

## Pyrene-1-carboxylic acid polyethylene glycol esters: synthesis and photophysical studies\*

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Monoesters of tri- and tetraglycol and 1-pyrenecarboxylic acid were characterized for the first time by NMR spectroscopy and elemental analysis. The photophysical properties of the compounds obtained were studied. A selective sensory response of the esters to nitro-containing explosives in an aqueous medium was revealed. The maximum value of the Stern–Volmer fluorescence quenching constant for 2,4,6-trinitrotoluene was found to be  $1.13 \cdot 10^4 \text{ L mol}^{-1}$ .

**Key words:** detection of explosives in aqueous medium, chemical sensors, podands, sensor compounds, pyrene-based luminophores, fluorescence quenching, nitro-containing compounds.

Currently, the danger posed by explosives lies not only in the threat of their use for terrorist acts, but also in the pollution of the environment by these compounds and products of their decay. The sources of pollution are landfills and places of military operations, as well as ammunition storage facilities, abandoned military equipment and ships; sites of manufacture, testing, and disposal of explosives, *etc.* In these areas, water bodies, soils, as well as surface and ground waters suffer pollution by explosives or products of their decomposition. In this connection, the development of methods for the detection of explosives and their decay products in aqueous medium seems an urgent issue.

Existing explosives detection techniques can be divided into laboratory (using chromatography; IR, UV, and Raman spectroscopy; mass spectrometry; X-ray; neutron activation analysis; biochemical and electrochemical methods; ion mobility spectrometry (IMS), *etc.*<sup>1,2</sup>) and field (trained dogs, portable devices based on IMS or gas chromatography). Unfortunately, each technique has its own disadvantages and limitations. For example, laboratory analysis requires expensive sophisticated equipment and skilled operators, as well as a significant investment of time. Detecting explosives with dogs gives very rough results. In addition, dogs require special training and care.

Given the shortcomings of the methods listed above and the importance of detecting explosives, new analytical techniques are being developed which should be highly

sensitive, portable, inexpensive, easy to use, and field-applicable.<sup>3</sup> Chemical sensors fully meet the specified criteria and are promising for use in this area.<sup>4</sup> Among them, fluorescence sensors based on pyrene stand out due to its unique photophysical properties, for example, high quantum yield, long fluorescence lifetime, and sensitivity to nitroaromatic compounds, which the most common explosives belong to.<sup>5</sup>

It should be noted that most chemosensors are used in the heterophase mode. This is a significant disadvantage, since the water-soluble analyzed nitro compound and the chemosensor soluble in organic solvents are in different phases. To get a sensory response, it is necessary to ensure the diffusion of the analyte to the periphery of the chemosensor. An analytical signal appears only after binding has taken place. The development of fluorophore sensors capable of dissolving in aqueous solutions, in our opinion, can neutralize this limitation and increase the efficiency of chemosensors.

Previously, pyrene-based sensors have been mentioned in the literature, for example, pyrene-labeled DNA probes for detecting point mutations<sup>6</sup> or 1-aminopyrene as a fluorescent sensor for terpene trilactones.<sup>7</sup> At the same time, it is known that polyethylene glycol was used as a linker in ligand design.<sup>8</sup> We decided to develop new sensors based on these compounds.

The purpose of the present work is to synthesize fluorescent chemosensors based on monoesters of tri- and tetraglycol and 1-pyrenecarboxylic acid for the *turn-off* detection of nitro-containing explosives in aqueous solutions.

