



HAL
open science

Original synthesis and spectroscopic study of thiophene triazine derivatives with enhanced luminescence properties

Alysson Duarte Rodrigues, Nathalie Marcotte, Françoise Quignard, Stefano Deabate, Mike Robitzer, Dan A. Lerner

► To cite this version:

Alysson Duarte Rodrigues, Nathalie Marcotte, Françoise Quignard, Stefano Deabate, Mike Robitzer, et al.. Original synthesis and spectroscopic study of thiophene triazine derivatives with enhanced luminescence properties. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* [1994-..], 2020, 227, pp.117708. 10.1016/j.saa.2019.117708 . hal-02433542

HAL Id: hal-02433542

<https://hal.umontpellier.fr/hal-02433542>

Submitted on 21 Jul 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

1 **Original Synthesis and Spectroscopic Study of Thiophene Triazine Derivatives** 2 **with Enhanced Luminescence Properties**

3 Alysson Duarte Rodrigues^{a,c}, Nathalie Marcotte^{a,c}, Françoise Quignard^a, Stefano Deabate^{b,c}, Mike
4 Robitzer^{a,c,*} and Dan A. Lerner^{a,c,*}

5 ^a ICGM, Univ Montpellier, ENSCM, CNRS, Montpellier, France

6 ^b Institut Européen des Membranes, IEM – UMR 5635, ENSCM, CNRS, Univ Montpellier,
7 Montpellier, France

8 ^c Ecole National Supérieure de Chimie de Montpellier, 240 Avenue du Professeur E. Jeanbrau, 34296
9 Montpellier Cedex 5, France

10 *mike.robitzer@enscm.fr and dan.lerner@enscm.fr*

11 **ABSTRACT**

12 A straightforward access to π -conjugated oligothiophenes bearing amino-rich groups was
13 developed. Palladium-catalyzed C-H arylation applied in the main step of the synthesis allowed to
14 couple 2-thiophenecarbonitriles and aryl bromides with moderate to excellent yields (35-93%). Then, to
15 improve their basic fluorescence properties, these compounds was transformed into their 2,4-diamino-
16 1,3,5-triazine derivatives, also with good to excellent yields (74-98%). UV-Visible absorption and
17 fluorescence studies identified a strongly emissive molecule (fluorescence quantum yield: $\Phi_F = 0.78 \pm$
18 0.05), which could find use in sensors for applications in biology and in material chemistry. We
19 observed an antagonistic effect in the spectroscopic properties of oligothiophenes bearing 2,4-diamino-
20 1,3,5-triazine, resulting in improved absorptive and emissive properties for more constrained structures
21 having shorter oligothiophenes chains.

22
23 **Keywords:** Thiophene, oligothiophene, triazine, palladium catalyzed C-H arylation, fluorescence,
24 fluorescent label

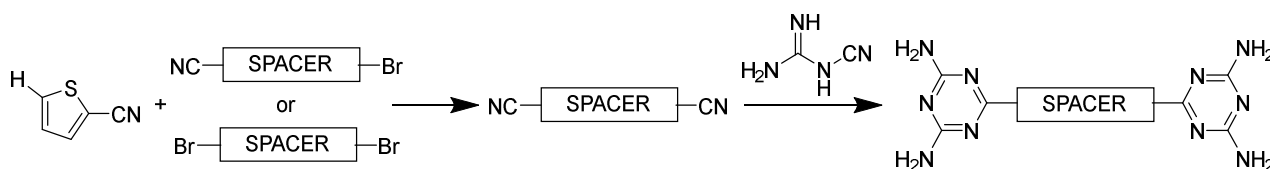
25 **1. Introduction**

26 Oligothiophenes (OTs) have proven to be one among the most promising functional materials for
27 a wide range of applications. The most notable properties of these compounds are related to their
28 electrical conductivity and light emitting characteristics sensitive to environmental stimuli [1]. Both
29 color and conductivity changes, induced by the same twisting mechanism of their mostly linear
30 molecular structures, have been intensely studied in conducting films for electrochromics [2-4] or in
31 solution for sensing applications [5-7].

1 2,4-Diamino-1,3,5-triazines (DATs) are polar, nitrogen-containing heterocycles widely used in
2 many domains of chemistry. They are involved in the development of conducting films [3-4], fire
3 resistant resins [8], polymers [9], therapeutic drugs [10], herbicides [11], gas storage [12] and some
4 DATs containing catalysts benefit from their nitrogen-rich content and high stability [13].

5 As discussed in our former work, the fluorescence properties of OT-DAT compounds might find
6 applications in biology as fluorescent sensitizers, due to their activity towards Prion proteins [14]. The
7 synthesis of OTs bearing amino-rich groups is a challenge due to their lack of solubility in the most of
8 laboratory common solvents, what obviously hinders purification. To catalytically couple thiophenes,
9 conventional cross-coupling reactions as those of Stille, Kumada, Negishi and Suzuki are most
10 frequently used [6, 15]. But such protocols are often time-consuming and require expensive and/or toxic
11 organometallic catalysts (e.g. Sn-based).

12 In order to improve the synthesis of OTs bearing amino-rich groups, we have developed an
13 adapted Fagnou's approach [16-18] using a palladium-catalyzed C-H arylation to promote C-C bond
14 formation. This pathway allows largely increased reactivity in the concerted metalation deprotonation
15 mechanism (CMD) of the reaction between 2-thiophenecarbonitrile and aryl bromides (**Scheme 1**). The
16 final compounds synthesized by this approach have been fully characterized and their basic absorption
17 and photoluminescence properties have been determined and compared.



