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Design and synthesis of a novel PET and ICT based 1,8-naphthalimide FRET bichromophore as a four-input Disabled–Enabled–OR logic gate

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ABSTRACT

The synthesis, sensor activity and logic behavior of a novel donor–acceptor system based on ICT and PET 1,8-naphthalimide fluorescent probes is reported. The system was configured on the “fluorophore₁–receptor₁–fluorophore₂–spacer–receptor₂” model where the two probes are integrated in a logic circuit comprising a FRET bichromophoric system with multilevel fluorescent output. The synthesized compound shows colorimetric and fluorescence signaling properties as a function of pH and in the presence of transition metal ions with emphasis on Cu²⁺ and Pb²⁺. Due to the remarkable fluorescence and absorption changes in the presence of protons, hydroxide anions, Cu²⁺ and Pb²⁺ ions the novel system executes four-input Disabled–Enabled–OR logic gate as well as two-input INHIBIT and IMPLICATION logic gates and is able to act as a three output combinatorial logic circuit with four chemical inputs. Due to the parallel action of four-input input₄–Disabled–input₃–Enabled–OR logic gate (Output 1) with INHIBIT (Output 2) and IMPLICATION (Output 3) gates, the system can be switched over Disable and Enable mode reversibly.

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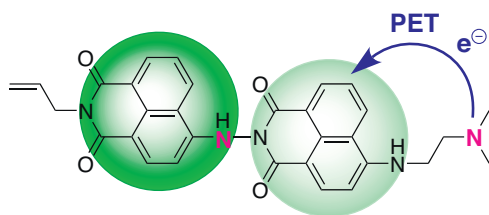
1. Introduction

A significant goal in the field of nanotechnology is the design of multi-functional molecular devices with built-in individually functional components which are working cooperatively as a whole [1]. Supramolecular devices that show large changes in their so called “off” and “on” states are currently of great interest as these can be modulated, or tuned, by employing external sources such as ions, molecules, light, etc. [2–5]. The “off” and “on” states of the molecular-level devices refer to their luminescence, magnetic or electronic properties. The binary possibilities where the signal change was large enough to be considered as “off-on” or “on-off” are increasingly conscious of information technology. Following the concept of molecular logic proposed by Aviram [6], de Silva demonstrated experimentally the analogy between molecular switches and electronic logic gates [7]. Since then, a large number of significant logic functions were exploited [8–10]. In particular, fluorescent systems and their excited-state processes (charge- or electron transfer, energy transfer, proton transfer) have been frequently employed in the rational design of molecular logic

devices [11]. These molecules capable of carrying out a variety of sensing functions simultaneously, and that compute a composite result autonomously, have great potential for real-life applications such as object coding and imaging, intelligent materials, drug delivery and activation, diagnostics or actuation [12–15]. In nearly two decades, all 16 fundamental logic gates [16–19] and more complex systems such as half-adder/subtractor [20], full-adder/subtractor [21], multiplexer [22], encoder/decoder [23], digital comparator [24,25] and keypad lock [26] were demonstrated. Also a smart oligonucleotide-based constructs playing simple games such as Tic–Tac–Toe [27] and molecular scale “anticancer destroyer” [28] have been reported. Nevertheless, the physical integration of molecular logic gates is especially important for rational design and implementation toward advanced molecular scale computing.

Two common principles for fluorescence molecular switches are used: photoinduced electron transfer (PET) and internal charge transfer (ICT) [29,30]. Fluorescent PET systems based on the “fluorophore–spacer–receptor” format are the most commonly exploited approach for the design of the fluorescent sensors and switches [31]. The components are chosen so that PET from electron rich receptor (usually an amino group) to the fluorophore excited state quenches the fluorescence of the system. Upon recognition of guest, which binds to the receptor, engaging its lone-pair electrons, the PET process is no longer possible and the fluorescence of

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Scheme 1. 1,8-Naphthalimide bichromophoric system based on ICT and PET.

the system is recovered [32]. In contrast with PET systems, in the ICT chemosensors the receptor is directly attached to the electron-donating/withdrawing unit that is conjugated to the fluorophore an electron-withdrawing/electron-donating unit [33,34]. During excitation of the system the fluorophore undergoes donor–acceptor intramolecular charge transfer which strongly depends on the microenvironment of the fluorophore. Thus recognition of guest affects the ICT efficiency that changes the energy between ground and excited state and results in shifting of the fluorophore electronic spectra [35,36]. The amalgamation of PET and ICT pathways has provided examples of multilevel logic systems with multiple logic functions, including arithmetic operations by modulation of the fluorescence output [37–40].

In the living organisms the molecular logic operations are realized by integration of parallel or successive chemical reactions that are controlled (disabled or enabled) by different chemical inputs the most important of which is the pH. That is why herein we pay attention on a molecular level logic gate with reversible pH dependent disabled/enabled mode. We propose a cascade of two molecular fluorescent probes that are integrated in logic circuit comprising a FRET bichromophoric system with multilevel output. We chose the FRET based bichromophore because it ensures a ratiometric fluorescent output. The single emission-based measurement by increasing fluorescence intensity without large shift of either excitation or emission wavelength can be influenced by many factors, such as the localization of the sensor, changes of environment around the sensor (e.g., pH, polarity and temperature), emission collection efficiency, effective cell thickness in the optical beam, and changes in excitation intensity [41]. These interferences can be eliminated by employing ratiometric fluorescent probes, which allow the measurement of changes of the intensity ratio at two emission bands to provide built-in correction for the above-mentioned environmental effects [42,43].

The examined bichromophoric system was constructed by coupling of a 1,8-naphthalimide acceptor dye with ICT chemosensing properties and a photoinduced electron transfer (PET) based 1,8-naphthalimide donor (Scheme 1).

The PET process results in an OR logic gate using metal cations as inputs while the ICT pH-sensing process serves as disabler or enabler of the observed PET based OR gate. The novel system operates with two amino-protons and therefore it needs strong acid–base balance. The disabling–enabling process is achievable by the acid amine and requires transition from neutral to strong alkaline media while the PET based OR logic gate works in neutral media using amine group with base properties.

2. Experimental

2.1. Materials

The intermediate *N*-allyl-4-nitro-1,8-naphthalimide **2** was prepared according to the reported procedure [44]. Commercially available 2-(dimethylamino)ethylamine, hydrazine monohydrate, 4-nitro- and 4-chloro-1,8-naphthalic anhydrides (Aldrich) were

used without purification. All solvents (Aldrich, Fisher Chemical) were pure or of spectroscopy grade. Commercial borate buffer (pH = 10, ACROS Organics™) was used. $\text{Zn}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, $\text{Hg}(\text{NO}_3)_2$, and AgNO_3 salts were the sources for metal cations (all Aldrich salts at p.a. grade).