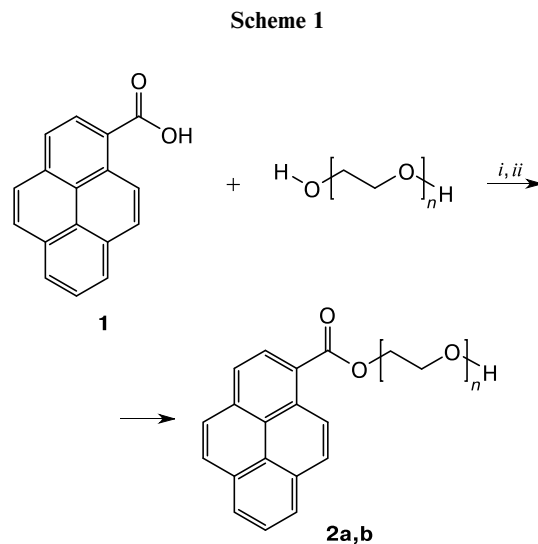
\* Dedicated to Academician of the Russian Academy of Sciences V. N. Charushin on the occasion of his 70th birthday.

## Results and Discussion

It is known that polyethylene glycols (PEGs) are incapable to form micelles. However, when modified with non-polar fragments, for example, with oleic acid residues, PEGs are converted into nonionogenic surfactants (for example, PEG 400 oleate) capable of forming micelles with a critical micelle concentration (CMC) of  $10^{-4}$ – $10^{-5}$  mol L $^{-1}$ .<sup>9</sup> In the present work, we made a successful attempt to modify triethylene glycol and tetraethylene glycol with the residue of 1-pyrenecarboxylic acid (**1**). To achieve this, the latter was refluxed with thionyl chloride in dichloroethane until a precipitate disappeared. The acid chloride formed *in situ* reacted with ethylene glycols in THF in the presence of triethylamine upon heating to 50 °C for 1 h. The reaction resulted in the formation of water-soluble monoglycol esters of 1-pyrenecarboxylic acid **2a,b** (Scheme 1). In aqueous media, these luminophores form micelles which can be used to detect explosives. Compounds **2a,b** were characterized for the first time. Compound **2b** has been obtained *in situ* earlier as an intermediate product<sup>10</sup> and has not been studied in detail.

To study the effect of solvent polarity on the photophysical properties of compounds **2a,b**, we used  $10^{-5}$  M solutions in H<sub>2</sub>O–THF (99.9 : 0.1 (vol.%)) and in cyclohexane to avoid possible self-quenching. The absorption and emission spectra of compounds **2a,b** are shown in Fig. 1.

The absorption spectra of compounds **2a,b** in H<sub>2</sub>O–THF and cyclohexane are similar (see Fig. 1). The S<sub>0</sub>→S<sub>3</sub> and S<sub>0</sub>→S<sub>4</sub> transition bands resemble those in the spectra of unsubstituted pyrene, while the S<sub>0</sub>→S<sub>2</sub> transition is represented by a broader and poorly structured band. The emis-