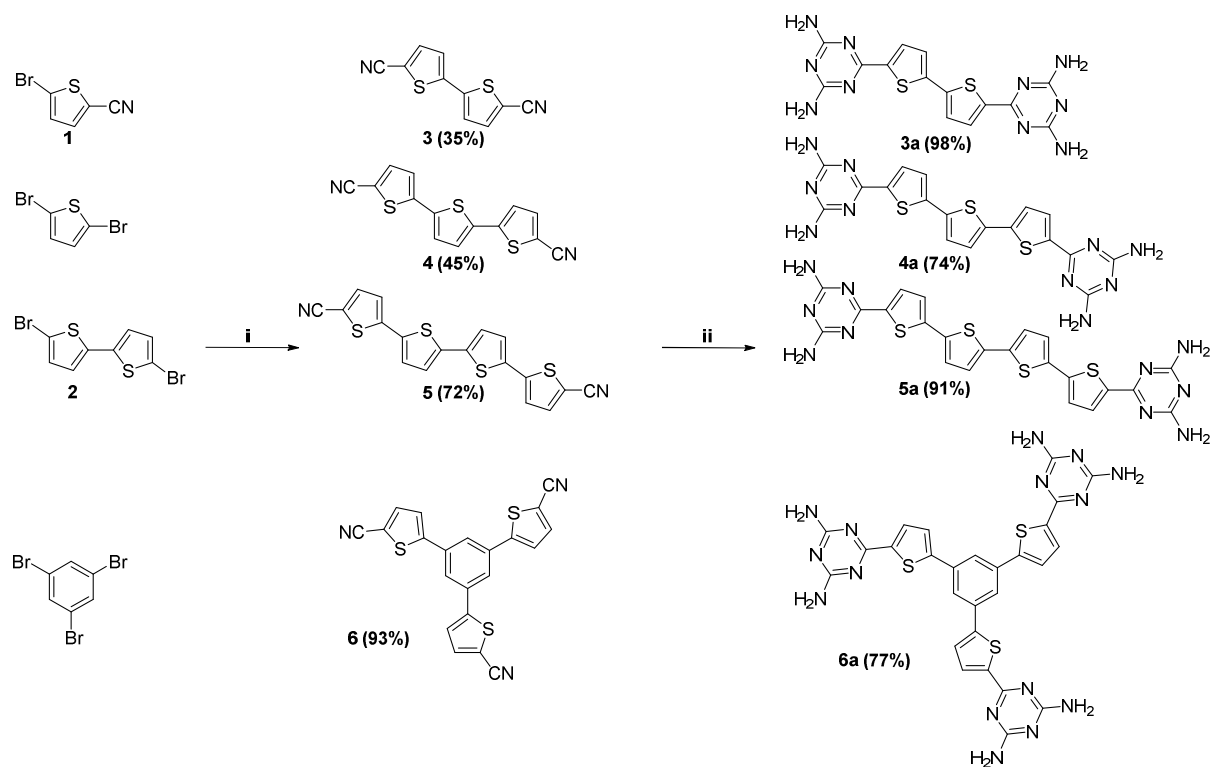
20 **Scheme 1.** Schematic pathway for the synthesis of thiophene diaminotriazine derivatives.

21 2. Results and discussion

22 2.1 A new and efficient synthetic route for the preparation of OT-DAT compounds

23 The aryl bromide precursors (**Scheme 2 – left side**) were commercially available or prepared
24 according to literature data [18]. 5-bromothiophene-2-carbonitrile (**1**) was obtained by reacting 2-
25 thiophenecarbonitrile with bromine (Br₂) and N-bromosuccinimide (NBS) in a solvent mixture of acetic
26 anhydride / acetic acid 50/50 (v/v %) during 14 h at room temperature. The final product was then
27 isolated by column chromatography using cyclohexane as eluent. The 5,5'-dibromo-2,2'-bithiophene (**2**)
28 was obtained in an acetic acid / chloroform 50/50 (v/v %) solvent mixture at room temperature using
29 NBS as brominating agent. The final product was isolated by successive recrystallizations in acetone.
30 All compounds have been characterized by ¹H and ¹³C NMR, UV-Vis, ATR-FTIR, HRMS (see 4-
31 experimental part).
32

1
2



3

4 **Scheme 2.** Molecular structure and synthesis yields (%) of OTs bearing nitriles and diaminotriazines (**3-**
5 **5** and **3a-5a**) or phenylthiophene bearing nitriles and diaminotriazines (**6** and **6a**): **i**) (3 eq.) 2-
6 thiophenecarbonitrile, (4 mol %) Pd(PPh₃)₄, (1.5 eq.) K₂CO₃, (0.15 eq.) pivalic acid, **N,N-**
7 **dimethylacetamide/toluene 50/50 (v/v %)**, C: 0.23 M, 110 °C, 48h and **ii**) (3 eq.) 2-cyanguanidine, (1
8 eq.) KOH, DMSO C: 0.1 M, 80°C, 16h. All amounts (eq.) are calculated according to the number of
9 precursor reactive sites (**(i)** -Br and **(ii)** -CN).

10

11 OTs bearing nitrile groups (**3-6**) (**Scheme 2 - middle**) were obtained in a single step by the
12 palladium-catalyzed C-H arylation pathway reacting 2-thiophenecarbonitrile and the respective aryl
13 bromides.

14 The palladium-catalyzed C-H arylations (**step i**, **Scheme 2**) were monitored by thin layer
15 chromatography (TLC) and UV-Vis absorption spectroscopy and were stopped when no more reactivity
16 was detected (after around 48h). The **N,N-dimethylacetamide/toluene 50:50 (v/v %)** solvent mixture
17 provided the best solubility at 110 °C among all solvents tested and was chosen as the standard solvent
18 mixture for all tries.

1 In the presence of tetrakis-(triphenylphosphine)palladium(0), K_2CO_3 and pivalic acid, the expected
2 products (**3-6**) were synthesized in moderate to excellent yields (35-93%). Purifications were carried out
3 by successive recrystallizations in appropriate solvents (**3, 4 and 6** in 1-butanol and **5** in toluene at room
4 temperature).

5 Yields were observed to improve with the number of reactive sites (-Br) of the precursor aryl
6 bromides and the OT chain length. This suggests phenyl-bromide intermediates to be more reactive than
7 thienyl ones. Results lead to the following reactivity scale in terms of isolated yields : 1,3,5-
8 tribromobenzene > 5,5'-Dibromo-2,2'-bithiophene > 2,5-dibromothiophene > 5-bromothiophene-2-
9 carbonitrile.

10 Further investigations carried out by GC-MS at the end of reactions revealed lower contents of
11 mono- (<1%) and di- (2.4%) arylated intermediates when 1,3,5-tribromobenzene was used as aryl
12 bromide. These results contrast with the higher contents of mono-arylated intermediates found using
13 5,5'-dibromo-2,2'-bithiophene (13%) and 2,5-dibromothiophene (31%) respectively. Although the better
14 electronic delocalization of benzene seems to favor the CMD mechanism, thienyl bromides allow good
15 conversions when less deactivating groups are substituted at the C2-position of the thiophene, giving to
16 the following reactivity scale: 5'-bromo-thiophene > -Br > -CN.