2.2. Methods

FT-IR spectra were recorded on a Varian Scimitar 1000 spectrometer. The ^1H NMR spectra (chemical shifts are given as δ in ppm) were recorded on a Bruker DRX-250 spectrometer operating at 250.13 MHz. TLC was performed on silica gel, Fluka F60 254, 20×20 cm, 0.2 mm. The UV–vis absorption spectra were recorded on a spectrophotometer Hewlett Packard 8452A. The fluorescence spectra were taken on a Scinco FS-2 spectrofluorimeter. The fluorescence quantum yields (Φ_F) were measured relatively to Coumarin 6 ($\Phi_F = 0.78$ in ethanol [45]) as a standard. All the experiments were performed at room temperature (25.0 °C). A 1×1 cm quartz cuvette was used for all spectroscopic analysis. To adjust the pH, very small volumes of hydrochloric acid and sodium hydroxide were used. The effect of the metal cations upon the fluorescence intensity was examined by adding portions of the metal cations stock solution (fresh prepared aqueous solutions) to a known volume of the fluorophore solution (10 mL, water/DMF 3:1, v/v). The addition was limited to 100 μL so that dilution remains insignificant.

2.3. Synthesis

2.3.1. Synthesis of 1,8-naphthalimide **3**

4-Nitro-1,8-naphthalimide **2** (0.85 g, 3.0 mmol) was added to 5 mL of hydrazine monohydrate. The reaction mixture was refluxed for 2 h under stirring then poured into water. The precipitate was collected by filtration, washed with water and dried to yield *N*-allyl-1,8-naphthalimide **3** as a yellow solid (0.78 g, 97%).

FT-IR (KBr) cm^{-1} : 3380 (νNH) and 3314 (νNH₂); 1673 (ν^{as}N–C=O); 1637 (ν^sN–C=O). ^1H NMR (CDCl_3 -d, 250.13 MHz) ppm: 8.60 (d, 1H, $J = 8.0$ Hz, Naphthalimide H-2); 8.53 (d, 1H, $J = 7.9$ Hz, Naphthalimide H-7); 8.29 (d, 1H, $J = 8.1$ Hz, Naphthalimide H-5); 7.73 (dd, 1H, $J = 7.9$ Hz, $J = 8.1$ Hz, Naphthalimide H-6); 7.34 (d, 1H, $J = 8.0$ Hz, Naphthalimide H-3); 5.98 (m, 1H, $\text{NCH}_2\text{CH}=\text{CH}_2$); 5.31 (d, 1H, $J_{\text{trans}} = 16.5$ Hz, allyl $\text{HCH}=\text{CH}_2$); 5.25 (d, 1H, $J_{\text{cis}} = 9.3$ Hz, allyl $\text{HCH}=\text{CH}_2$); 4.79 (br.s, 1H, NH); 4.58 (d, 2H, $J = 5.7$ Hz, $\text{CH}_2\text{CH}=\text{CH}_2$); 2.38 (br.s, 2H, NH₂). Elemental analysis: Calculated for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_2$ (MW 267.28) C 67.40, H 4.90, N 15.72%; Found C 67.65, H 5.08, N 15.39%.

2.3.2. Synthesis of light emitting bisnaphthalimide **5**

1,8-Naphthalimide **3** (0.7 g, 2.6 mmol) was added to a solution of 4-chloro-1,8-naphthalic anhydride (0.61 g, 2.6 mmol) in 20 mL of acetic acid. The resulting solution was refluxed for 16 h. After cooling the yellow–orange precipitate was filtered off and dried to afford 1.10 g (88%) of bisnaphthalimide **4**.

To a suspension of 2-(dimethylamino)ethylamine (0.37 mL, 4.0 mmol) and 0.5 g of bisnaphthalimide **4** (1.0 mmol) in 15 mL of DMF, 0.1 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were added. The resulting mixture was heated to reflux for 5 h with stirring. After cooling to room temperature, the mixture was filtrated and filtrate was poured into 20 mL of water. The desired compound **5** that precipitated was collected by filtration, washed with water and dried (0.41 g, 76%).

FT-IR (KBr) cm^{-1} : 3328 (νNH); 1706 (ν^{as}N–C=O); 1688 (ν^sN–C=O); 1684 (ν^{as}N–C=O); 1652 (ν^sN–C=O). ^1H NMR (CDCl_3 -d, 250.13 MHz) ppm: 8.64–8.42 (m, 6H, $2 \times$ Naphthalimide H-2, $2 \times$ Naphthalimide H-7 and $2 \times$ NH); 8.36 (d, 1H, $J = 8.1$ Hz, Naphthalimide-1 H-5); 8.25 (d, 1H, $J = 8.2$ Hz, Naphthalimide-2 H-5); 7.64 (t, 1H, $J = 7.9$ Hz, Naphthalimide-1 H-6); 7.37 (t, 1H,

$J = 7.7$ Hz, Naphthalimide-2 H-6); 7.06 (d, 1H, $J = 8.3$ Hz, Naphthalimide H-3); 6.63 (d, 1H, $J = 8.2$ Hz, Naphthalimide H-3); 5.93 (m, 1H, $\text{NCH}_2\text{CH}=\text{CH}_2$); 5.21 (d, 1H, $J_{\text{trans}} = 17.2$ Hz, allyl $\text{HCH}=\text{CH}_2$); 5.12 (d, 1H, $J_{\text{cis}} = 10.0$ Hz, allyl $\text{HCH}=\text{CH}_2$); 4.72 (d, 2H, $J = 5.2$ Hz, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$); 3.42 (t, 2H, $J = 5.6$ Hz, ArNHCH_2); 2.71 (t, 2H, $J = 5.5$ Hz, NCH_2); 2.30 (s, 6H, $2 \times \text{NCH}_3$); Elemental analysis: Calculated for $\text{C}_{31}\text{H}_{27}\text{N}_5\text{O}_4$ (MW 533.58) C 69.78, H 5.10, N 13.13%; Found C 70.14, H 5.37, N 12.85%.