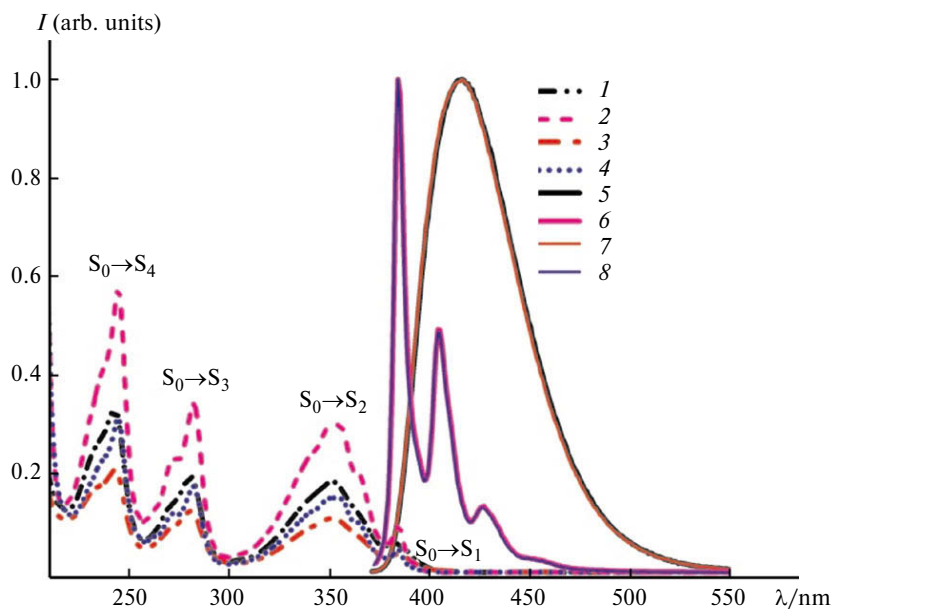


$n = 3$  (a),  $n = 4$  (b)

**Reagents and conditions:** *i.* 15 equiv. of SOCl<sub>2</sub>, DCE, 2 h with a reflux condenser; *ii.* 5 equiv. of glycol, 6 equiv. of NEt<sub>3</sub>, anhydrous THF, heating.

sion spectra differ radically depending on the solvent nature. In both solvents, compounds **2a,b** exhibit strong emission in the blue region of the spectrum. The emission spectrum of compounds **2a,b** in cyclohexane is largely similar to that of unsubstituted pyrene, while the formation of a broad unstructured peak with a bathochromic shift up to 416 nm is observed in the spectrum of a solution in H<sub>2</sub>O–THF.

The absorption and emission spectra of compounds **2a,b** recorded in the same solvent are almost identical,



**Fig. 1.** The absorption (*I*–*4*) and emission spectra (*5*–*8*) of sensors **2a** (*1*, *2*, *5*, *6*) and **2b** (*3*, *4*, *7*, *8*) in H<sub>2</sub>O–THF (*1*, *3*, *5*, *7*) and cyclohexane (*2*, *4*, *6*, *8*).

**Table 1.** Photophysical characteristics of compounds **2a,b**

Com- pound	$\lambda_{\text{abs}}/\text{nm}$		$\lambda_{\text{em}}/\text{nm}$		$\Phi_{\text{f}}(\%)$		$\tau/\text{ns}$ at $\lambda/\text{nm}$		
	H <sub>2</sub> O—THF	Cyclohexane	H <sub>2</sub> O—THF	Cyclohexane	H <sub>2</sub> O—THF	Cyclohexane	416 <sup>a</sup>	384 <sup>b</sup>	405 <sup>b</sup>
	<b>2a</b>	243, 280, 351, 383	244, 272, 282, 354, 364, 384	416	385, 405, 427	58.23	45.28	2.25	4.04
<b>2b</b>	243, 280, 351, 383	244, 271, 282, 354, 364, 384	416	384, 404, 426	62.05	34.65	2.86	3.68	4.97

<sup>a</sup> Solution in THF—H<sub>2</sub>O.<sup>b</sup> Solution in cyclohexane.

which indicates that the length of the PEG fragment does not affect the spectral characteristics of fluorophores.

The photophysical characteristics of the compounds obtained are given in Table 1. The absolute quantum yield of compounds **2a,b** in the polar solvent system is higher, which generally corresponds to the photophysical properties of the pyrenecarboxylic acid methyl ester. The parent 1-pyrenecarboxylic acid shows the opposite result.<sup>10</sup> From the above, one can conclude that esterification leads to an increase in the quantum yield of pyrenecarboxylic acid esters in polar solvents and to its decrease in nonpolar ones. The high quantum yields of compounds **2a,b** within 35–62% were obtained both in water and in cyclohexane. Such excellent fluorescent properties are possibly related to the absence of  $n-\pi^*$ -transitions, which would lead to quenching of fluorescence by intersystem crossing or internal conversion, as was shown by the TD—DFT calculations.<sup>11</sup>

