

Dedicated to Professor Bogdan C. Simionescu  
on the occasion of his 65<sup>th</sup> anniversary

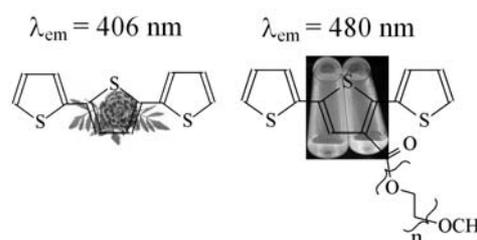
## POLY(ETHYLENE GLYCOL) – FUNCTIONALIZED, WATER SELF-DISPERSIBLE $\alpha$ -TERTHIOPHENES

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The aim of this work was the synthesis, structural characterization and photophysical properties investigation of two  $\alpha$ -terthiophenes ( $\alpha$ -TT) containing the poly(ethylene glycol) (PEG) of different lengths as substituents. For their synthesis, the Suzuki condensation between 2-thiophene boronic acid and two functionalized PEG ( $M_n = 1000$  and  $M_n = 2000$ ) with 2, 5 dibromothiophene moieties was employed and structural characterization of obtained  $\alpha$ -TT were performed by  $^1\text{H-NMR}$  and FT-IR spectral methods. Photophysical properties of the synthesized  $\alpha$ -TT in solutions were evaluated by UV-Vis and fluorescence measurements and the influence of different solvents polarity on the oligomers fluorescence behavior was also investigated.



### INTRODUCTION

Functional oligothiophenes (OTFs) have attracted comprehensive interest among researchers all over the world and can be considered as a third generation of advanced conjugated materials.<sup>1</sup> A renaissance of oligothiophenes was launched in 1989 when Garnier and Fichou realized that also shorter conjugated oligomers such as  $\alpha$ -sexithiophene can be used as active semiconductor materials in organic field-effect transistors.<sup>2</sup> Later on, the implementation of structurally defined end-capped oligothiophenes in organic light emitting diodes<sup>3</sup> was demonstrated in 1993, and that of  $\alpha$ -quinquethiophene and  $\alpha$ -octithiophene in organic solar cells<sup>4</sup> was demonstrated in 1995. While the vast majority of conjugated polymers and oligomers research focuses on microelectronic and optoelectronic applications,

researchers are applying increasingly the knowledge gained in these areas toward biomedical applications.<sup>5,6</sup> Used formerly as biosensors materials,<sup>7,8</sup> due to their variable absorption and emission wavelengths, OTFs were used further as photostable fluorescent markers for biomolecules.<sup>9</sup> Nowadays their bioapplications expand, OTFs that can overcome the limits of currently available organic dyes in live-cell staining<sup>10</sup>, useful in optical imaging of a plethora of protein aggregates in cerebral amyloidoses<sup>11</sup> or which presented organelle-selective imaging and anticancer activity<sup>12</sup> being reported. Moreover OTFs are good singlet oxygen sensitizers and biophotosensitizers<sup>13-15</sup> and  $\alpha$ -terthienyl, a secondary metabolite extracted from the root of the Marigold (*Tagetes erecta Asteraceae*), is a natural plant defense,<sup>16</sup> which together with its derivatives was used as photodynamic killing of

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insects, in photodynamic therapy for dermatophytes, in human immunodeficiency virus.<sup>17-19</sup> Following our previous interest in the thiophene-containing monomers and polymers with designed architectures and tuned photophysical properties,<sup>20, 21</sup> the present work reports on the synthesis of two amphiphilic structures based on poly(ethylene glycol)(PEG) and  $\alpha$ -terthienyl. In the light of the recent obtained results<sup>22, 23</sup> we expect that these new OTFs, due to the structural peculiarities could self-assemble in water as "stealth" nanoparticles with a biocompatible PEG corona and a fluorescent  $\alpha$ -terthienyl core useful for both cell-imaging and photodynamic therapy. Moreover, due to their specific structure, these compounds can be considered as macromonomers for eventually further polymerization reactions by chemical or electrochemical oxidative couplings of  $\alpha$ -TT.

