent properties of the sensor element, its luminescence spectra excited by photons with energies in the range 280–425 nm were measured. The excitation photoluminescence spectra for luminescence bands of the sensor element were also measured. Excitation source was light emitting diode (375 nm), and luminescent signal receiver was a photodiode (430–650 nm) in the device. The device was operating under control of the program algorithm, which provides multiple operating modes (configuration, calibration, measurement etc.). The advantages of this device are autonomic power, a low weight and small sizes, as well as simplicity of operations for measurements. The calibration of the device « Zaslon-M» was carried out by using the internal software. The fluorescence measurements (excited at 375 nm) for nitroaromatic vapors were performed with the device « Zaslon-M » connected with a computer.

The sensor for detection of NACs in vapor phase has been designed as cartridge [16]. The cartridge has two parts which are connected at the contour of the framework. In previous investigation, it has been shown that non-woven spunlace fabric (70% viscose, 30% polyester, Industrial Spunlace purchased from Afalina Co., Ltd., Russia) is the best porous substrate for fabrication of sensors [19]. The parts of cartridge made from Plexiglas were connected to each other along the contour by means of acrylonitrile glue. A piece of spunlace (50 mm in diameter) was immersed in the fluorophore solution with a concentration 1.0×10^{-3} M for 5 min. Then, spunlace with immobilized fluorophore **5a** (**5b**, **5c** or **5d**) was removed from the solution and dried at 70–80 °C for 30 min. To demonstrate its application as a fluorescence sensor for NAC detection, the obtained spunlace was placed in cartridge.

To detect vapors of nitroaromatic compounds, such as TNT (400 mg), 2,4-DNT (1.0 g) and nitrobenzene (1 mL) in open glass tubes (150 mm in diameter), they were placed in a hermetic glove-box (0.8 m × 0.6 m × 0.4 m). Explosive was kept in this box during 48 h at room temperature until saturated vapor was formed. Similar protocol was used for interferents (15 mL), such as ammonia, ethanol, ethylene glycol, acetone, acetic acid and toluene.

2.2. *2,4-Di(thiophen-2-yl)pyrimidine (2)*

A mixture of 2,4-dichloropyrimidine (**1**) (500 mg, 3.36 mmol), 2-thienylboronic acid (1.29 g, 10.07 mmol), $Pd(PPh_3)_4$ (388 mg, 10 mol %) and K_3PO_3 (3.56 g, 16.78 mmol) was dissolved in 1,4-dioxane (50 mL). The reaction mixture was degassed and refluxed for 10 h under an argon atmosphere. The solvent was removed under reduced pressure, and the residue was extracted with EtOAc. The organic layer was washed with water and then saturated sodium chloride solution, dried over anhydrous Na_2SO_4, and then evaporated in vacuum to dryness. The residue was purified by silica gel column chromatography with ethyl acetate/hexane (1:2, v/v) as an eluent to give the target compound **2**. Yield 820 mg (87%), beige powder, mp 79–81°C.^{1}H NMR