The fluorescence lifetime for compounds **2a,b** varies within 2–5 ns, which is two orders of magnitude shorter than the corresponding parameter for pyrene (100 ns or more, depending on the medium<sup>12–21</sup>). These relatively low values also are similar to the fluorescence lifetime values of pyrenecarboxylic acid methyl ester.<sup>11</sup>

Experiments using dynamic light scattering were carried out in order to study compounds **2a,b** in the micelle formation (Table 2). Thus, a standard solution ( $1 \cdot 10^{-4}$  mol L<sup>-1</sup>) of compounds **2a,b** was stepwise diluted to a concentration of  $5 \cdot 10^{-7}$  mol L<sup>-1</sup>. In the case of compound **2a**, it was found that the micelle size gradually decreased from 112 to 22.7 nm with dilution of the solution. A very low concentration of micelles in the solution was observed from approximately  $5 \cdot 10^{-6}$  mol L<sup>-1</sup>. In a solution of compound **2b**, micelles were present in sufficient quantities only at a concentration of  $1 \cdot 10^{-4}$  mol L<sup>-1</sup>; upon dilution, the micelle concentration and the signal intensity rapidly decreased. In contrast to compound **2a**, the change in the size of micelles with decreasing concentration of the solution had in this case a haphazard character, which may be associated with errors due to insufficient intensity of the signal.

Despite the low concentration, micelles are still present in dilute solutions of compounds **2a,b**. It should be

noted that micelle formation is a dynamic process, *i.e.*, the amount of micelles and their size can vary over time.

The possibility of using compounds **2a,b** as sensors for the detection of nitro-containing analytes by fluorescence quenching was tested by their fluorometric titration with the most common components of explosives, namely, dinitrotoluene (DNT), trinitrotoluene (TNT), as well as pentaerythritol tetranitrate (PETN) (Table 3). The experiment was preceded by a blank titration with acetonitrile. The addition of acetonitrile had no effect on the emission intensity of solutions of compounds **2a,b**. The test compounds **2a,b** did not have a sensory response in the presence of DNT, either, but both showed it to TNT. Compound **2b** also demonstrated a sensory response to PETN. To sum up the studies, compound **2b** showed the best result as a sensor: in the presence of TNT, the Stern—Volmer fluorescence quenching constant reached  $1.13 \cdot 10^4$  L mol<sup>-1</sup>, which is similar or higher than the values for structurally similar compounds.<sup>23,24</sup> Meanwhile, we note that the sensors described in the literature<sup>23,24</sup> required an increase in sensitivity through micelle form-

**Table 2.** Experimental results on dynamic light scattering

Concentration /mol L <sup>-1</sup>	Micelle sizes/nm	
	<b>2a</b>	<b>2b</b>
$1 \cdot 10^{-4}$	13.07 <sup>a</sup>	19.34 <sup>a</sup>
	112	88.9
$5 \cdot 10^{-5}$	20.59 <sup>a</sup>	— <sup>b</sup>
	92.49	
$2 \cdot 10^{-5}$	52.95	— <sup>b</sup>
$1 \cdot 10^{-5}$	37.09	30.53
$5 \cdot 10^{-6}$	24.91	29.83
$1 \cdot 10^{-6}$	22.73	44.73
$5 \cdot 10^{-7}$	— <sup>c</sup>	33.42
$2 \cdot 10^{-7}$	— <sup>d</sup>	— <sup>c</sup>

<sup>a</sup> Micelle fractions are given.<sup>b</sup> Not measured.<sup>c</sup> Very weak signal, so it is difficult to reliably determine the particle size.<sup>d</sup> No micelles are present.