17 The transition state (TS) involving both substrates in the palladium-catalyzed C-H arylations was
18 consistent with the presence of a pivalate anion assisting the deprotonation of 2-thiophenecarbonitrile in
19 C5 position and favoring its oxidative addition in the palladium catalyst [16-17]. The desired products
20 were obtained by a reductive elimination step [18].

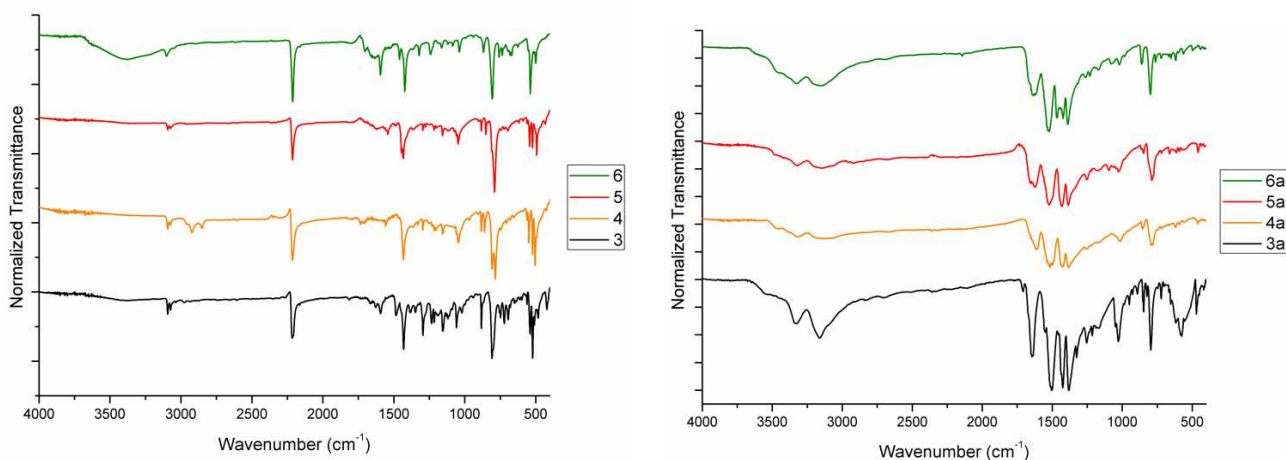
21 The diaminotriazine derivatives **3a-6a** (**Scheme 2 – right side**) were easily obtained by
22 cycloaddition between the nitrile precursors (**3-6**) and 2-cyanoguanidine. Reactions were carried out in
23 DMSO at 80 °C using KOH as base, and the pure compounds (**3a-6a**) were isolated following
24 successive recrystallizations in THF. The compounds solubility decreased with the addition of the DAT
25 groups.

26 2.2 Infrared spectroscopy

27 **Figure 1** compares normalized infrared (ATR-FTIR) spectra of compounds **3-6** and **3a-6a**. As
28 expected, spectral changes are mostly observed in the spectral domains of nitrile ($C\equiv N$)_{str} and amine ($N-$
29 H)_{str} stretching vibrational modes (2260-2210 and 3400-3250 cm^{-1} ranges respectively) as well as in the
30 region of the ($N-H$)_{bend} bending mode (1650-1580 cm^{-1}). Compounds **3-6** display the characteristic
31 bands due to the ($C-H$)_{str} and ($C-H$)_{bend} modes of thiophenes, at 3000-2850 and \sim 1400 cm^{-1}
32 respectively. The nitrile function can be identified with the narrow band at 2212 cm^{-1} due to the ($C\equiv N$)_{str}
33 mode. Spectra of compounds **3a-6a** show the disappearance of the latter and the appearance of the

1 primary amine bands at 3327 cm^{-1} ($(\text{N-H})_{\text{str}}$ mode) and 1647 cm^{-1} ($(\text{N-H})_{\text{bend}}$). The aromatic DATs are
2 identified by the presence of the $(\text{C-N})_{\text{str}}$ mode typical of heterocycles at 1379 cm^{-1} .

3



4

5

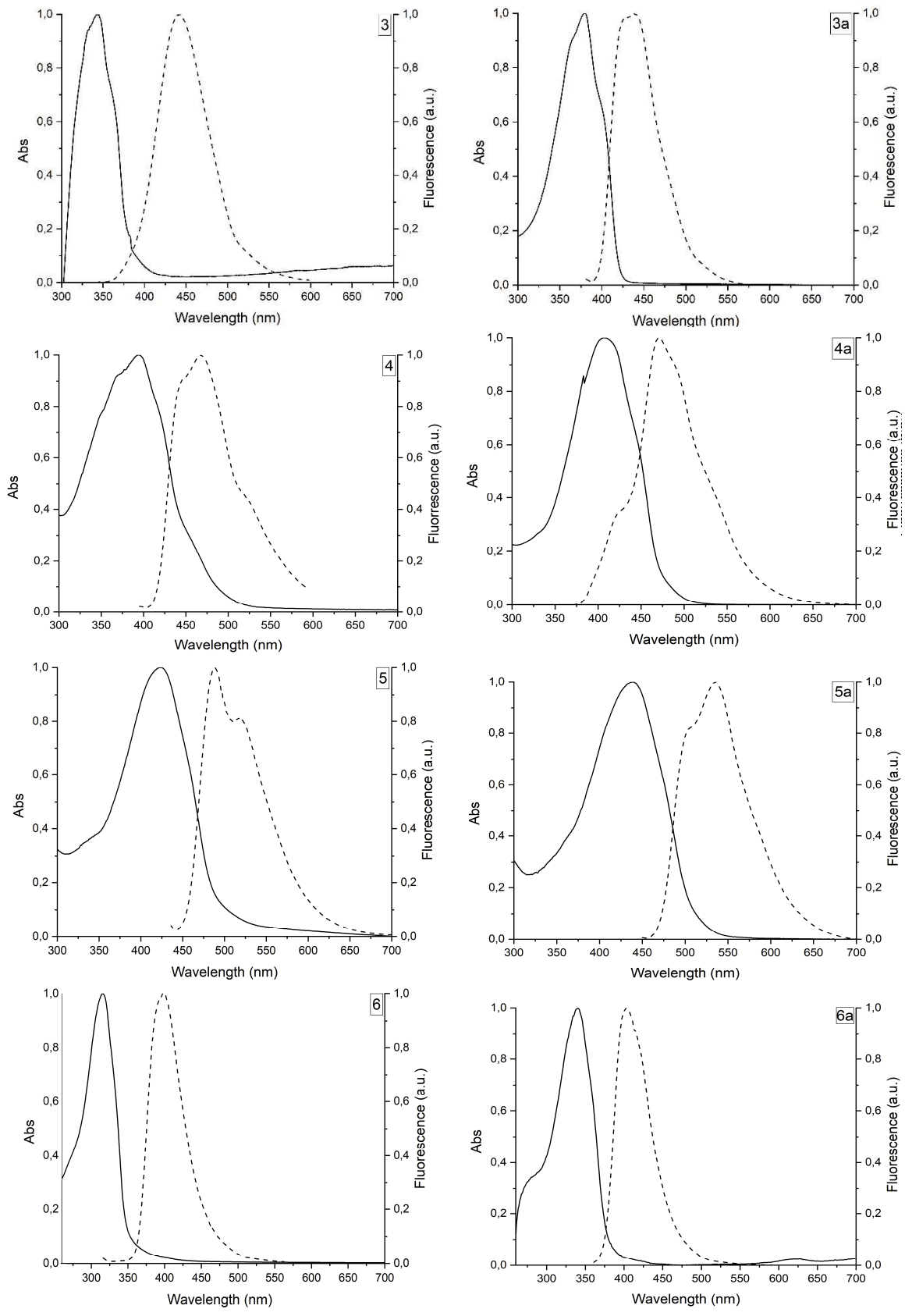
6 **Fig. 1.** ATR-FTIR spectra of compounds (**3-6**) (left) and (**3a-6a**) (right).