3. Results and discussion

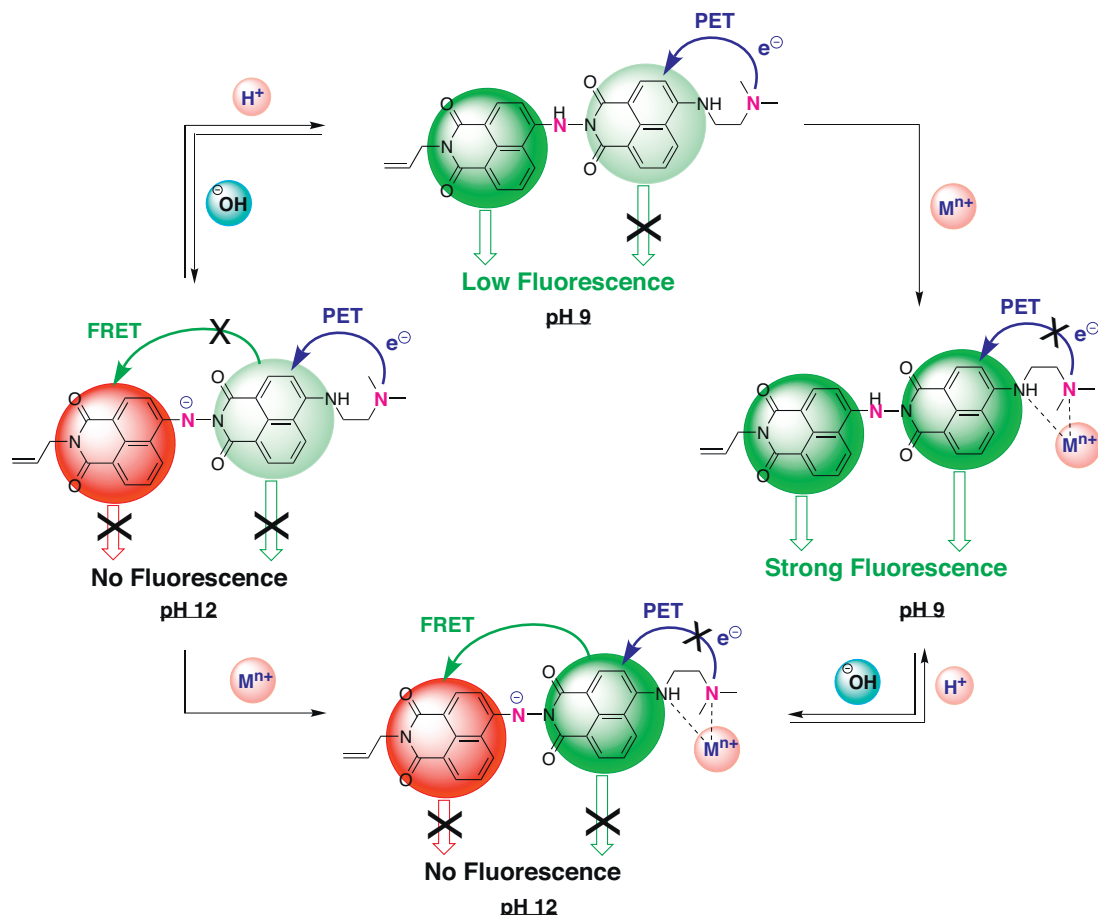
3.1. Design and synthesis of bichromophoric system 5

The novel 1,8-naphthalimide bichromophoric system **5** was configured on the “fluorophore₁–receptor₁–fluorophore₂–spacer–receptor₂” model. The both fluorophores are 4-amino-1,8-naphthalimides with very similar absorption and emission properties, that is why they absorb and emit light in the same spectral region. As a result the bichromophoric system **5** has typical for 4-amino-1,8-naphthalimides excitation input in range of 350–450 nm and fluorescence output between 450 and 650 nm [46]. The 4-(*N*-dimethyl)ethylamino-1,8-naphthalimide comprises the “fluorophore₂–spacer–receptor₂” part in which the PET process from tertiary alkylamino nitrogen quenches the 4-amino-1,8-naphthalimide fluorophore excited state. This represents the “fluorophore₂” “off-state” and the bichromophore **5** has medium fluorescence output owing to the “fluorophore₁” emission (Scheme 2). However upon cation recognition, which binds to the tertiary amine receptor, engaging its lone-pair electrons, the PET process is no longer possible and the fluorescence of the

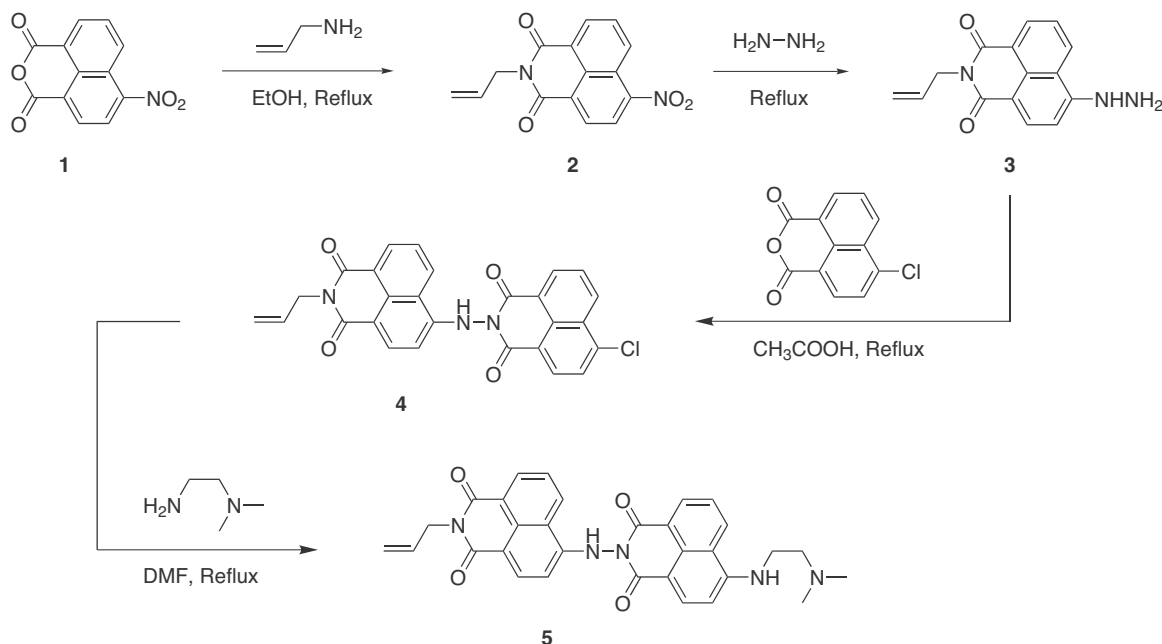
system is recovered [47]. In this state “fluorophore₂” is “switched-on” and the system has strong fluorescence owing to the simultaneous emission of the both fluorophores in Dyad **5**.

The 4-imidoamino-1,8-naphthalimide part in Dyad **5** represents the “fluorophore₁–receptor₁” architecture with ICT chemosensing properties, where the 4-amino-1,8-naphthalimide is fluorophore and imidoamine group possessing labile hydrogen is a receptor moiety. The fragments with labile N–H bonds are widely used for anion recognition because the acidity of the NH group can be easily tuned by adjusting the electronic properties of the neighboring substituents so that it can recognize anions through hydrogen-bonding or deprotonation interactions [48,49].

It is well known that absorption and fluorescence characteristics of the 1,8-naphthalimides depend on the nature of the substituent at C-4 position of the 1,8-naphthalimide ring [50]. The 4-amino-1,8-naphthalimide is a “push–pull” π -electron system in which the light absorption generates a charge transfer interaction between C-4 amine donating substituent and the both peri-positioned carbonyl acceptors. When an anion, such as OH^- , interacts with the amino group in 4-amino-1,8-naphthalimide fluorophore, the amine electron-donating ability is increased due to the deprotonation which generates a strong electron density around amino nitrogen. As a result the ICT efficiency in the 1,8-naphthalimide fluorophore strongly increases and red shifting (colorimetric changes from yellow to red color) along with lower quantum yield are expectable [51]. This would represent the “fluorophore₁” “off-state”. In this state “fluorophore₁” absorption is in a range of about $\lambda_A = 400$ –600 nm, where the emission of 4-alkylamino-1,8-naphthalimide appears. This opens pathway for possible FRET from “fluorophore₂” to “fluorophore₁” and quenching the “fluorophore₂”



Scheme 2. Fluorescence changes of Dyad **5** in the presence of protons (0.01 M HCl), hydroxide anions (0.01 M NaOH) and analyte (Me^{n+} , 1 eq.).



