SENSOR ACTIVITY AND LOGIC BEHAVIOUR OF SOME 2-AMINOTEREPhTHALIC DERIVATIVES

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ABSTRACT

Herein we report on the sensor activity of three blue-emitting triazine derivatives of 2-aminoterephthalic acid. The novel compounds are configured as a “fluorophore-receptor” system. The fluorophores designed can act as a pH-probe via an “off-on-off” fluorescence sensing mechanism due to an internal charge transfer. The sensor activity towards cations and anions in water/DMF (1:1, v/v) media is studied by monitoring the fluorescence intensity changes. The ions tested exert a high quenching effect suggesting that the compounds are sensitive to strong acid (pH<3) and strong alkaline media (pH>8). The logic function XNOR can be performed using an acid and a base as chemical inputs, while a digital comparator can be designed on the ground of pH induced changes in the spectral properties of the novel molecule.

Keywords: 2-aminoterephthalic derivatives, ICT (intramolecular charge transfer), pH molecular sensors, molecular logic gates.

INTRODUCTION

The rapid grow of nanotechnology extends the concept of a macroscopic device to a molecular level and which is why the design and synthesis of (supra-)molecular species capable of mimicking the functions of macroscopic devices are currently of great interest [1-3]. Molecular devices operate via electronic and/or nuclear rearrangements and just like macroscopic devices require energy, provided as chemical, electrical energy, or light for their elements' operation and communication. The luminescence is one of the most useful techniques to monitor the operation of molecular-level devices [4-6]. This determines the interest towards synthesis of novel fluorescence compounds as a considerable and inseparable part of nanoscience development.

Further semiconductors miniaturization reaches its limit. Therefore, the design and construction of molecular systems capable of performing complex logic functions is of great scientific interest now [7-9]. The logic gates in semiconductor devices work using binary logic, where the signals are encoded as 0 and 1 (low and high current). This process is executed on a molecular level using different procedures, but the most common are based on the optical properties of the molecule switches. They encode the low and high concentrations of the input guest molecules and the output fluorescent intensities by the binary 0 and 1, respectively [10-12]. The first proposal to execute logic operations at a molecular level was made in 1988, but the field developed only five years later, when the analogy between molecular switches and logic gates was experimentally demonstrated by de Silva [13]. The field has recently extended from simple switches to more complex molecular systems which can perform a variety of classical logic functions [14-16] and act as a half-adder [16-18], a full-adder [19, 20], a keypad lock [21, 22], a half-subtractor [23, 24], a full-subtractor [19, 20], an encoder-decoder [25, 26], a digital comparator [27, 28]. The fluorescence switching development is attractive to analytical chemistry as well.
due to the increasing requirements in connection with
the environment pollution and the further development
of the diagnostic medicine and biology [29-31].

The fluorescence molecular sensors are designed
at present using three basic approaches based on intra-
molecular charge transfer (ICT), photoinduced electron
transfer and energy transfer [32 - 33]. The receptor in the
ICT chemosensors is directly attached to the electron-
donating/withdrawing unit that is conjugated to the
fluorophore electron-withdrawing/electron-donating
unit. During system's excitation the fluorophore un-
dergoes donor-acceptor intramolecular charge transfer.
The subsequent change in the dipole moment results in
a Stokes shift that depends on the microenvironment of
the fluorophore. Changes in quantum yields and lifetimes
are often observed [34, 35] in addition to these shifts.

The derivatives of 2,5-diaminoterephthalate are
organic chromophores that being in solid state exhibit
fluorescence of high efficiency in the visible region. They attract increasing attention in the field of functional
materials and optoelectronic devices such as organic
light-emitting diodes (OLEDs), light-emitting field-
effect transistors, semiconductor lasers and fluorescent
solid sensors [36]. 2-aminodimethylterephthalates are
organic chromophores that exhibit fluorescence in the
visible region too. They find application in textiles and
polymers production [37 - 39], but there is no informa-
tion on their possible use chemosensors. With this in
mind, the study of their sensor activity is of interest.