**Table 3.** Results of fluorimetric quenching of sensors **2a,b**

Sensor	$K_{SV}/L \text{ mol}^{-1}$		LOD (ppb)		Quenching efficiency (%)	
	TNT	PENT	TNT	PENT	TNT	PENT
<b>2a</b>	$1.00 \cdot 10^4$	—	302	—	4.27	—
<b>2b</b>	$1.13 \cdot 10^4$	$0.50 \cdot 10^4$	533	1040	3.52	2.46

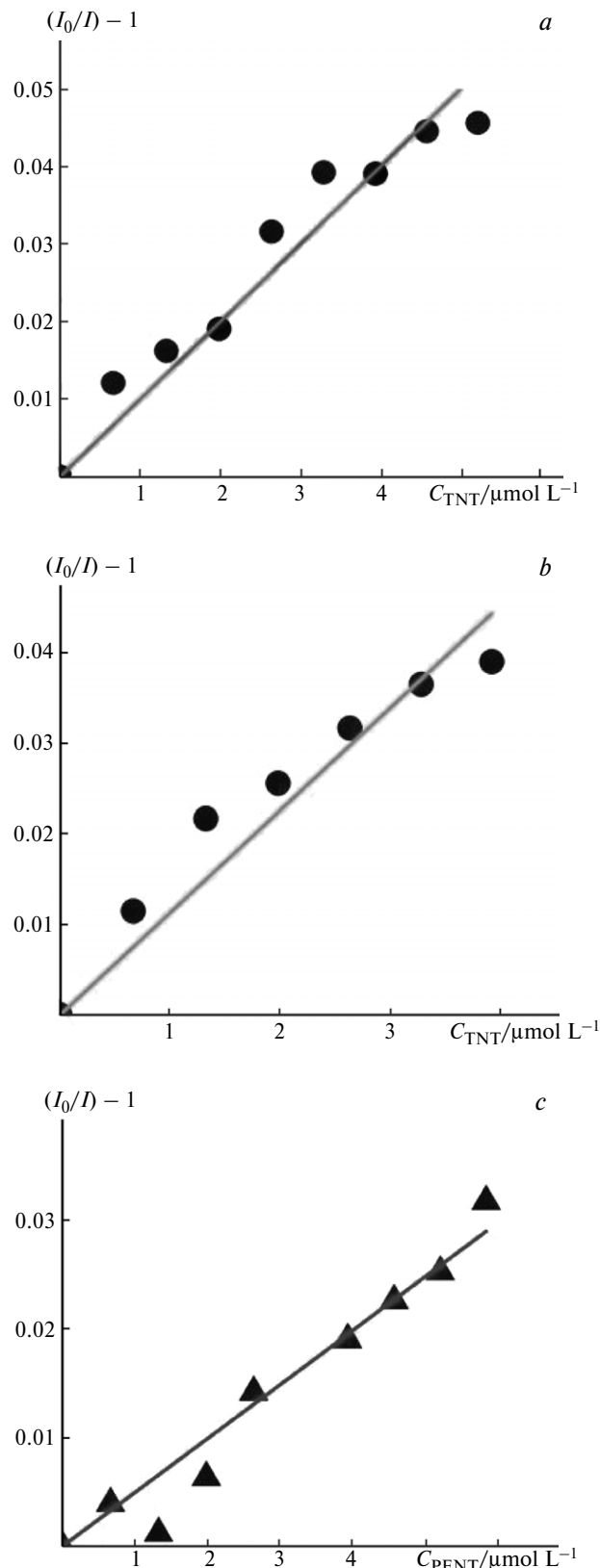
ation by the addition of external surfactants. Sensors **2a,b** do not have this disadvantage, since they are soluble in water and possess surface-active properties.

The dependence of the fluorescence quenching of sensors **2a,b** on the analyte (Stern–Volmer plot) is static at low concentrations of the latter, which becomes dynamic at high concentrations, thus indicating a mixed type of quenching (Fig. 2). However, the calculation using the static quenching equation gave a high approximation rate (coefficient of determination ( $R^2$ )) equal to 0.98 for all three titrations, which indicates the predominance of the static mechanism. Since no peaks corresponding to the formation of the sensor–nitroanalite complex appeared in the absorption spectra, we finally adopted the model of pseudostatic quenching.