Scheme 3. Synthesis of bichromophoric system 5.

excited state. That is why, when the “fluorophore₁” is in “off-state” the system always shows low fluorescence output, even in a case when the PET process in “fluorophore₂–spacer–receptor₂” is cut off (Scheme 2).

The synthesis of bichromophoric system 5 was performed as shown in Scheme 3. First, the intermediate 4-nitro-1,8-naphthalimide 2 was obtained by reaction of 1,8-naphthalic anhydride 1 with allylamine as we reported before [44]. Then the nitro group in 2 was nucleophilically substituted with hydrazine by analogy with a previously reported procedure [52] to give 4-hydrazino-1,8-naphthalimide 3. The final Dyad 5 was obtained by reaction of 4-chloro-1,8-naphthalic anhydride with 3 and subsequent substitution of the chlorine at C-4 position with N-dimethylethylenediamine.

The structure and purity of the synthesized compounds were characterized and confirmed by conventional techniques—elemental analysis data, UV-vis, fluorescence, FT-IR and ¹H NMR spectroscopy. For instance, in the ¹H NMR (CDCl₃-d, 250.13 MHz) spectrum of Dyad 5 a resonances at 7.06 ppm and 6.63 ppm (Fig. 1A and B) were observed which are characteristic for protons in position C-3 of the yellow-green emitting 1,8-naphthalimide, substituted in C-4 position with an electron-donating amino group. The resonance of 4-imidoamino-1,8-naphthalimide (7.03 ppm) is different from the corresponding resonance for the 4-alkilamino-1,8-naphthalimide moiety (6.63 ppm) due to the lower electron donating ability of imidoamino fragment and logically appears in low field. The presence of the both resonances in ratio of 1:1 is solid evidence that the target bichromophoric system was successfully synthesized.

3.2. Effect of pH on the photophysical properties of probe 5

Photophysical properties of Dyad 5 were determined in water/DMF (3:1, v/v) solution at different pHs. The effect of pH was studied in pH range from 3 to 13.5 maintained by NaOH starting from acidic solution of Dyad 5 (Figs. 2 and 3).

In acid media (ca. pH = 3) bichromophore 5 shows fluorescence signal in a range of 450–700 nm with maximum at 534 nm (Fig. 2A) which is usual for 4-amino-1,8-naphthalimides. Under these

conditions, the PET quenching effect from the tertiary alkylamine receptor is not possible and the both fluorophores are in their “on states” whereupon the system has strong emission.

The quantum yield of fluorescence $\Phi_F = 0.12$ was calculated for Dyad 5 using Coumarin 6 ($\Phi_F = 0.78$ in ethanol) as a standard according to Eq. (1) [53], where A_{ref} , S_{ref} , n_{ref} and A_{sample} , S_{sample} , n_{sample} represent the absorbance at the exited wavelength, the integrated emission band area and the solvent refractive index of the standard and the sample, respectively.

$$\Phi_F = \Phi_{\text{ref}} \left(\frac{S_{\text{sample}}}{S_{\text{ref}}} \right) \left(\frac{A_{\text{ref}}}{A_{\text{sample}}} \right) \left(\frac{n_{\text{sample}}^2}{n_{\text{ref}}^2} \right) \quad (1)$$

The calculated quantum yield of fluorescence was relatively low compared to the other 1,8-naphthalimide derivatives. The reason for such behavior of the novel compound could be twofold: (i) Dyad 5 is highly hydrophobic and probably quenches its emission in the aqueous solution due to the aggregation process; (ii) It is well known that the water is an effective fluorescence quencher, which additionally decreased the quantum yield in the aqueous medium.

The addition of NaOH to Dyad 5 in acid media converts the quaternary PET receptor fragment in neutral amine with strong electron donating ability which makes the PET quenching process in “fluorophore₂” faceable. As a result the fluorescence intensity of Dyad 5 gradually decreases with the pH increase (Fig. 2B). For the decrease of fluorescence intensity, the qualitative parameter fluorescence quenching $FQ = 2.11$ have been obtained. The $FQ = I/I_0$ is the ratio between the maximum fluorescence intensity I_0 at ca. pH 3 and the minimum fluorescence intensity I at pH 9. At pH 9 the system shows medium fluorescence due to the emission of the 4-imidoamino-1,8-naphthalimide moiety (“fluorophore₁”). The calculated quantum yield of fluorescence for Dyad 5 at pH 9 was $\Phi_F = 0.07$. Analysis of the fluorescence changes in pH window 3–9 according to Eq. (2) [54], gives pK_a value of 7.54 ± 0.03 for the mono-protonated form of Dyad 5.

$$\log \left[\frac{(I_F^{\text{max}} - I_F)}{(I_F - I_F^{\text{max}})} \right] = \text{pH} - pK_a \quad (2)$$

In acid media (ca. pH = 3) Dyad 5 shows an absorption band in range between 350 and 540 nm with maximum at 436 nm

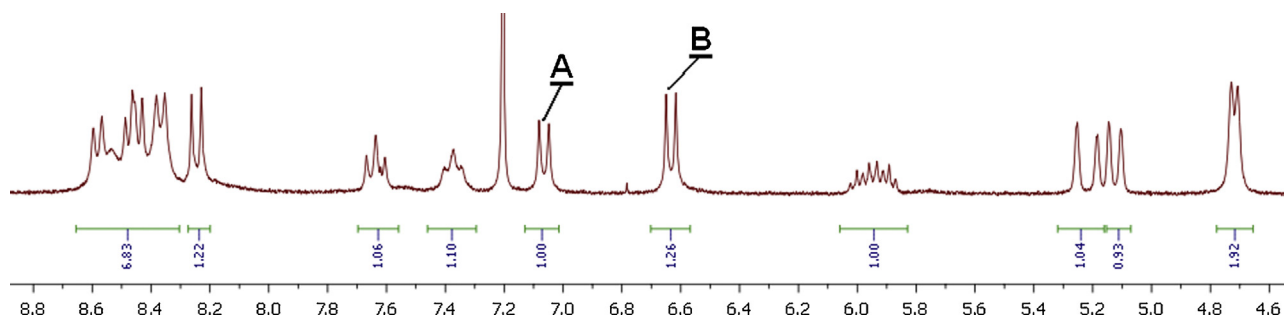


Fig. 1. ^1H NMR ($\text{CDCl}_3\text{-d}$, 250.13 MHz) spectrum of Dyad 5.