7

8 2.3 Electronic spectroscopy:

9 The photo-physical properties of the different compounds were firstly investigated by UV-Visible
10 absorption spectroscopy, in the range of 200 to 700 nm. The emission properties were then
11 characterized by excitation at different wavelengths. Absorption and emission spectra of compounds (**3-**
12 **6**) and their DAT derivatives (**3a-6a**) (**Figure 2** and **3** respectively) were all obtained in air equilibrated
13 DMSO solutions and at room temperature ($23\text{ °C} \pm 2\text{ °C}$). Relevant data are summarized in **Table 1**.
14 Emission spectra stayed unchanged whatever the excitation wavelength.

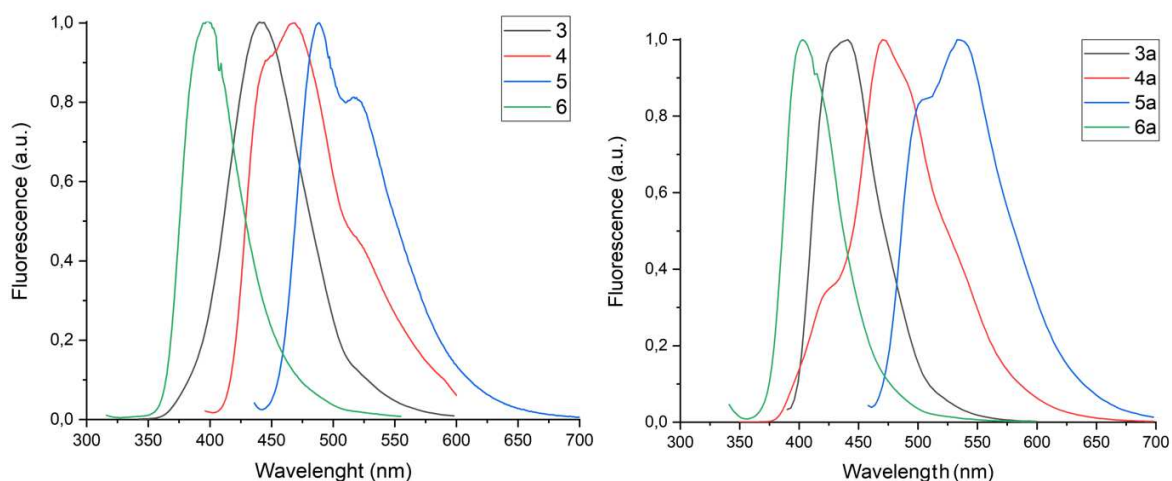
15



1
2
3

Fig. 2. Normalized absorption (solid line) and emission (dashed line) spectra of compounds **3-6** and **3a-6a** in air equilibrated DMSO solutions at T_{room} .

1



2

3

4

Fig. 3. Normalized emission spectra of derivatives **3-6** (left) and **3a-6a** (right) (air equilibrated DMSO solutions at T_{room}).

5

6

Compound	λ_{max} Absorption (nm) / ϵ (L. mol ⁻¹ cm ⁻¹)	Excitation wavelength (nm)	λ_{max} Emission (nm)	Stokes shift (cm ⁻¹)	E_{00} , (E_g) (eV)	Φ_F (± 0.05)
3	346 / (9862)	342	442	6280	3.18 (3.6)	0.05
4	396 / (16905)	394	468	3885	2.85 (3.1)	0.41
5	431 / (25404)	422	488	2710	2.64 (2.9)	0.55
6	317 / (39921)	307	398	6420	3.40 (3.9)	0.18
3a	377 / (37909)	380	442	3900	3.3 (3.3)	0.78
4a	419 / (36196)	404	474	2770	2.76 (2.9)	0.59
5a	447 / (30151)	439	538	3785	2.55 (2.7)	0.26
6a	344 / (26628)	342	405	4380	3.26 (3.6)	0.22

7

8

9

10

11

12

13

14

15

16

Table 1: UV-visible and fluorescence spectroscopic data for compounds **3-6** and their DAT derivatives **3a-6a** in air equilibrated DMSO solutions. For compounds **3**, **3a**, **6** and **6a**, Anthracene (A) in ethanol ($\Phi_F = 0.28 \pm 0.02$) [19] has been used as a standard for fluorescence quantum yields calculations. Perylene (P) in DMSO ($\Phi_F = 0.78 \pm 0.02$) [20] has been used for compounds **4**, **4a**, **5** and **5a**. Stokes shifts are calculated from the difference between the emission λ_{max} and the excitation λ_0 (nm) and then converted in cm⁻¹. E_{00} transitions are obtained from the spectral position corresponding to the crossing of excitation and emission spectra (**Figure 2**). E_g were optical estimates of the band gaps (see explanation in the text).