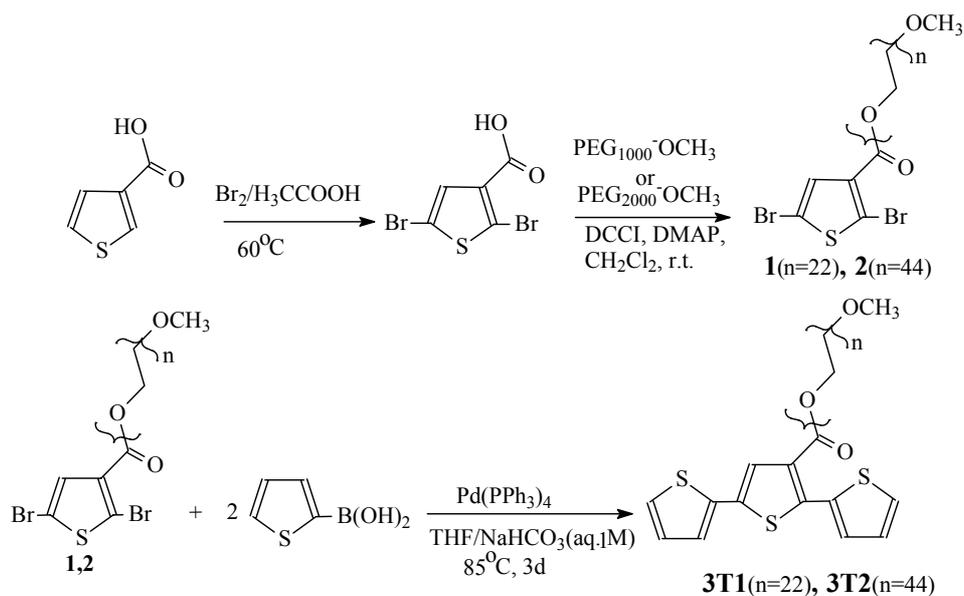
## RESULTS AND DISCUSSION

### Synthesis and Structural Characterization

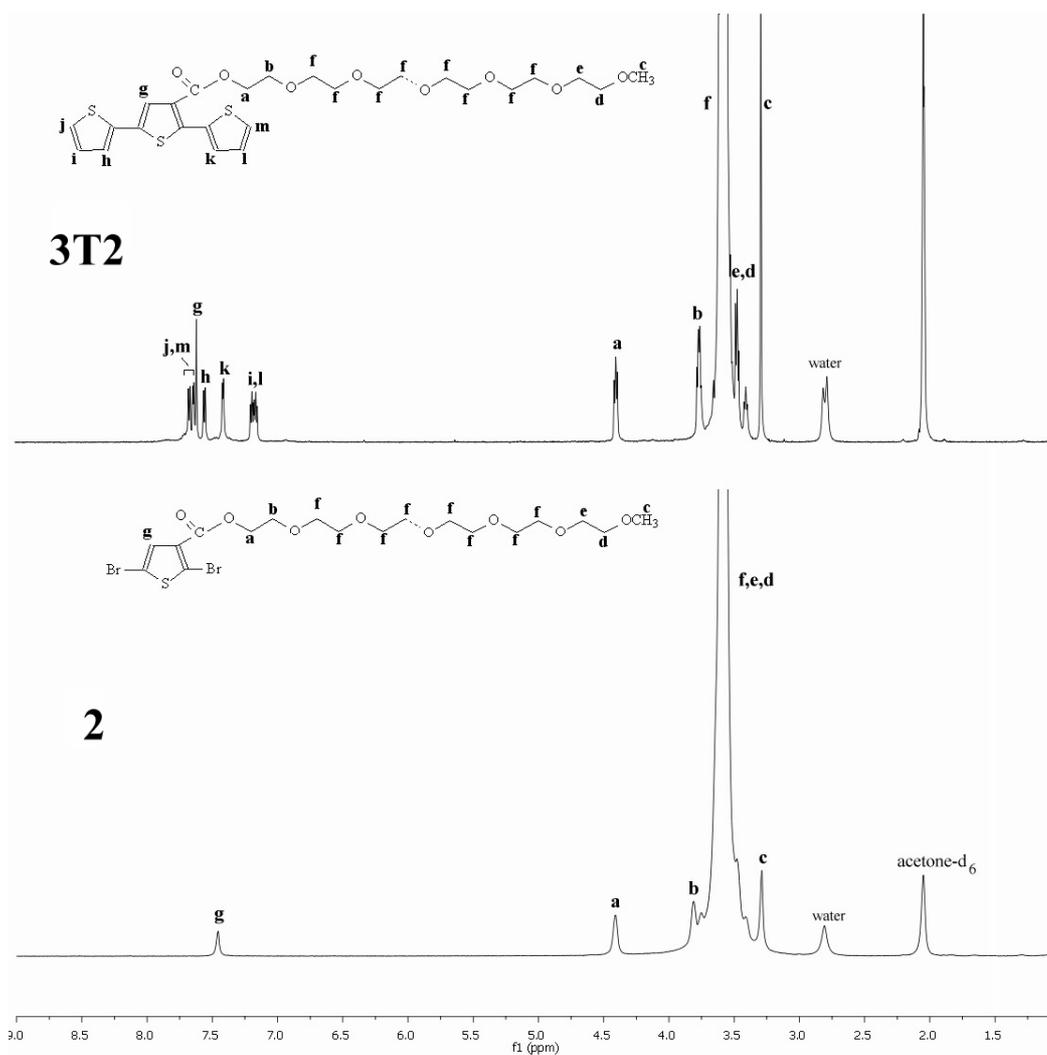
For any fluorescent material to be used for biological applications and to function as desired, it should be nontoxic, non-immunogenic, non-aggregating, and should not accumulate in the body, decompose in ambient conditions, or adsorb non-specifically to other biological molecules.<sup>24</sup> PEG is one of the most effective biocompatible building blocks that has been widely integrated into biomaterials to suppress nonspecific adsorption of biological substances. PEG has also been reported to serve as a steric repulsion and hydration molecular layer to reduce electrostatic and hydrophobic interactions with biomolecules that could mitigate nonspecific cellular uptake. In addition, PEG-containing amphiphilic polymers are prone to self-assemble into micelles in aqueous solution, which can offer a hydrophobic microenvironment for charge-transfer based fluorophores to enhance their fluorescence.<sup>25</sup> In our attempt for synthesis of water self-dispersible, fluorescent  $\alpha$ -TT, the first step of the followed strategy was the chain-end functionalization of commercially available poly(ethylene glycol)methyl ether ( $M_n=1000$ , **PEG**<sub>1000</sub>;  $M_w=2000$ , **PEG**<sub>2000</sub>) with 2,5-dibromothiophene

moieties through a Steglich esterification reaction.<sup>26</sup>

2,5-Dibromothiophene-3-carboxylic acid (**DBrThi-COOH**) used for esterification (top line in Scheme 1) was synthesized by bromination of 3-thiophene carboxylic acid using a method reported in the literature.