We have recently synthesized six blue-emitting tri-
azine derivatives of 2-aminothephthalic acid [38]. Herein
we report on the ability of three of them (Scheme 1) to serve
as pH chemosensing materials and molecular logic gates.

EXPERIMENTAL

Materials and methods

A pH meter Metrohm 704 (www.metrohm.com)
coupled with a combined pH electrode was used for
the pH measurements. Commercial standard buffers
for pH 2, 7 and 10 (Aldrich) were used for calibration.
The absorption spectra were obtained using Hewlett
Packard 8452A spectrophotometer (www.gecltoronto.
com) against water or the buffers described above. The
fluorescent spectra were recorded on a Scinco FS-2
fluorescence spectrophotometer (www.scinco.com). The
excitation source was a 150 W Xenon lamp. Excitation
and emission slit width was 5 nm. The fluorescence
measurement was carried out in right angle sample
geometry. A 1×1 cm quartz cuvette was used for the
spectroscopic analysis. The quantum yields of fluores-
cence were calculated using 9,10-Diphenylanthracene
(Φ_F = 0.95 in ethanol) [40] as a standards according to
Eq. (1) [41]:

Φ_F = Φ_ref \left( \frac{S_{sample}}{S_{ref}} \right) \left( \frac{A_{sample}}{A_{ref}} \right) \left( \frac{n^2_{sample}}{n^2_{ref}} \right)

where A_ref, S_ref, n_ref and A_sample, S_sample, n_sample stand for the
absorbance at the excitation wavelength, the integrated
emission band area and the solvent refractive index of
the standard and the sample, respectively.

The effect of pH on the absorption and fluorescence
properties of compounds 1-3 were studied by multiple
addition of amounts of 0.1 M NaOH or 0.1 M HCl to
250 mL of 1x10^{-5} M of the respective compound. The
solution pH as well as the absorption and the fluores-

![Scheme 1](image-url)
Fluorescence spectra were recorded following each addition of NaOH or HCl solution. The fluorescence intensity of each mixture was measured at 470 nm. The spectral data were collected using FluoroMaster Plus 1.3 and processed further by OriginPro 6.1 software.

All experiments were performed at room temperature.

RESULTS AND DISCUSSION

The basic spectral characteristics of 2-aminoterephthalic derivatives depend on the terephthalic molecule polarization due to the electron donor-acceptor interaction occurring between the amino substituent and the carbonyl groups from the chromophoric system. Thus it can be predicted that the interaction of a guest with the donor or acceptor moiety will change the photophysical properties of the fluorophore. We chose compounds 1-3 because of their remarkable structure containing both amino and amido fragments in their chromophoric system. The amide fragments are widely used functional groups in anion recognition because the acidity of the NH group can be easily tuned by adjusting the electronic properties of neighboring substituents so that it can recognize anions through hydrogen-bonding and deprotonation interactions [42, 43]. Additionally, the 2-amino moiety in the terephthalic fluorophore is a strong electron donating group and it can serve as a cation receptor fragment [44, 45]. Hence compounds 1-3 are expected to detect cations as well as anions. When a cation interacts with the terephthalic fluorophore amino group, the latter reduces its electron-donating character.

![Scheme 2](image)

Table 1. Quantum yields and pKa values of compounds 1, 2 and 3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Phi_F$</th>
<th>pH 2</th>
<th>pH 7</th>
<th>pH 10</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.006</td>
<td>0.011</td>
<td>0.003</td>
<td>2.6</td>
<td>9.9</td>
</tr>
<tr>
<td>2</td>
<td>0.012</td>
<td>0.021</td>
<td>0.009</td>
<td>2.5</td>
<td>10.1</td>
</tr>
<tr>
<td>3</td>
<td>0.032</td>
<td>0.090</td>
<td>0.021</td>
<td>2.5</td>
<td>10.0</td>
</tr>
</tbody>
</table>