1 In view of the potential use of some of these compounds in organic semiconductors, for which the
2 knowledge of the band gap is essential, we estimated E_g (**Table 1**) in addition to the value of the 0-0
3 energy transitions. E_g values were obtained from the absorption edge of the lowest energy band of the
4 UV-visible spectrum, as described for instance in the work of Bhadwal [21] or Costa [22]. The two sets
5 of data, E_{00} and E_g , based on purely optical parameters of individual molecules, were expected to give
6 nearly identical values, even if approximated for E_g .

7 It should then be point out that the 0-0 gap of a molecule can be computed with all the desired
8 accuracy whereas obtaining the true values of E_g would require the theory of electronic band structures
9 specially derived for crystals with a lattice periodicity. So, E_g values may be very different, depending
10 on the molecules packing and orientation (see [23] for more details about this issue). Ideally the E_g
11 notation for a single molecule should be renamed “the optical band gap” with a symbol like OE_g or $E0-0_g$
12 for instance to avoid confusion. Experimentally, the actual value of E_g may be obtained by various
13 methods such e.g. running reflectance spectra, cyclic voltammetry, etc. [23].

14 2.3.1 UV-Vis spectroscopy.

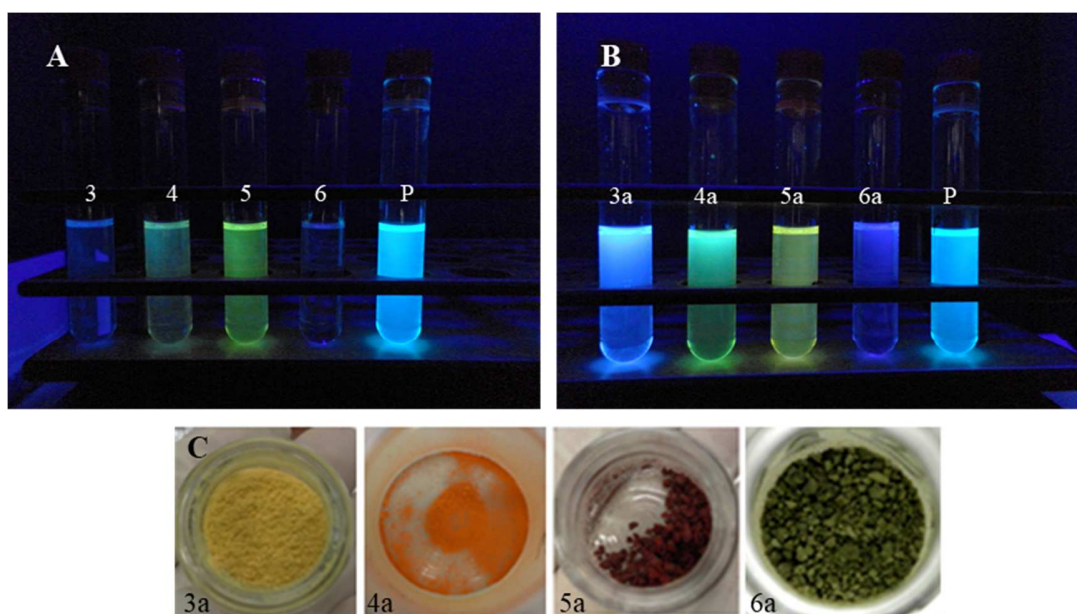
15 The absorption maxima of the different compounds are observed to red-shift with the increase of the
16 chain length of oligothiophenes i.e. λ_{\max} bithiophenes (**3** and **3a**) < λ_{\max} terthiophenes (**4** and **4a**) < λ_{\max}
17 quaterthiophenes (**5** and **5a**) (**Figure 2**). As shown by E_{00} (eV) values (**Table 1**), this evolution results
18 from the progressive reduction of the HOMO-LUMO energy gaps. Due to their specific structures,
19 tripodes (**6** and **6a**) exhibit higher energy band gap values (3.9 eV and 3.6 eV for **6** and **6a** respectively),
20 with λ_{\max} red-shift when going from nitrile (**6**) to the DAT derivative (**6a**). These compounds, with more
21 compact molecular structures, might find applications in material chemistry as insulators for instance.

22 Nitrile derivatives (**3-5**) exhibit the increase of the molar absorptivity with the increase of the OT
23 chain length: on average of 7700 L. mol⁻¹ cm⁻¹ per added thiophene. Furthermore, the transformation of
24 **3** into **3a** by the double cycloaddition reaction increases the molar absorptivity up to about 28000 L.
25 mol⁻¹ cm⁻¹. Compound **3** presents $\epsilon = 9860$ L. mol⁻¹ cm⁻¹ and **3a** $\epsilon = 37910$ L. mol⁻¹ cm⁻¹, which means
26 that compound **3a** absorbs light 3.8 times more than compound **3**. According to the above, direct
27 observations for the **3-5** serie and the **3-3a** transformation, one would expect **3a-5a** DAT derivatives to
28 exhibit the same ϵ increase trend.. On the contrary, the molar absorptivity of compounds **3a-5a** decreases
29 with the increase of the OT chain length. Compound **3a** presents $\epsilon = 37910$ L. mol⁻¹ cm⁻¹, **4a** $\epsilon = 36200$
30 L. mol⁻¹ cm⁻¹ and **5a** $\epsilon = 30150$ L. mol⁻¹ cm⁻¹. This is the hint of an antagonistic phenomenon affecting
31 the absorption properties of DAT derivatives.
32

1 Although tripods **6** and **6a** do not present the same molecular structures as OT derivatives, we
2 observe the same decrease of the ϵ values in the **6** \rightarrow **6a** transformation (from 39920 L. mol⁻¹ cm⁻¹ to
3 26630 L. mol⁻¹ cm⁻¹). This confirms that the antagonistic effect brought by the DAT function is also
4 found in molecules with less conjugated systems and different molecular structures.

6 2.3.2 Fluorescence.