<sup>27</sup> In order to assure a complete conversion of the hydroxylic chain ends of **PEG**<sub>1000</sub> and **PEG**<sub>2000</sub> a high excess of **DBrThi-COOH** was used. In the second step, the Suzuki coupling between **1** or **2** and 2-thiophene boronic acid was used for the obtainment of the coloured **3T1** and **3T2**. (Scheme 1, bottom line). The PEG substituted  $\alpha$ -TT show similar solubilities as PEG itself, including solubility in water. Because there were not obvious differences in the <sup>1</sup>H-NMR spectra of both **1** and **2** and also in <sup>1</sup>H-NMR spectra of **3T1** and **3T2**, in Fig. 1 the spectra of intermediate **2** and the one of **3T2** are given. They confirm the proposed structures in Scheme 1. In <sup>1</sup>H-NMR spectrum of **2** in acetone-*d*<sub>6</sub>, the ratio of the integration area of signals at chemical shifts  $\delta$  at 7.46ppm (thiophene protons) or  $\delta$  at 4.41 ppm (CO-OCH<sub>2</sub>) to that of  $\delta$  at 3.29 ppm (OCH<sub>3</sub>) is 1/3 or 2/3 respectively, as expected. The GPC traces of **1** and **2** were unimodal and narrow and show slightly different values as compared with the starting commercially PEGs. Using THF as eluent in GPC measurements,  $M_{n1}=1208$  and PDI=1.04 values were obtained for **1**(as compared to  $M_{nPEG1000}=1125$  and PDI=1.06) and  $M_{n2}=2436$  and PDI=1.05 values were obtained for **2** (as compared to  $M_{nPEG2000}=2543$  and PDI=1.06). The new introduced 2, 5-dibromothiophene chain ends to PEGs are responsible for these modifications. The GPC measurements of PEGs using columns calibrated with polystyrene (PSt) standards usually furnish overestimated values of molecular weights due to the difference in polarity of the two polymers. Also <sup>1</sup>H-NMR calculations based on the end groups can induce some errors due to the fact that bonding water or other traces of solvents can affect the overall integral of CH<sub>2</sub> groups of PEGs. Therefore in our further calculations we assumed theoretical values of  $M_n=1268$  for **1** and  $M_n=2268$  for **2**.