In conclusion, we have synthesized surface-active chemosensors, fluorophores based on two polyethylene glycol esters of 1-pyrenecarboxylic acid, studied their photophysical properties and the ability to detect explosives, as well as examined and confirmed by experiments on dynamic light scattering their ability to form micelles in an aqueous medium. The advantages of the sensors we obtained are their selectivity (especially for the hard-to-detect pentaerythritol tetranitrate) and the ability to work in an aqueous medium due to the hydrophilic polyethylene glycol residue. In our case, there is no necessity to increase the sensor sensitivity through the micelle formation by the addition of external surfactants.

### Experimental

$^1\text{H}$  NMR spectra were obtained on a Bruker AVANCE II spectrometer (400.13 MHz) (USA) with TMS as an internal standard. Elemental analysis was performed on a Perkin Elmer 2400 II CHN analyzer (USA) by the elemental analysis laboratory team of the I. Ya. Postovsky Institute of Organic Synthesis of the Ural Branch of the Russian Academy of Sciences. Mass spectra were recorded on a Shimadzu GCMS-QP2010 Ultra spectrometer (Japan), using electron impact for ionization. The reaction progress and the purity of the products were monitored by TLC on Macherey-Nagel DC-Fertigfolien Alugram ALOX N/UV<sub>254</sub> plates (Germany). The products were purified by flash chromatography on alumina (Acros Organics, 50–200 nm, 60 Å (Belgium)). UV absorption spectra were obtained on a Shimadzu UV-1600 spectrophotometer (Japan). Emission spectra were recorded on a Horiba-FluoroMax-4 spectrofluor-



**Fig. 2.** The Stern–Volmer plots of fluorescence quenching for sensor **2a** in the presence of TNT (*a*), sensor **2b** in the presence of TNT (*b*), PENT (*c*).

rometer (USA). The graphic processing of the absorption and emission spectra was performed using the OriginPro 2015 software (64-bit) b9.2.196. All electronic spectra were normalized in the Overlay mode automatically using the "Normalize columns" option in the same software. The absolute quantum yields of fluorophores were determined using an integrating sphere of the FluoroMax-4 instrument (Horiba, USA). The fluorescence lifetime of the sensors was measured on a FluoroMax-4 instrument (Horiba, USA) using the Time Correlated Single Photon Counting (TCSPC). Fluorescence titration experiments were carried out using a FluoroMax-4 spectrofluorometer (Horiba, USA) by Single Point technique. The micelle diameter was determined by dynamic light scattering (DLS) using a Photocor Compact analyzer (Photocor, Russia). The water used to prepare solutions of sensors **2a,b** for recording spectra and fluorometric titration was purified using a Millipore Simplicity UV type I high purification system (Merck, Germany).

We used commercially available 1-pyrenecarboxylic acid (**1**). It can also be obtained according to the described procedure.<sup>7</sup> Solvents (1,2-dichloroethane, tetrahydrofuran, toluene, ethyl acetate, ethanol), starting materials (thionyl chloride, triethylene glycol, tetraethylene glycol, triethylamine, sodium chloride, sodium hydroxide, sodium sulfate), and alumina for chromatography were commercially available. Chromatographically pure acetonitrile and tetrahydrofuran were used for spectral studies.