7 The **Figure 4-A** and **B** compare fluorescence brightness of compounds **3-6** and **3a-6a** respectively, in
8 DMSO solution. Perylene is used, as standard (**P**, $\Phi_F = 0.78 \pm 0.02$ in DMSO). **Figure 4-C** shows the
9 colored compounds **3a-6a** at the solid state. A brightness increase is observed for all compounds in
10 DMSO solutions when going from nitriles to DAT derivatives. The emitted colors shifts from blue to
11 yellow with the OT chain length increase. Compound **3a** exhibits spectroscopic and visual properties
12 similar to those of **P** standard.



13 **Figure 4:** A) compounds **3-6** and standard **P** at 1.0×10^{-6} M in DMSO solutions irradiated with an UV
14 lamp ($\lambda = 366$ nm); B) **3a-6a** and standard **P** at 1.0×10^{-6} M in DMSO solutions irradiated with an UV
15 lamp ($\lambda = 366$ nm) and C) **3a-6a** at solid state in day-light.

16
17
18 Our molecules, since quite stable towards temperature and chemical degradation, might be useful
19 as fluorescent probes in biological applications as well as components in molecular devices for energy
20 conversion. Therefore, because of their potential interest in the biological field, their fluorescence
21 quantum yields have been estimated with samples diluted in DMSO at ambient conditions (**Table 1** -
22 Φ_F). Due to the large spectral span of our compounds, we used Perylene or Anthracene as actinometers.

1 We used perylene standard (**P**) for compounds **4**, **4a**, **5** and **5a** and anthracene standard (**A**) for
2 compounds **3**, **3a**, **6** and **6a**. UV absorption and fluorescence emission of both standards are shown in
3 **Figure S11**.

4 When compared to their nitrile precursors (**4 - 6**), compounds **4a**, **5a** and **6a** display a significant
5 red-shifted emission, indicative of an electronic distribution more delocalized over the OT chain and the
6 DAT groups in agreement with the extended π - π conjugation (**Figure 3**). Otherwise, **Figure S12** shows
7 that no shift occurs between the fluorescence λ_{\max} of compounds **3** and the DAT derivative **3a** ($\lambda_{\max} =$
8 442 nm), with an almost perfect overlap of the two transitions but much larger emission intensity of the
9 DAT product (**Table 1**).

10 In the series of oligothiophenes bearing nitrile groups (**3-5**), the better electronic delocalization in
11 the molecular structure and the fluorescence quantum yields went along with the displacement of the
12 emission maxima wavelengths. The quantum efficiency increases with the OT chain length ($\Phi_F = 0.05$
13 ± 0.05 for bithiophene (**3**), $\Phi_F = 0.41 \pm 0.05$ for terthiophene (**4**) and $\Phi_F = 0.55 \pm 0.05$ for
14 quaterthiophene (**5**)). Otherwise, as previously observed for the molar absorptivity values (ϵ), the
15 quantum efficiency of DAT derivatives (**3a-5a**) show the opposite behavior i.e. decrease of Φ_F with the
16 increase of the OT chain length. This phenomenon is probably related to the formation of more
17 constrained structures with lower degrees of torsional freedom.

18 Compound **3a** exhibits a highly efficient fluorescence emission, with a quantum yield $\Phi_F = 0.78 \pm$
19 0.05 resulting from the extended π - π conjugation and, probably, the higher steric hindrance of such a
20 small molecule. Similarly, compound **4a** shows good fluorescence emission properties with $\Phi_F = 0.59$
21 ± 0.05 and green fluorescence brightness when irradiated with a UV light at 366 nm (**Figure 4**).

22 Compound **5a** presents lower quantum yield $\Phi_F = 0.26 \pm 0.05$ when compared to the
23 corresponding nitrile precursor **5** ($\Phi_F = 0.55 \pm 0.05$). However, the following interesting behavior was
24 observed visually: fluorescence brightness changes from green-yellow to yellow when **5** is converted
25 into **5b** (compare the related test tubes in **Figures 4-A** and **4-B**), which is the hint of a slightly extended
26 electronic delocalization in the molecular structure of the last compound. The antagonistic effect
27 brought by the DAT groups in structure and fluorescence properties makes compound **5** behave
28 similarly to compound **4a** i.e. greenish fluorescence brightness and close quantum yields ($\Phi_F = 0.55 \pm$
29 0.05 and $\Phi_F = 0.59 \pm 0.05$ respectively)..

30 Contributions of the DAT function to the molecular structure of the samples (**3a-5a**) seem to
31 induce an improved electronic delocalization and more rigid structures increasing the fluorescence
32 quantum yield.

1 Compound **6** ($\Phi_F = 0.18 \pm 0.05$) shows a fluorescence quantum yield higher than **3** ($\Phi_F = 0.05 \pm$
2 0.05) but both display a large Stokes shift linked to a major change in the geometry of the excited state
3 related to the ground state.
4

5 **3. Conclusions:**

6 We report a straightforward access to π -conjugated oligothiophenes and phenylthiophenes bearing
7 amino-rich groups. The compounds were synthesized using a palladium-catalyzed C-H arylation in the
8 main step of the synthesis, leading to nitrile derivatives (**3-6**) in moderate to excellent yields. Further
9 cycloaddition reactions with 2-cyanoguanidine led to DAT derivatives (**3a-6a**) in good to excellent
10 yields. UV-Vis absorption and fluorescence studies were performed with all compounds to determine
11 their basic spectroscopic properties. We have identified a strongly emissive molecule (compound **3a**)
12 with fluorescence quantum yield $\Phi_F = 0.78 \pm 0.05$, which could find applications in biology and
13 material chemistry. We have observed an antagonistic effect in the spectroscopic properties of
14 oligothiophenes bearing DATs, resulting in more constrained structures with improved absorptive and
15 emissive properties when decreasing the OT chain length. The spectroscopic study of this new family of
16 compounds showed such differences in the absorption properties of the different molecules to preclude
17 any global guess relative to their excited state property. Anyhow, some of these DAT substituted
18 compounds have an actual potential interest as fluorescent labels while others might be of interest for
19 the conception of molecular electronic devices,
20

21 **4. Experimental**

22 All reactions were carried out in anhydrous or freshly distilled solvents in oven dried Schlenk
23 flasks under argon atmosphere or air (when not mentioned). Commercial reagents have been used
24 without any further purification.