Scheme 1 – Synthesis of 3T1 and 3T2.

Fig. 1 –  $^1\text{H-NMR}$  spectra in  $\text{acetone-d}_6$  of 2 and 3T2.

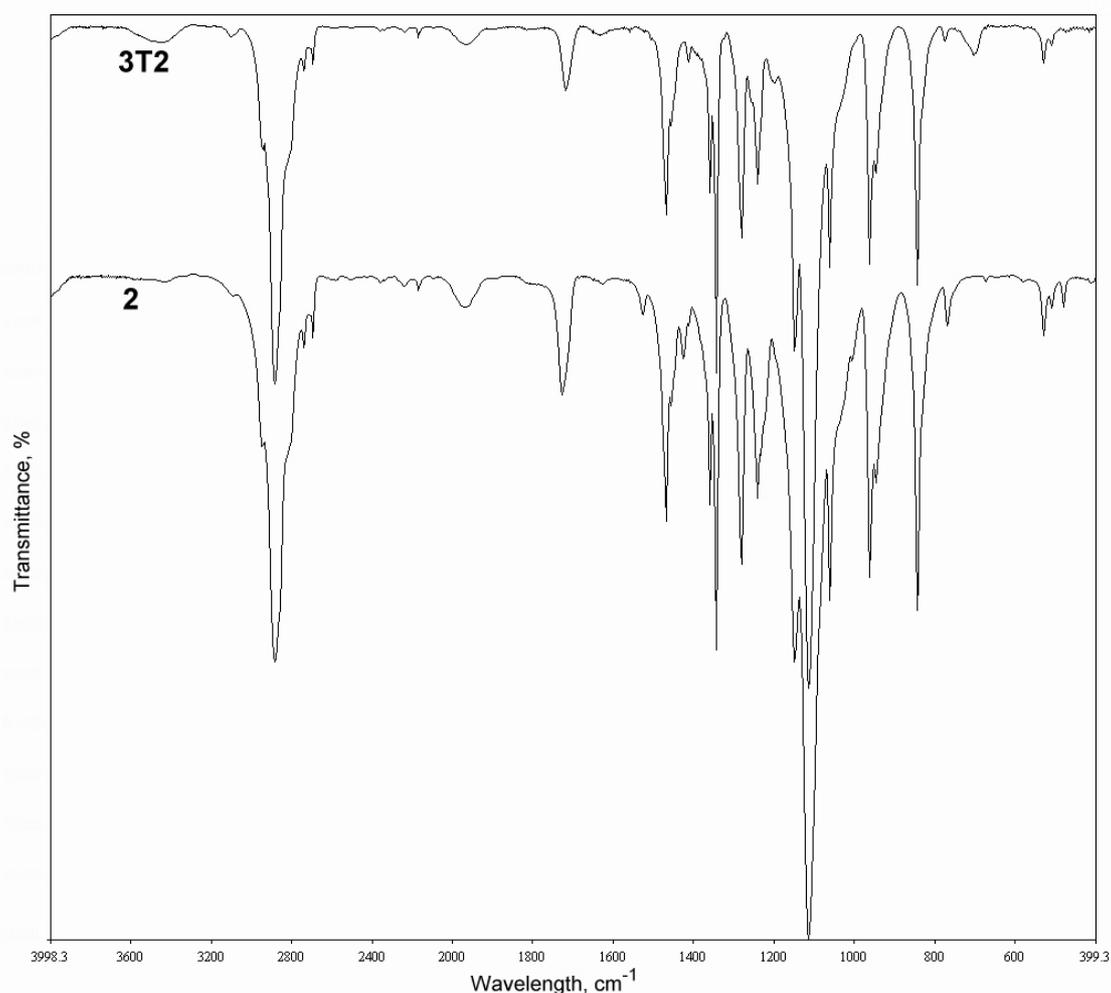


Fig. 2 – IR spectra of 2 and 3T2.