![Fig. 1](image)

 getPath 1. Absorption spectra of sensor 3 in water/DMF (1:1, v/v) solution at different pH values.
Because of the resulting reduction in polarization, a blue shift of the absorption spectrum is expected, together with a decrease in the quantum yield of fluorescence (Scheme 2). The anion effect is similar. In case of an anion interaction with the terephthalic fluorophore amides, the carbonyl electron-accepting ability decreases due to the amides deprotonation which generates a strong electron density near the carbonyl group. This results in decrease of the ICT efficiency in the 2-aminoterephthalic fluorophores, which in turn leads to blue shifting and lower quantum yield.

This was the reason to investigate the photophysical behaviour of compounds 1-3 in water/DMF (1:1, v/v) solution at different pH values (in presence of protons as cations and a hydroxide as anions). Compounds 1-3 show the longest-wavelength absorption band in the range of 280 nm - 430 nm in the media pointed above. It is attributed to the typical 2-aminoterephthalic ICT process. The pH effect on the absorption properties of the compounds examined is negligible in a wide pH range. This is illustrated by the absorption spectra of compound 3 at pH 2, pH 7 and pH 10 presented in Fig. 1.

The emission spectra of the compounds under study (1-3) do not show significant pH-dependent changes in the pH window of 3.5-8, since 2-aminoterephthalic fluorophore does not affect the ICT excited state. The calculated quantum yields of fluorescence are in the range between 0.011-0.09 (Table 1, pH 7). These values are very low and can be explained taking into consideration that water is an effective fluorescent quencher. Besides, the high hydrophobicity of the compounds examined results a self-quenching effect in aqueous media due to fluorophore aggregation.

pH decrease from 3.5 to 2 results in a blue shifting ($\Delta \lambda = 4$ nm) and a quenching effect of the fluorescence of probes 1-3 (Fig. 2A) because of protonation of 2-aminoterephthalic nitrogen, which in turn decreases the ICT efficiency. Fluorescence quenching (FQ) determined as the ratio of the maximum fluorescence intensity $I_0$ at pH 3.5 and the minimum fluorescence intensity $I$ at pH 2 is found equal to 1.52, 1.58 and 1.44 for compounds 1, 2 and 3, correspondingly.

At high pH values (pH > 8) the amido groups are deprotonated and an anion is formed. The latter decreases the electron deficiency at the adjacent carbonyl groups which in turn decreases the ICT efficiency. This is related
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Fig. 4. Fluorescence spectra of compound 3 in presence of a chemical input of 20 µL of 0.1 mol L⁻¹ HCl (Input 1) and of 20 µL of 0.1 mol L⁻¹ NaOH (Input 2) to water/DMF (1:1, v/v).

to the lower electron accepting ability of terephthalic carbonyls. As a result, a hypsochromic shift (Δλ = 13 nm) and fluorescence quenching effect are observed (Fig. 2A). The values of FQ determined as the ratio of the maximum fluorescence intensity I₀ at pH 8 and the minimum fluorescence intensity I at pH 14 are found equal to 10.88, 11.94 and 11.24 for compounds 1, 2 and 3, correspondingly.

In general, bell-shaped pH titration curves reflecting the “off-on-off” fluorescence response of compounds 1-3 are obtained (Fig. 3). The analysis of the fluorescence changes as a function of pH according to Eq. (2) [47] gives two pKₐ values for each compound, for the protonated and the deprotonated form, respectively.

\[
\log \left( \frac{(I_{\text{Fmax}} - I_{\text{f}})}{(I_{\text{f}} - I_{\text{Fmin}})} \right) = \text{pH} - \text{pK}_a
\]  

(2)

The significant pH effect on the emission spectra of sensors 1-3 provides to conclude that they can execute logic operation upon addition of H⁺ and OH⁻ as inputs. The fluorescence of sensors 1, 2 and 3 monitored at 470 nm in the presence of an acid and a hydroxide shows that a XNOR molecular logic gate (Table 2) can be constructed starting off a neutral solution. It is seen that the emission output is low (coded for binary 0) with the input either of an acid or a base (Fig. 4). The simultaneous input of an acid and a base annihilates each other’s effect and generates high emission (coded for binary 1) at 470 nm mimicking thus the XNOR logic function.