25 Analytical thin layer chromatography (TLC) was performed using Merck silica gel 60 F₂₅₄ pre-
26 coated plates. Chromatograms were observed under UV light at 254 nm and/or 366 nm. NMR
27 spectroscopic data were obtained with a Bruker Advance 300 and 600 MHz and chemical shifts were
28 quoted in parts per million (ppm) relative to residual solvent peak. *J* values are given in hertz. High
29 performance liquid chromatography (HPLC) was performed on an Alliance 2795-Waters with mass
30 spectrometry (MS) detection ESI-QTOF-Waters using electrospray ionization (ESI) or by direct
31 introduction. GC-MS (QP2010 plus – Shimadzu) analyses were performed to follow the reactions
32 depending on the polarity of the products. FTIR analyses were done with purified solid samples in the
33 attenuated total reflectance (ATR) mode on a Vector22 Bruker equipment. Elemental analysis was
34 performed on a FlashEA® 1112-Thermo equipment.

1 UV-Vis spectra were performed in a Lambda 35 double beam spectrophotometer (Perkin Elmer),
2 using DMSO (Sigma-Aldrich, 99.9%) as solvent and a scan speed of 120 nm.min⁻¹. DMSO was chosen
3 as solvent due to the lack of solubility of the DAT derivatives in other low toxicity solvent. Total
4 dissolution of the samples was carefully checked before running the spectra. The molar extinction
5 coefficients (ϵ) were calculated following precise controlled dilutions of mother solutions.

6 HOMO-LUMO energy gap (eV) was estimated directly from UV-Vis λ_{\max} absorption according to
7 $E_g = h.c / \lambda$ formula where h is Planck's constant (J.s), c is the speed of light (m/s) and λ is the
8 absorption wavelength (nm), resulting (after conversion) in the simplified formula $E_g = 1240/\lambda_{\max}$.

9 Fluorescence studies were performed on a spectrofluorimeter (K2-001, ISS, Champaign, USA)
10 running in the steady state mode and using a right-angle geometry. The instrument was fitted with a 300
11 W xenon short arc lamp (Excelitas Technologies' Cermax[®]) and single concave holographic grating
12 monochromator with interchangeable slits ranging from 0.4 to 32 nm. Emission spectra were carried out
13 using excitation wavelengths reported in **Table 1** and all spectroscopic data relative to a given
14 compound were measured using the same 1 cm Hellma fluorescence cell for absorption, excitation and
15 emission.

16 Quantum yields were obtained by the relative method using optically dilute solutions (Abs. <
17 0.02), with samples at room temperature (23 °C \pm 2 °C) in a dark room. Data are for air equilibrated
18 samples and are not corrected from instrument response. Perylene (**P**) in DMSO and anthracene (**A**) in
19 ethanol have been used as standards, with the respective literature values of $\Phi_F = 0.78 \pm 0.02$ for **P** in
20 DMSO [19] and $\Phi_F = 0.28 \pm 0.02$ for **A** in ethanol [20], considering the differences in refractive indexes
21 of solvents for analyzed samples (always in DMSO) and standards when necessary. Refractive index of
22 DMSO ($n = 1.4793$) and ethanol ($n = 1.3617$) were used in the calculations. The relative fluorescence
23 quantum yields were determined using the same cells, excitation wavelengths for emission spectra of
24 samples and standards, same gain and slit bandwidths applying the following formula for the
25 estimations:

$$\phi = \phi_{ref} \frac{I}{I_{ref}} \frac{1-10^{A_{ref}}}{1-10^A} \frac{n^2}{n_{ref}^2}$$

26
27
28 where Φ and Φ_{ref} were the fluorescence quantum yields of the unknown sample and the respective
29 reference, η and η_{ref} are the refractive indexes of the solvents used to dilute the samples and references,
30 I and I_{ref} are the integrated fluorescence intensities of the samples and references respectively and A and
31 A_{ref} are the absorbances at the excitation wavelengths of the samples and references respectively.

1 *General procedure for the synthesis of 3-6*

2 A mixture of aryl bromide (1 eq.), 2-thiophenecarbonitrile (3 eq. per site), K₂CO₃ (1.5 eq. per
3 site), pivalic acid (0.15 eq. per site) and Pd(PPh₃)₄ (4 mol % per site) in a solvent mixture of dry **N,N-**
4 **dimethylacetamide/toluene 50:50 (v/v %)**, C :0.23 M, was stirred under argon atmosphere at 110 °C
5 during 48h. The reaction mixture was then diluted with water, filtered on Celite and washed with diethyl
6 ether. The solid was resolubilized in THF/diethyl ether 50:50 (v/v %) and centrifuged (15 min, 4000
7 rpm, rt). The white solid was eliminated and the solution evaporated to give a product which was
8 purified by successive recrystallizations in appropriate solvents: **3**, **4** and **6** in 1-butanol and **5** in toluene
9 at room temperature. Yields: (**3**) 35%, yellow solid; (**4**) 45%, orange solid; (**5**) 72%, red solid; (**6**) 93%,
10 green solid. All amounts were calculated based on each reactive site (-Br) of the starting precursor.

11 **[2,2'-bithiophene]-5,5'-dicarbonitrile (3)**: ¹H NMR (DMSO-*d*₆, 600 MHz.) δ (ppm): 8.02 (d, *J* =
12 4.18 Hz, 1H), 7.71 (d, *J* = 3.96 Hz, 1H), ¹³C NMR (DMSO-*d*₆, 150 MHz.) δ (ppm): 141.2, 140.4, 127.2,
13 113.8, 108.6, GC-MS: *m/z* = 216.20, HRMS (ESI+): *m/z* = 216.9894, UV-*vis* (λ_{max}): 346 nm, IR (ATR
14 cm⁻¹): 3093, 3073, 2215, 1594, 1480, 1430, 1295, 1151, 1058, 882, 809, 522.

15 **[2,2':5',2''-terthiophene]-5,5''-dicarbonitrile (4)**: ¹H NMR (DMSO-*d*₆, 600 MHz) δ (ppm): 7.95
16 (d, *J* = 3,96 Hz, 2H), 7.595 (s, 2H), 7.54 (d, *J* = 3.96 Hz, 2H), ¹³C NMR (DMSO-*d*₆, 150 MHz) δ (ppm)
17 : 142.7, 140.2, 135.1, 128.1, 125.3, 113.9, 106.9, HRMS (ESI+) : *m/z* = 297.9695, UV-*vis* (λ_{max}): 396
18 nm IR (ATR cm⁻¹): 3094, 3071, 2924, 2824, 2214, 1431, 1045, 806, 784.