In Fig. 1  $^1\text{H-NMR}$  spectrum of **3T2** in acetone- $d_6$  is also given and the following peaks could be identified: ( $\delta$ , ppm): 7.66-7.61 (2H, 2d, **j,m**); 7.59 (1H, s, **g**); 7.54-7.53 (1H, d, **h**); 7.40-7.39 (1H, d, **k**); 7.18-7.13 (2H, m, **i,l**), 4.41-4.38 (2H, t, **a**), 3.78-3.75 (2H, **m, b**), 3.58-3.39 (about 180H, m, **f,e,d**), 3.29 (3H, s, **c**). The ratio between the integrals of aromatic protons and the peak from 4.41-3.38 is 7/2 proving the fully functionalization of **3T2**. Similar observations could be made in the case of  $^1\text{H-NMR}$  spectrum of **3T1**. The GPC traces ( $M_{n3T1}$  = 1460; PDI=1.05 and  $M_{n3T2}$  = 2591; PDI= 1.03) were also unimodal and slightly narrower than **1** and **2**, respectively. The IR spectra of 2,5-dibromo thiophene functionalized PEGs **1** and **2** show strong absorptions originating from PEG components at  $2884\text{ cm}^{-1}$  ( $\nu_{\text{as}}\text{CH}_2$ ),  $2738\text{ cm}^{-1}$  ( $\nu_{\text{s}}\text{CH}_2$ ),  $1464\text{ cm}^{-1}$  ( $\delta\text{CH}_2$ ),  $1359\text{ cm}^{-1}$ ,  $1342\text{ cm}^{-1}$  ( $\text{CH}_2$  wagging),  $1277\text{ cm}^{-1}$  ( $\text{CH}_2$  twisting),  $1241\text{ cm}^{-1}$  ( $\text{CH}_2$  twisting and C-O-C stretching),  $1148\text{ cm}^{-1}$  ( $\nu\text{ CO}$ ),  $1112\text{ cm}^{-1}$  (C-O-

C stretching),  $1059\text{ cm}^{-1}$  ( $\text{CH}_2$  rocking and C-O-C stretching),  $964\text{ cm}^{-1}$  ( $\text{CH}_2$  rocking) (Fig. 2).

Supplementary peaks (that are missing in the IR spectra of the starting PEGs), that can be attributed to the 2,5-bromo-thiophene moiety, appear at  $3091\text{ cm}^{-1}$  (shoulder),  $1524\text{ cm}^{-1}$ ,  $1423\text{ cm}^{-1}$ ,  $1005\text{ cm}^{-1}$  (shoulder),  $765\text{ cm}^{-1}$  and  $497\text{ cm}^{-1}$ . The last two signals can be attributed to the  $\nu\text{C-Br}$  bonds. The strong peak from  $1728\text{ cm}^{-1}$  belong to  $\nu\text{C=O}$  of the new formed ester group. The IR spectrum of **3T2** shows no obvious differences as compared with the starting intermediated **2** (Fig. 2). Despite this, one can notice two important changes: (i) the appearance of a relatively strong peak at about  $700\text{ cm}^{-1}$  ( $\nu\text{CH}$  thiophene ring) that can be explained by the presence of two supplementary monosubstituted thiophene rings in its oligomeric structure; (ii) the disappearance of the peak at  $497\text{ cm}^{-1}$  attributed to the C-Br linkage.