**Synthesis of pyrenecarboxylic acid polyethylene glycol esters (2a,b) (general procedure).** 1-Pyrenecarboxylic acid (1.22 mmol) was suspended in 1,2-dichloroethane (20 mL), followed by the addition of thionyl chloride (18.27 mmol). The mixture was refluxed until the precipitate was dissolved and completely converted to the pyrenecarboxylic acid chloride. The resulting chloride was concentrated *in vacuo* and dissolved in anhydrous THF (10 mL). Polyethylene glycol (6.09 mmol) was dissolved in anhydrous THF (15 mL), followed by the addition of triethylamine (7.31 mmol). A solution of pyrenecarboxylic acid chloride was added dropwise to the resulting solution with continuous stirring. The reaction mixture was stirred at 50 °C for 1 h, then concentrated *in vacuo*. The residue was dissolved in toluene, the resulting solution was washed sequentially with brine (10 × 2 mL) and 5% aqueous sodium hydroxide (10 mL). The extract was dried with Na<sub>2</sub>SO<sub>4</sub>, concentrated *in vacuo*, and applied to a short column with alumina. The product was eluted with an ethyl acetate–ethanol mixture with an ethanol gradient from 5 to 10% and concentrated *in vacuo*.

**2-[2-(2-Hydroxyethoxy)ethoxy]ethyl pyrene-1-carboxylate (2a).** The yield was 0.284 g (62%). A yellowish oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 2.25 (br.s, 1 H, OH); 3.62–3.64 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>OH), 3.73–3.75 (m, 4 H, OCH<sub>2</sub>CH<sub>2</sub>OH, CH<sub>2</sub>); 3.78–3.80 (m, 2 H, CH<sub>2</sub>); 3.97–3.99 (m, 2 H, C(O)OCH<sub>2</sub>CH<sub>2</sub>O); 4.67–4.69 (m, 2 H, C(O)OCH<sub>2</sub>), 8.04–8.10 (m, 2 H, Pyr (pyrene)); 8.17–8.19 (m, 2 H, Pyr (pyrene)); 8.23–8.28 (m, 3 H, Pyr (pyrene)); 8.67 (d, 1 H, Pyr (pyrene), H(3), *J* = 8.03 Hz); 9.28 (d, 1 H, Pyr (pyrene), H(2), *J* = 9.54 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ: 61.81, 64.13, 69.36, 70.48, 70.75, 72.52, 99.96, 123.38, 124.09, 124.17, 124.80, 124.87, 126.17, 126.28, 127.14, 128.51, 129.43, 129.63, 130.35, 130.98, 131.16, 134.37, 167.91. Found (%): C, 72.75; H, 6.24. C<sub>23</sub>H<sub>24</sub>O<sub>5</sub>. Calculated (%): C, 72.61; H, 6.36. MS (EI, 70 eV), *m/z* (*I*<sub>rel</sub> (%)): 380 [M]<sup>+</sup> (100).

**2-[2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy]ethyl pyrene-1-carboxylate (2b).** The yield was 0.300 g (58%). A yellowish oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 2.41 (br.s, 1 H, OH); 3.54–3.57 (m, 2 H,

OCH<sub>2</sub>CH<sub>2</sub>OH); 3.62–3.64 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>OH); 3.66–3.68 (m, 4 H, O(CH<sub>2</sub>)<sub>2</sub>O); 3.71–3.75 (m, 2 H, CH<sub>2</sub>); 3.78–3.80 (m, 2 H, CH<sub>2</sub>); 3.96–3.98 (m, 2 H, C(O)OCH<sub>2</sub>CH<sub>2</sub>O); 4.66–4.69 (m, 2 H, C(O)OCH<sub>2</sub>CH<sub>2</sub>O); 8.04–8.09 (m, 2 H, Pyr (pyrene)); 8.17 (dd, 2 H, Pyr (pyrene), *J* = 8.66 Hz, *J* = 3.39 Hz); 8.22–8.28 (m, 3 H, Pyr (pyrene)); 8.66 (d, 1 H, H(3), Pyr (pyrene), *J* = 8.03 Hz); 9.27 (d, 1 H, H(2), Pyr (pyrene), *J* = 9.29 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ: 61.71, 64.23, 69.34, 70.33, 70.63, 70.68, 70.71, 72.43, 99.95, 123.47, 124.08, 124.15, 124.78, 124.90, 126.14, 126.25, 127.13, 128.51, 129.40, 129.60, 130.34, 130.97, 131.13, 134.33, 167.92. Found (%): C, 70.88; H, 6.57. C<sub>25</sub>H<sub>28</sub>O<sub>6</sub>. Calculated (%): C, 70.74; H, 6.65. MS (EI, 70 eV), *m/z* (*I*<sub>rel</sub> (%)): 424 [M]<sup>+</sup> (100).