The XNOR logic gate is actually a comparator as the output is 1 only when both inputs are of an identical value playing thus the role of the mathematical symbol “equal”. XNOR cannot however say which input is higher than the other. An additional output value serving as the mathematical symbol “greater than” or “lower than” is required to construct a magnitude digital comparator. In fact the compounds examined are able to act as a magnitude digital comparator in a three-valued logic output mode (the output has three values “low”, “medium” and “high”) due to the different quenching effect of the cations and anions present. For example, the quantum yield of fluorescence of compound 3 in a neutral solution is 0.09 and can be coded as “high”. In presence of NaOH the quantum yield decreases to 0.021

Table 2. The truth table for the logic behaviour of compound 3.

<table>
<thead>
<tr>
<th></th>
<th>Input 1</th>
<th>Input 2</th>
<th>Output Fl₄₇₀</th>
<th>Qₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.090 (High)</td>
</tr>
<tr>
<td>OH⁻</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0.021 (Low)</td>
</tr>
<tr>
<td>H⁺</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.032 (Medium)</td>
</tr>
<tr>
<td>OH⁻</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.090 (High)</td>
</tr>
</tbody>
</table>
to be referred as a “low value”, while the addition of HCl decreases the quantum yield to 0.032 corresponding to a “medium” value, i.e. a value between 0.021 (the “low value”) and 0.09 (the “high value”). When both inputs are equal (H⁺ = OH⁻), the output (Fl₁υ₀) is “high”. In case H⁺ > OH⁻, the output (Fl₁υ₀) refers to the “medium value”, while the addition of a base, i.e. when H⁺ < OH⁻, the output refers to the “low” value.

The compounds acting as molecular logic gates of chemical inputs are actually complex chemosensors. This feature is revealed in case the sample analyzed responses to a predefined standard. If the fluorescence output of novel sensors 1, 2 and 3 is 1, then the solution tested is in the pH window of 3-8. If the fluorescence output is 0, then the solution tested has a strong acid (pH < 3) or a strong alkaline (pH > 8) reaction. In other words compounds 1, 2 and 3 are sensors with neither fast response that the analyzed sample is nor strong acid and nor strong alkaline.

CONCLUSIONS

Three new fluorescent pH sensors 2-aminoterephthalic acid derivatives are presented and their photophysical behavior in water/DMF (1:1, v/v) media as a function of pH is studied. The compounds studied show low fluorescence emission intensity in alkaline and acid media. It is enhanced upon further acidification or alkalization. The system is in “on” state in pH range of 3-8. The effect is suggested to result from the amine receptor’s protonation, when pH < 3 and deprotonation, when pH > 8. The fluorescence changes indicate that sensors 1, 2 and 3 can act as an efficient “off-on-off” switch for pH determination. The sensors’ logic behavior is also examined using fluorescence as output and H⁺ and OH⁻ as chemical inputs. The logic function XNOR is achieved and the logic circuit of a digital comparator is demonstrated.

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REFERENCES

14. J. Andréasson, U. Pischel, Smart molecules at work-
Polya Miladinova, Nikolai Georgiev

17. C. Xu, W. Sun, C. Zhang, Y. Bai, C. Fang, W. Li, Y. Huang, C. Yan, Chemicals for mimicking logic functions within fluorescent MPT dyes, Science China, Series B, 52, 2009, 700-714.
39. P. Miladinova, On the photostability of some blue-emitting derivatives of 2-aminoterephthalic acid and
their copolymers with methyl methacrylate, Polym Degr Stab, 98, 2013, 2347-2350.