### Optical properties

Due to the amphiphilic nature of the investigated compounds, the used solvents for photophysical characterization were deliberately chosen to change their selectivity toward the different hydrophilic/hydrophobic character of the PEG and  $\alpha$ -TT chain, respectively. Therefore water (H<sub>2</sub>O) and methanol (MeOH) are selective solvents for PEG, while they are non-solvents for aromatic sequence. Dichloromethane (DCM) could be considered good solvent for both moieties. Dioxane (DOX) could be considered selective for thiophene, as long as its interaction parameter with PEG,  $\chi$  is 0.2 by comparing with DCM that has  $\chi = -0.51$  (liquids with the smallest  $\chi$ 's are usually the best solvents).<sup>28</sup> Taking into account these aspects, micelles-like aggregates with  $\alpha$ -TT core and PEG corona in H<sub>2</sub>O and MeOH, could be expected due to microphase separation, while inverse micelles with PEG core and  $\alpha$ -TT corona could be formed in DOX. In the DCM the tendency for aggregation is strongly diminished. Absorption and photoluminescence maximum wavelengths ( $\lambda_{\max}$  abs,  $\lambda_{\max}$  em.), molar absorption coefficients ( $\epsilon$ ), and Stokes shift of **3T1** and **3T2** are given in Table 1. The photophysical properties of analyzed compounds are influenced by the adopted conformation of both PEG and  $\alpha$ -TT in the solvents used for the measurements, by the aggregation tendency in those solvents and also by the length of the PEGs chains. These influence factors are more evident for the fluorescence behaviour than for the absorption. A comparison of UV spectra of **3T1** and **3T2** measured in solvents with different polarities shows a slightly difference in the position of the peak of  $\lambda_{\max}$  absorption (the

$\pi$ - $\pi^*$  transition), the values ranging between 348 nm – 354 nm. The differences are also not significant even in comparison with bare  $\alpha$ -terthienyl that shows  $\lambda_{\max}$  absorption at 350 nm for a solution in chloroform<sup>29</sup> and an absorption peak at 351 nm in ethanol.<sup>30</sup> However the absorption spectra are broad (280 nm-480nm) which provide flexibility in the choice of excitation wavelength when cell imaging applications are intended.

For fluorescence behaviour two aspects must be emphasized, namely the values of the  $\lambda_{\max}$  emission and the fluorescence intensity. As can be seen in Fig. 3, the PEGs chain length influences the fluorescence intensity, it being higher for **3T2** in all investigated solvents. This behaviour can be explained if the PEG conformation in investigated solvents is taken in account. PEG chains benefit from strong stabilizing interaction with water and methanol molecules having the most extended conformation in this two solvents. As the core-shell nanoparticles formation is supposed for these solvents, the PEG shell act as an “insulating” cover that prevent the exposure of the thiophene oligomeric chains to solvent molecules and consequently prevent deactivation of the excited state. As the shell is thicker fluorescence intensity is higher. In the case of DOX, when inverse micelles-like aggregate are expected, even in coiled conformation, the PEG chains could have higher size for **3T2** than **3T1** which better prevent the thiophene interchains aggregation by  $\pi$ - $\pi$  staking a phenomenon that usually conduct to excimer formation and to a decreased fluorescence intensity. A similar explanation can be considered for the DCM where the PEGs chains are enough extended to prevent better the  $\pi$ - $\pi$  staking.

Table 1

The photophysical properties of the synthesized  $\alpha$ -TT

Code	$\lambda_{\max}$ abs(nm)		$\lambda_{\max}$ em.(nm) <sup>a</sup>		Stokes shift (cm <sup>-1</sup> )		$\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> )	
	3T1	3T2	3T1	3T2	3T1	3T2	3T1	3T2
H <sub>2</sub> O	350	354	475	481	7590	7458	495.467	447.252
MeOH	348	348	462	469	7090	7413	492.639	439.671
DCM	350	352	462	465	6926	6904	495.467	444.725
DOX	350	352	455	460	6593	6431	495.467	444.725