($\varepsilon = 13,200 \text{ L mol}^{-1} \text{ cm}^{-1}$), which is typical for the internal charge transfer process occurring in the 4-amino-1,8-naphthalimide chromophores. The observed absorption spectrum do not show significant pH-dependent changes in pH window 3.8–9, since the PET process does not affect the 1,8-naphthalimide chromophoric system (Fig. 3).

Further increase of pH from pH 9 to pH 13 leads to additional quenching process in the emission of Dyad 5 (Fig. 2B). This fluorescent quenching effect is accompanied with a gradually red shifting of the absorption maximum of Dyad 5 (Fig. 3A) from 436 nm to 504 nm ($\varepsilon = 15,900 \text{ L mol}^{-1} \text{ cm}^{-1}$). These results suggest the

deprotonation of the imidoamino moiety in Dyad 5 by OH^- which causes a significant increase in the charge density on the amino nitrogen and bathochromically shifting the absorption due to the enhancement in the push–pull character of the ICT transition. Additionally an increase of the band centered at 330 nm was observed which was explained by Gunnlaugsson and coworkers with the $n \rightarrow \pi^*$ transition in the deprotonated 4-amino-1,8-naphthalimide fluorophore [55].

At ca. pH 13 the both fluorophores in Dyad 5 are in “off-state” and the system completely lost its fluorescence. The fluorescent enhancement value of $\text{FQ} = 12.03$ was calculated for Dyad 5 after

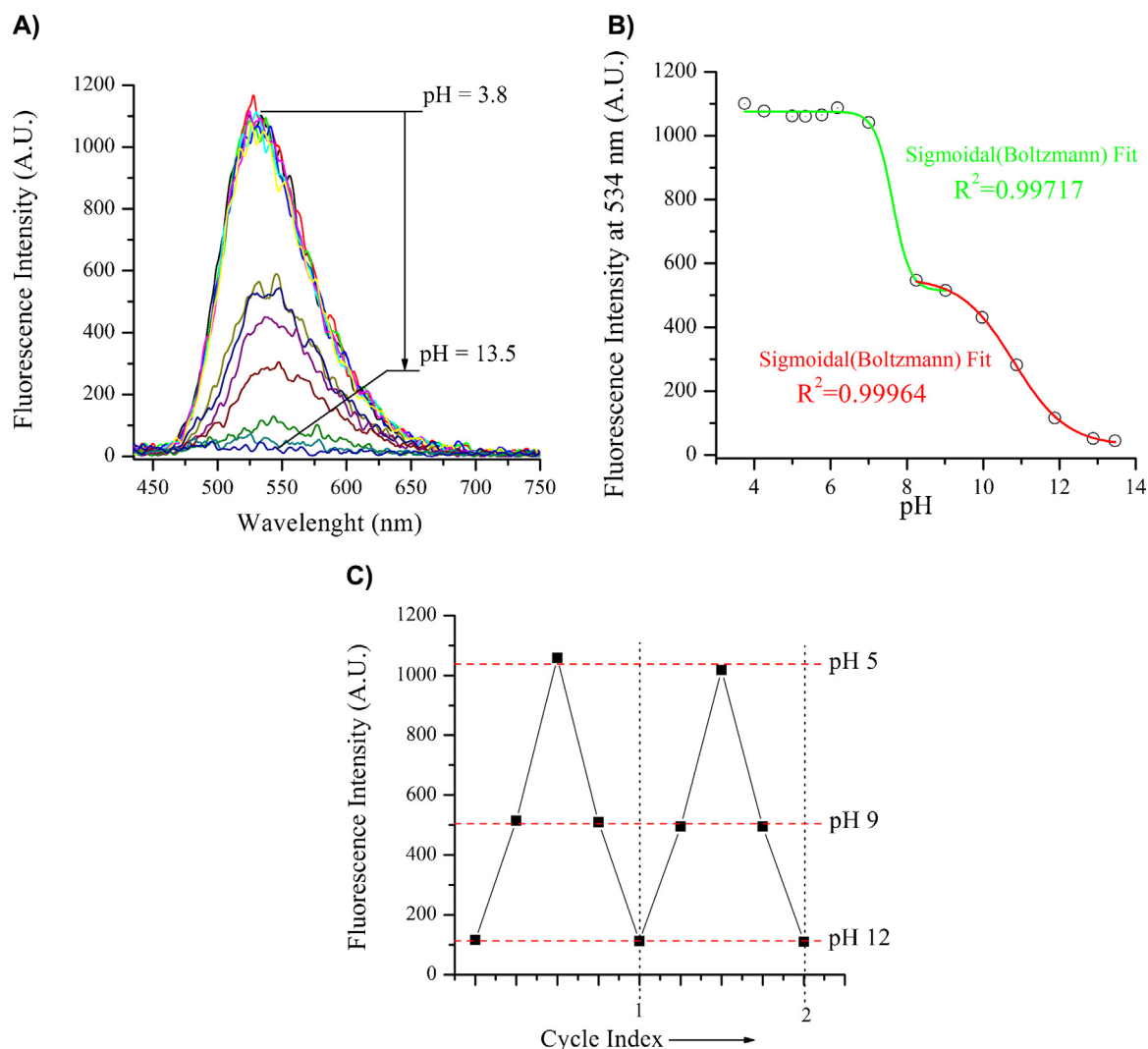


Fig. 2. Effect of pH on the fluorescence intensity of Dyad 5 (A), titration plot of Dyad 5 at $\lambda_F = 534 \text{ nm}$ in a pH range of 3.8–13.5 (B) and fluorescence pH reversibility of Dyad 5 between pH 5, pH 9 and pH 12 (C).

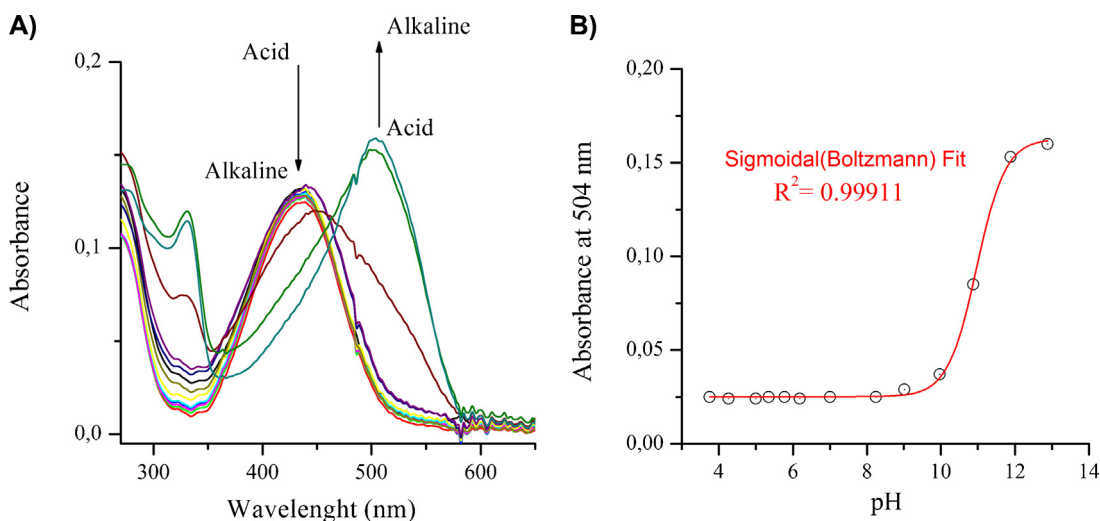


Fig. 3. Absorption changes of Dyad 5 as a function of pH (A) and titration plot of Dyad 5 at $\lambda_A = 504$ nm in a pH range of 3.7–12.9 (B).