**Fluorometric titration.** The absorption and emission spectra of sensors **2a,b** were measured in solutions in H<sub>2</sub>O–THF (99.9 : 0.1 (vol. %)). After determining the wavelengths of absorption and emission, single point technique was used to quench fluorescence. A sensor solution with a concentration of 10<sup>-6</sup> mol L<sup>-1</sup> (3 mL) was placed in a quartz cuvette, followed by sequential addition of aliquots (10 μL each) of nitroanalyte in acetonitrile with a concentration of 2 · 10<sup>-4</sup> mol L<sup>-1</sup>. The Stern–Volmer fluorescence quenching constant (*K*<sub>SV</sub>) was calculated as the slope of the intensity graph ((*I*<sub>0</sub>/*I*) – 1) versus the quencher concentration ([*Q*]):

$$\frac{I_0}{I} = 1 + K_{SV}[Q]. \quad (1)$$

**Fluorescence lifetime measurement.** In order to avoid self-quenching, solutions for sensors **2a,b** were prepared with such a concentration that the absorption intensity at a selected wavelength did not exceed 0.1. The lifetime was measured using a time-correlated single-photon counter (TCSPC) with a nano-second LED (λ = 370 nm).

**Limit of detection calculation.** The limit of detection (LOD) was determined based on the data from fluorescence quenching experiments in accordance with the method published earlier.<sup>25</sup> To obtain the equation of the regression curve, a calibration graph of the sensor fluorescence intensity versus the analyte concentration was plotted. The limit of detection was calculated using the equation

$$\text{LOD} = 3\sigma/k,$$

where σ is the standard deviation of the fluorophore intensity in the absence of the analyte obtained using the STEYX function in Excel, *k* is the slope of the calibration curve.

**Determination of the presence and the size of micelles.** The micelle diameter was determined by the of dynamic light scattering using a Photocor Compact analyzer (Photocor, Russia), which was equipped with a temperature-stabilized 25 mW diode laser operating at a wavelength of 633 nm and a built-in Photocor-FC correlator for auto- and cross-correlation measurements. The scattered light was detected at an angle of 90°.

The autocorrelation function of the scattered light intensity was analyzed using the DynaLS software. The correlation function of the scattered light intensity contains information on the coefficient of particle diffusion in the sample. The relationship between fluctuations in the intensity of the optical signal (field) and fluctuations in the measured photocurrent was found using the Siegert relation:

$$g^{(2)}(\tau) = 1 + |g^{(1)}(\tau)|^2, \quad (2)$$

where  $g^{(2)}(\tau)$  is the normalized correlation function of the scattered light intensity;  $g^{(1)}(\tau)$  is the normalized autocorrelation function of the field. The spectral characteristics of the optical signals can be calculated by measuring the correlation function of the signal as a discrete sequence of pulses at the output of the detector.

The half-width of the scattered light spectrum ( $\Gamma$ ) and the correlation time of the scattered light intensity ( $T_c$ ) are related to the coefficient of particle diffusion ( $D$ ) by the relation

$$\Gamma = Dq^2 = 1/T_c, \quad (3)$$

where  $q$  is the modulus of oscillation of the wave vector on which the light is scattered.

The diffusion coefficient ( $D$ ) was determined by the Einstein–Stokes equation:

$$D = \frac{kT}{6\pi R\eta}, \quad (4)$$

where  $R$  is the hydrodynamic radius of micelles,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\eta$  is the solution viscosity.

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This paper does not contain descriptions of studies on animals or humans.

The authors declare no competing interests.

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