a-  $\lambda_{ex} = \lambda_{\max}$  abs

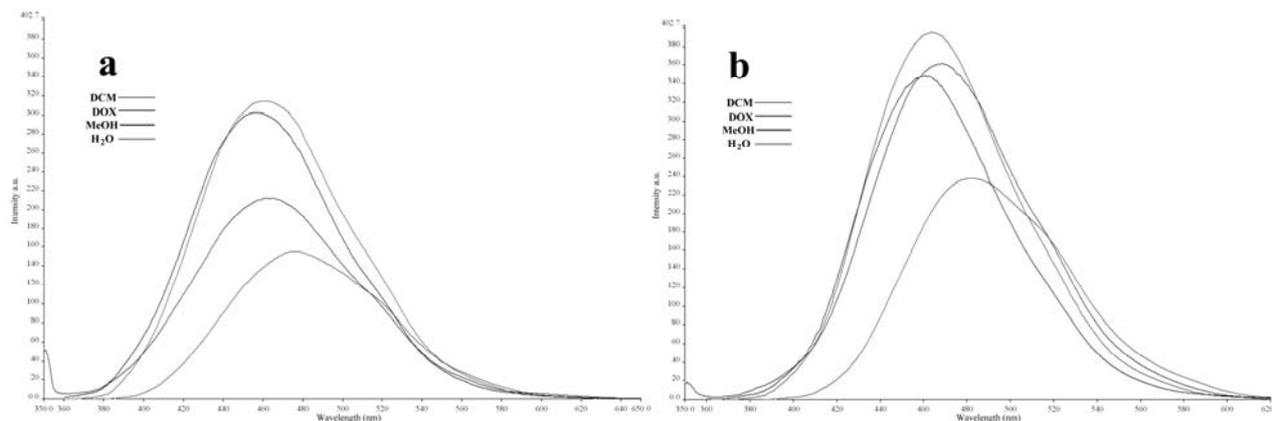


Fig. 3 – Fluorescence spectra of 3T1 (a) and of 3T2 (b).



Fig. 4 – 3T1 and 3T2 in water in the day light (left side) and under excitation with a 365 nm UV lamp (right side).

But this aggregation is not totally avoided, it is stronger in water and methanol for both **3T1** and **3T2**, the fluorescence intensity being significantly reduced by comparing with DCM and DOX. Due to the solvents polarity the PEG chains conformation can influence also the conformation of the thiophene short oligomeric chains. It seems that they are more planar when the PEGs chains are more extended and could be twisted in DCM. Certainly the thiophene chains interaction with solvents it is also important, the overall fluorescence behaviour being a result of both these effects. Consequently the fluorescence spectra of **3T2** are bathochromically shifted with respect to the same spectra of **3T1**, the magnitude of the shift being relatively small (3-7 nm) when the same solvent are considered and more higher (20 nm) when the most polar solvent ( $\text{H}_2\text{O}$ ) is compared with the less polar one (DOX) for both **3T1** and **3T2**. The highest bathochromical shift magnitude is obtained if the  $\lambda_{\text{max}}$  em. of **3T2** is compared with the  $\lambda_{\text{max}}$  em. of bare  $\alpha$ -terthienyl (406 nm).<sup>29</sup> In the case of the fluorescence traces in water of both **3T1** and **3T2** an evident red-shifted shoulder must to be remarked around 520 nm (Fig. 3). Such a behaviour was attributed in the literature to the nanoparticles formation and its appearance was

ascribed to energy transfer to low energy chromophores, that increases with increasing chain-chain interactions in nanoparticles core.<sup>31</sup>

The presence of this shoulder in a spectral region commonly used for biological imaging increase the benefit of the synthesized compounds. They also present high values of the Stokes shift, which is one of the most important request for a fluorescent compound to be used in fluorescence bioimaging. It must have sufficiently large Stokes shifts to filter out the exciting light.<sup>32</sup> In Fig. 4 photos of both **3T1** and **3T2** water-self-dispersible compounds are presented showing a strong fluorescence at low concentration ( $0.7 \times 10^{-3}$  mol/L) under excitation with a 365 nm UV lamp.

## EXPERIMENTAL

### Materials

All the used solvents were purified and dried by usual methods. Poly(ethylene glycol)methyl ether Mn=2000 (**PEG<sub>2000</sub>**) (Aldrich), poly(ethylene glycol) methylether Mn=2000 (**PEG<sub>1000</sub>**), 3-thiophene carboxylic acid (Aldrich), 2-thiophene boronic acid (Aldrich), N,N'-dicyclohexylcarbodiimide (DCCI) (Merk), 4-dimethylamino pyridine (DMAP) (Aldrich), Pd(PPh<sub>3</sub>)<sub>4</sub> (Aldrich) were used as received.