transition from pH 9 to pH 13 (Fig. 2B). The analysis of the fluorescence changes according to Eq. (2) in pH range 9–13 gives pK_a value of 10.89 ± 0.03 for the deprotonated form of Dyad 5. According to Eq. (3) [56], a very similar pK_a value ($pK_a = 10.94 \pm 0.03$) was calculated from the absorption changes at 504 nm as a function of pH (Fig. 3B) which suggests a simple equilibrium by the deprotonation of Dyad 5. This switching process was also found to be reversible and Dyad 5 was able to perform at least two cycles (Fig. 2C).

$$\log \left[\frac{(A_{\max} - A)}{(A - A_{\min})} \right] = \text{pH} - pK_a \quad (3)$$

3.3. Influence of metal cations on the fluorescence intensity of Dyad 5

The signaling fluorescent properties of bichromophore 5 in the presence of transition metal ions have been investigated in water/DMF (3:1, v/v) at pH 10 with regard to potential application of the system as a PET sensor. For a constant pH, the examined solutions were buffered with addition of 1 mmol borate buffer solution (pH = 10). The borate buffer was chosen because it ensures pH value about pH = 10 where the PET process in the 4-(*N*-dimethyl)ethylamino-1,8-naphthalimide moiety of bichromophore 5 is feasible and the “fluorophore₂” is in its “off-state”. Experiments have been performed in the presence of different metal cations: Cd^{2+} , Co^{2+} , Cu^{2+} , Fe^{3+} , Ni^{2+} , Pb^{2+} , Zn^{2+} , Hg^{2+} and Ag^+ .

The enhancement of the fluorescence emission (FE) has been used as a qualitative parameter (Fig. 4). The $\text{FE} = I/I_0$ is determined as the ratio between the maximum fluorescence intensity (I —after metal ion addition) and the minimum fluorescence intensity (I_0 —free of metal cations solution).

Dyad 5 do not show well pronounced PET sensor selectivity. As can be seen the cations of Cd^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , and Ag^+ caused a minor effect with FE values lower than 1.1. However, the calculated FE for the other cations was higher than 1.3. The Fe^{3+} and Hg^{2+} showed a medium effect with FE of the system between 1.3 and 1.4, while the higher sensitivity ($\text{FE} > 1.4$) was observed after addition of Cu^{2+} and Pb^{2+} . The fluorescence enhancement of the system was $\text{FE} = 1.60$ in the presence of Cu^{2+} and $\text{FE} = 1.45$ in the presence of Pb^{2+} . The higher sensitivity toward Cu^{2+} and Pb^{2+} is consistent with the previously reported data for 1,8-naphthalimide derivatives with a similar PET receptor [57].

Furthermore, the presence of Cu^{2+} and Pb^{2+} induces a hypsochromic shift of the fluorescence maximum ($\Delta\lambda_F = 6$ nm and

$\Delta\lambda_F = 5$ nm, respectively) due to the complexation with the receptor group of the chemosensing system (Fig. 5A and B).

This indicates that the aromatic nitrogen atom in the substituent at C-4 position of the 1,8-naphthalimide (“fluorophore₂”) is subjected to coordination with metal cations (Scheme 2). It is well known that the light absorption properties of the naphthalimide derivatives are basically related to the polarization of their chromophoric system. Light absorption in this molecule generates a charge transfer interaction between the substituent at C-4 position and the imide carbonyl functions. The coordination of cation with the aromatic amine partially reduces the push–pull character of the ICT state which results in a hypsochromic shift. The illustrated on Scheme 2 binding mechanism was proposed according to previously reported compounds with a similar nature [58,59]. Obviously the higher sensitivity of Dyad 5 toward Cu^{2+} and Pb^{2+} is probably due to the cooperating of several combined influences, such as the suitable coordination geometry, the proper radius and charge density around the both nitrogen atoms in the ethylenediamine receptor moiety.

The stoichiometry of the complex between the ligand and metal cations (Cu^{2+} and Pb^{2+}) was determined using the method of continuous variations (Job’s method). Job plot analysis of the titrations revealed a maximum at about 0.5 mol fraction indicating 1:1 binding stoichiometry (Fig. 5A and B, Insets).

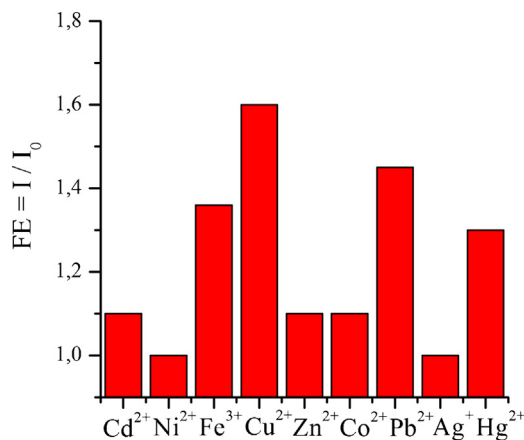


Fig. 4. Effect of the metal cations at concentration $C = 10^{-4}$ mol L⁻¹ on the fluorescence of Dyad 5 ($C = 10^{-5}$ mol L⁻¹) in water/DMF (3:1, v/v) solution buffered with 1 mmol borate buffer (pH = 10).