### Measurements

$^1\text{H-NMR}$  spectra were recorded at room temperature on a Bruker Avance DRX-400 spectrometer (400 MHz) as solutions in acetone  $d_6$  and chemical shifts are reported in ppm. The relative molecular weights were determined by gel permeation chromatography (GPC) using a PL-EMD instrument, polystyrene standards for the calibration plot and THF as elution solvent. FT-IR spectra were recorded on a Bruker Vertex 70 FTIR spectrometer, equipped with a diamond ATR device (Golden Gate, Bruker) in transmission mode, by using KBr pellets. UV-Vis and fluorescence measurements were carried out on Specord 200 spectrophotometer and Perkin Elmer LS 55 apparatus, respectively using the solutions of compounds at concentration of  $0.7 \times 10^{-3}$  (mol/L) in different solvents.

#### Synthesis of 2, 5-dibromothiophene-3-carboxylic acid (DBrThi-COOH)

The reaction was performed using a method adapted from literature.<sup>27</sup>  $^1\text{H-NMR}$  (acetone  $d_6$ ): 10.86 ppm (COOH), 7.4 ppm (TiH).

#### Synthesis PEG polymers functionalized with 2, 5 dibromothiophene moieties (1, 2)

8 g (0.008 mol) of PEG<sub>1000</sub>, and 3,432 g (0.012 mol) of DBrThi-COOH were placed into a three-neck round-bottom flask equipped with a dropping funnel, under  $\text{N}_2$ . 70ml of  $\text{CH}_2\text{Cl}_2$  and 0,1452g (0.0012 mol) DMAP were added to the flask. 2,4624g (0,012mol) DCCI in 6 ml  $\text{CH}_2\text{Cl}_2$  were placed in the dropping funnel and added in about 15 min. The mixture was stirred at room temperature for three days. The resulting solution was filtered and precipitated in cold diethyl ether to remove the catalyst and unreacted reagents. After filtration and drying a white solid **1** was obtained. Intermediate **2** was obtained in a similar manner using 8g (0.004 mol) of PEG<sub>2000</sub>, 1.716g (0.006 mol) of DBrThi-COOH, 0.0726g (0.00006 mol) of DMAP and 1.2312g (0.006mol) of DCCI.

$^1\text{H-NMR}$  (**2**) (acetone- $d_6$ ): 7.46 ppm (TiH), 4.41 ppm; (CO-OCH<sub>2</sub>), 3.91 ppm (second CH<sub>2</sub>O), 3.45-3.41 ppm (CH<sub>2</sub>O from PEG, 3.29 OCH<sub>3</sub>).

#### Synthesis of PEG substituted $\alpha$ -Terthiophenes (3T1, 3T2)

A 20 mL three neck round bottom flask equipped with a condenser, a rubber septum, nitrogen inlet-outlet and magnetic stirrer was charged under inert atmosphere with 0.416 mmol dibrominated compounds **1** or **2**, 1.66 mmol 2-thiophene boronic acid and 0.0166 mmol Pd(PPh<sub>3</sub>)<sub>4</sub>. Then 8 mL mixture of solvents (THF/1M NaHCO<sub>3</sub>, 3/2 v/v) was introduced with a syringe through the septum. The reaction was maintained under vigorous stirring and with the exclusion of oxygen and light. The mixture was refluxed under nitrogen for 3 days. The reaction was stopped and the mixture was extracted several times with dichloromethane. The organic layer was dried over MgSO<sub>4</sub>, concentrated by rotary evaporation and precipitated in cold diethyl ether. After filtration and drying under vacuum, **3T1** and **3T2** were obtained as reddish (**3T1**) and yellowish (**3T2**) powders. Their purification was performed by passing the solutions in dichloromethane through a silicagel filled column and then reprecipitated in cold diethyl ether.

### CONCLUSIONS

Using the versatile thiophene chemistry, two stimuli-sensitive, water self-dispersible, fluorescent

$\alpha$ -terthiophenes were successfully synthesized, the properties of which can be modulated to make them more robust, more brightly fluorescent, and easier to be adapted for biological interest. Their photophysical properties in different solvents were also emphasized in conjunction with their structural peculiarities and the solvents properties. The water self-dispersible micelles of both newly synthesized  $\alpha$ -TT show a strong fluorescence and a remarkable Stokes shift in water that make them potentially applicable in cell-imaging. Based on the already reported photosensing properties of the bare  $\alpha$ -terthienyl, the applications of **3T1** and **3T2** in photodynamic therapy could be also expected.

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