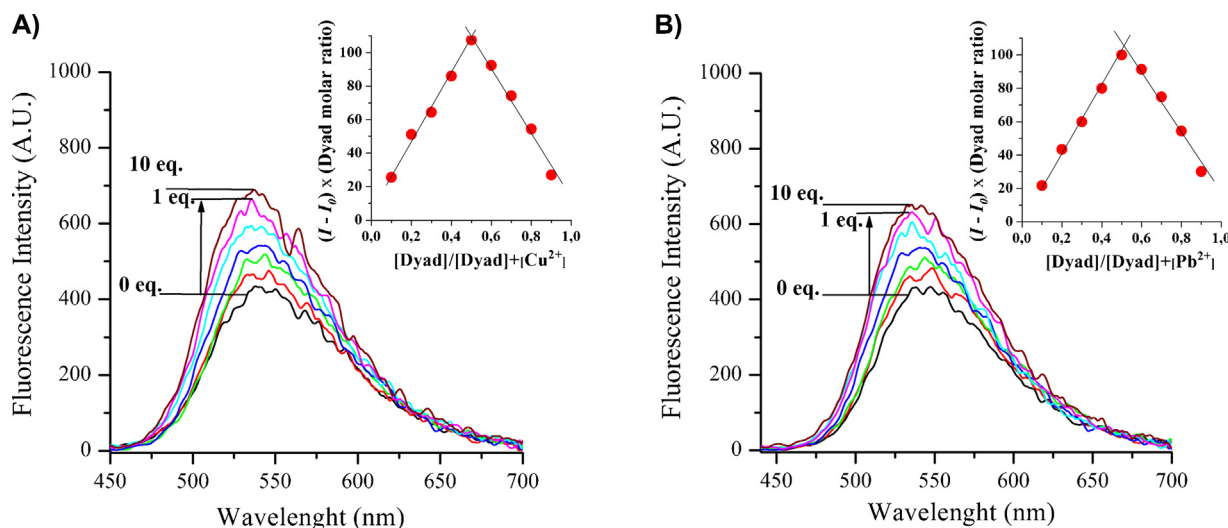


Fig. 5. Effect of Cu^{2+} (A) and Pb^{2+} (B) on the fluorescence of Dyad **5** ($C = 10^{-5} \text{ mol L}^{-1}$) in water/DMF (3:1, v/v) solution buffered with 1 mmol borate buffer (pH = 10). Insets: Job's plots.

3.4. Logic behavior of Dyad **5**

Due to the remarkable fluorescence changes of Dyad **5** in the presence of protons (0.01 M HCl), hydroxide anions (0.01 M NaOH), Cu^{2+} (1 eq.) and Pb^{2+} (1 eq.) it would be able to act as a three output combinatorial logic circuit with four chemical inputs. We chose the Cu^{2+} (1 eq.) and Pb^{2+} (1 eq.) as inputs because of the higher sensitivity of Dyad **5** toward these ions. The Fe^{3+} and Hg^{2+} ions also can be used as chemical inputs for the construction of the presented molecular logic device, however their lower FE values increase the possibility of errors due to the reaching of the threshold value.

Starting from strong alkaline media, by monitoring the emission of Dyad **5** (Output 1, fluorescence at 534 nm) a four-input input₄-Disabled-input₃-Enabled-OR logic gate can be constructed, where the enabling Input 3 is H^+ , the disabling Input 4 is OH^- , Pb^{2+} and Cu^{2+} are Input 1 and Input 2, respectively. The starting conditions were prepared after addition of 0.01 M NaOH to a solution of Dyad **5** at ca. pH 9 in water/DMF (3:1, v/v).

It is well known that the OR gate requires a nonselective receptor which gives a positive optical response upon cation binding [60]. The fluorescence output is high if either one or the other or both of the cation input values are high. If both inputs are low, then the output is low. The less selective receptor have a better OR action. Due to the lack of PET sensing selectivity toward transition metal cations Dyad **5** is able to work as a OR logic gate at molecular level. However the OR logic gate is achievable at slightly alkaline media where the Dyad **5** is in a neutral form and the PET process is feasible. In the starting strong alkaline solution (ca. pH = 12) the 4-imidoamino-1,8-naphthalimide in Dyad **5** ("fluorophore₁") is in its deprotonated form and absorb light in the region where the emission of 4-alkylamino-1,8-naphthalimide ("fluorophore₂") appears. Thus the path for FRET process is opened. Nevertheless, the fluorescence of the "fluorophore₂" is PET quenched and FRET to the "fluorophore₁" is not possible (Scheme 2).

The addition of Cu^{2+} (1 eq., Input 1) and Pb^{2+} (1 eq., Input 2) as inputs to the starting alkaline solution of Dyad **5** cuts off the PET process in "fluorophore₂". However, under these conditions the fluorescence of the system remains quenched due to the energy transfer from "fluorophore₂" to "fluorophore₁" and the OR logic gate in Dyad **5** is not achievable. As can be seen from Table 1 and Fig. 6, only the simultaneous action of Cu^{2+} (1 eq.) and/or Pb^{2+} (1 eq.) with protons (0.01 M HCl, Input 3) results in a high fluorescence output of the system (Fig. 6A). The acid input itself results in a

medium fluorescence enhancement below the threshold and does not affect the fluorescence output of Dyad **5** in presented binary mode. The role of the acid input is to convert the Dyad **5** in neutral molecule which enables the cation OR gate action. Furthermore the addition of hydroxide (0.01 M NaOH) as chemical input (Input 4) would be annihilate the enabler acid input and as such disables the OR gate. As a whole four-input input₄-Disabled-input₃-Enabled-OR logic gate is constructed.

By monitoring the absorption, actually, Dyad **5** works as two two-inputs logic gates because Cu^{2+} (Input 1) and Pb^{2+} (Input 2) do not affect remarkably the 1,8-naphthalimide ICT process (Fig. 5). First, using the absorption at 436 nm (Output 2) an INHIBIT gate at a molecular level can be achieved. In starting alkaline solution Dyad **5** is in deprotonated form with red color and low absorption band at 436 nm (coded for binary 0). After addition of protons (Input 3) Dyad **5** is converted in neutral form with yellow-green color and high absorption at 436 nm. The simultaneous inputs of acid and base annihilated each other and the system remains in deprotonated form with low absorption at 436 nm. So, the absorption at 436 nm (Output 2) of Dyad **5** is high (Fig. 6B, Table 1) only in the presence of H^+ (Input 3) and in the absence of OH^- (Input 4) which is correlated very well with INHIBIT gate [61]. Due to the inverse connection between the absorptions at 436 nm and 504 nm (when the absorption at 436 is high the absorption at 504 is low and when

Table 1

The truth table for the operation of Dyad **5**.

	Input Cu^{2+}	Input Pb^{2+}	Input H^+	Input OH^-	Output ₁ F ₅₃₄	Output ₂ A ₄₃₆	Output ₃ A ₅₀₄
A	0	0	0	0	0	0	1
B	0	1	0	0	0	0	1
C	1	0	0	0	0	0	1
D	1	1	0	0	0	0	1
E	0	0	1	0	0	1	0
F	0	1	1	0	1	1	0
G	1	0	1	0	1	1	0
H	1	1	1	0	1	1	0
I	0	0	0	1	0	0	1
J	0	1	0	1	0	0	1
K	1	0	0	1	0	0	1
L	1	1	0	1	0	0	1
M	0	0	1	1	0	0	1
N	0	1	1	1	0	0	1
O	1	0	1	1	0	0	1
P	1	1	1	1	0	0	1

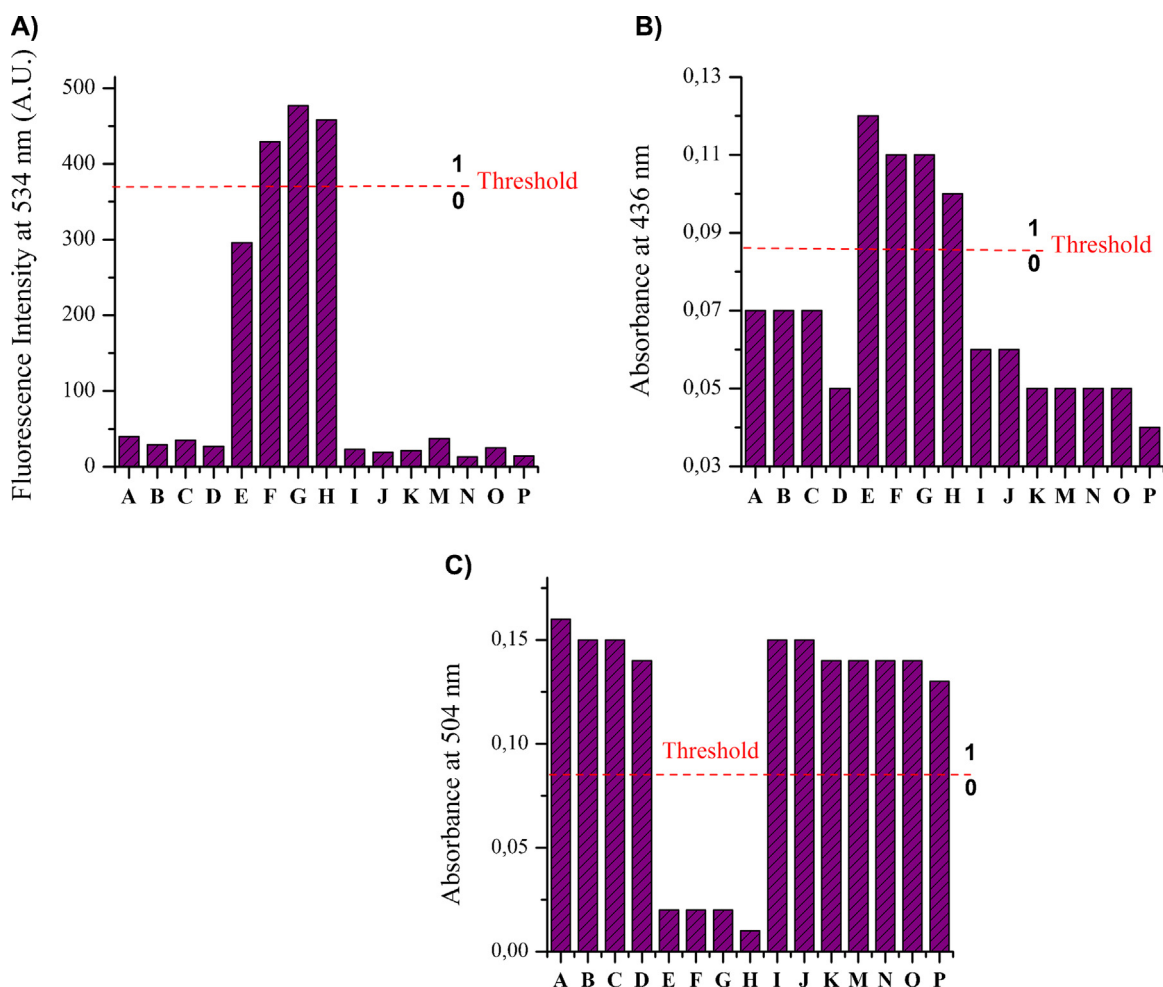
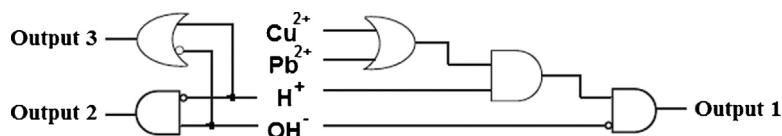


Fig. 6. The changes in fluorescence intensity of Dyad **5** at 534 nm (A), absorbance at 436 nm (B) and absorbance at 504 nm (C) with four chemical inputs (the values of A–P are illustrated in Table 1).



Scheme 4. Combinatorial logic circuit on the basis of Dyad **5**.

the absorption at 436 is low the absorption at 504 is high) in Dyad **5** the latter is able to execute IMPLICATION gate which is related inversely (negative logic) to the above INHIBIT gate. As can be seen from Fig. 6C and Table 1 the absorption output of Dyad **5** at 504 nm (Output 3) is low only in the presence of protons and absence of OH^- . In all other cases the Output 3 is high. This behavior mimics IMPLICATION logic gate [62].

Moreover, due to the parallel action of Dyad's **5** four-input input₄-Disabled-input₃-Enabled-OR logic gate (Output 1) with INHIBIT (Output 2) and IMPLICATION (Output 3) gates, the system can be switched over Disable and Enable mode reversibly. If the Output 2 is high (coded in binary as 1) then the Dyad's **5** molecular OR logic gate is in enabled mode and it can be disabled by addition of OH^- as chemical input. If the Output 3 is high then the Dyad's **5** based OR gate is in disabled mode and it can be enabled only after addition of protons Input.

On the basis of the present study and results obtained the logic behavior of Dyad **5** could be summarized with the electronic representation in Scheme 4.

4. Conclusions

A novel fluorescent 1,8-naphthalimide bichromophoric system with sensing properties based on FRET, PET and ICT was synthesized. Photophysical behavior of the compound as a function of pH and in the presence of different metal cations was studied. The system was configured on the “fluorophore₁–receptor₁–fluorophore₂–spacer–receptor₂” model and as such the two fluorophores were able to act as ICT and PET based probes, respectively. In acid media the PET quenching effect in “fluorophore₂” is not possible and the both fluorophores are in their “on states” whereupon the system showed strong emission. In neutral to slightly alkaline media the fluorescence of the system was low due to the fluorescence of only “fluorophore₁” because the PET quenching process in “fluorophore₂” is faceable. Under strong alkaline conditions the fluorescent quenching effect was accompanied with deprotonation of the imine “receptor₁” causing a red shifting of the “fluorophore₁” absorption due to the enhancement in the push–pull character of the ICT transition. At ca. pH 13 the

both fluorophores in Dyad **5** are in “off-state” and the system completely lost its fluorescence. In the presence of representative metal ions Dyad **5** did not show well pronounced PET sensor selectivity. In all cases the binding metal ions enhanced the fluorescence of the system as that effect was most pronounced in the presence of Cu^{2+} and Pb^{2+} . Due to the remarkable absorption and fluorescence changes as a function of pH and in the presence of Cu^{2+} and Pb^{2+} ions novel compound is able to act as a three output (Fl_{534} , Abs_{436} and Abs_{504}) combinatorial logic circuit with four chemical inputs (H^+ , OH^- , Cu^{2+} and Pb^{2+}). The four-input input₄-Disabled-input₃-Enabled-OR as well as two-input INHIBIT and IMPLICATION logic gates were achieved. Due to the parallel action of four-input input₄-Disabled-input₃-Enabled-OR logic gate (Output 1) with INHIBIT (Output 2) and IMPLICATION (Output 3) gates, the system can be switched over Disable and Enable mode reversible.

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