19 **[2,2':5',2''':5'',2''''-quaterthiophene]-5,5''''-dicarbonitrile (5)**: ¹H NMR at 40 °C (DMSO-*d*₆, 600
20 MHz) δ (ppm): 7.94 (d, *J* = 3,8 Hz, 2H), 7.56 (d, *J* = 3.8 Hz, 2H), 7.51 (d, *J* = 3.8 Hz, 2H), 7.46 (d, *J* =
21 3.8 Hz, 2H), ¹³C NMR at 40 °C (DMSO-*d*₆, 150 MHz) δ (ppm): 143.1, 140.1, 136.6, 133.4, 128.1,
22 126.3, 124.78, 113.9, 106.3, HRMS (ESI+): *m/z* = 380.9644, UV-*vis* (λ_{max}): 431 nm, IR (ATR cm⁻¹):
23 3094, 3078, 2215, 1542, 1446, 1433, 1047, 852, 789.

24 **5,5',5''-(benzene-1,3,5-triyl)tris(thiophene-2-carbonitrile) (6)**: ¹H NMR (DMSO-*d*₆ 600 MHz)
25 δ (ppm): 8.077 (s, 2H), 8.072 (s, 2H), 7.97 (d, *J* = 3.81 Hz, 2H), ¹³C NMR (DMSO-*d*₆ 150 MHz)
26 δ (ppm): 148.8, 140.1, 133.9,126.6,124.5, 114.1, 108.0 HRMS (ESI+): *m/z* = 400.0037, UV-*vis* (λ_{max}):
27 317 nm, IR (ATR cm⁻¹): 3395, 3106, 2214, 1594, 1422, 1323, 1238, 1038, 807

28 *General procedure for the synthesis of 3a-6a*

29 A mixture of the nitrile derivatives (**3-6**) (1 eq.), 2-cyanoguanidine (3 eq. per site) and KOH (1 eq.
30 per site) in DMSO (C: 0.1M) was stirred at 80 °C for 16h. Distilled water was added and the crude was
31 recrystallized at 80 °C during 15 min. The precipitated solid was then hot filtrated on celite, washed
32 with acetonitrile and purified by recrystallizations in THF. Yields: **3(a)** 98%, yellow solid; (**4a**) 74%,
33 orange solid; (**5a**) 91%, dark red solid; (**6a**) 77%, green solid. All amounts are calculated based on each
34 reactive site (-CN) of the starting precursor.

1 **6,6'-([2,2'-bithiophene]-5,5'-diyl)bis(1,3,5-triazine-2,4-diamine) (3a):** ¹H NMR (DMSO-*d*₆,
2 600 MHz) δ (ppm): 7.77 (d, *J* = 3.96 Hz, 2H), 7.42 (d, *J* = 3.96 Hz, 2H), 6.71 (bs, 8H, NH₂), ¹³C
3 (DMSO-*d*₆, 150 MHz) δ (ppm): 166.9, 166.1, 142.3, 139.7, 129.6, 125.3, HRMS (ESI+) : *m/z* =
4 385.0758, UV-*vis* (λ_{max}): 377 nm, IR (ATR cm⁻¹): 3329, 3166, 1644, 1499, 1424, 1379, 1027, 795, 574.

5 **6,6'-([2,2':5',2''-terthiophene]-5,5''-diyl)bis(1,3,5-triazine-2,4-diamine) (4a):** ¹H NMR
6 (DMSO-*d*₆, 600 MHz) δ (ppm): 7.75 (d, *J* = 3.81 Hz, 2H), 7.430 (s, 2H), 7.39 (d, *J* = 3.81 Hz, 2H), 6.78
7 (bs, 8H, -NH₂), ¹³C NMR (DMSO-*d*₆, 150 MHz) δ (ppm): 166.9, 166.1, 141.8, 139.2, 135.9, 129.6,
8 126.1, 125.0, HRMS (ESI+): *m/z* = 467.0645, UV-*vis* (λ_{max}): 419 nm, IR (ATR cm⁻¹): 3454, 3316,
9 3121, 1614, 1515, 1429, 1382, 1013, 794.

10 **6,6'-([2,2':5',2''':5''',2''''-quaterthiophene]-5,5''''-diyl)bis(1,3,5-triazine-2,4-diamine) (5a):** ¹H
11 NMR (DMSO-*d*₆ 600 MHz) δ (ppm): 7.75 (d, *J* = 3.81 Hz, 2H), 7.42 (d, *J* = 3.81 Hz, 2H), 7.38 (m, *J* =
12 6.74 Hz, 4H), 6.77 (bs, 8H, -NH₂), ¹³C NMR (DMSO-*d*₆ 150 MHz) δ (ppm): 166.9, 166.1, 141.7, 139.3,
13 135.5, 135.4, 129.7, 126.0, 125.7, 124.9, HRMS (ESI+): *m/z* = 549.0527, UV-*vis* (λ_{max}): 447 nm, IR
14 (ATR cm⁻¹): 3324, 3153, 1622, 1524, 1429, 1386, 848.

15 **6,6',6''-(benzene-1,3,5-triyltris(thiophene-5,2-diyl))tris(1,3,5-triazine-2,4-diamine) (6a):** ¹H
16 NMR (DMSO-*d*₆ 600 MHz) δ (ppm): 7.96 (s, 2H), 7.85 (d, *J* = 3.81 Hz, 2H), 7.81 (d, *J* = 3.81 Hz, 2H),
17 6.78 (bs, 8H, -NH₂), ¹³C NMR (DMSO-*d*₆ 150 MHz) δ (ppm): 168.4, 167.6, 146.7, 144.2, 136.7, 131.1,
18 127.2, 123.3, HRMS (ESI+): *m/z* = 652,1349, UV-*vis* (λ_{max}): 344 nm, IR (ATR cm⁻¹): 3326, 3154,
19 1633, 1518, 1461, 1423, 1384, 863, 797.

21 Acknowledgments:

22 The authors would like to thank the "Ministère de l'Éducation Nationale, de l'Enseignement
23 Supérieur et de la Recherche" (MENESR) and The "Ecole Nationale Supérieure de Chimie de
24 Montpellier" (ENSCM) for supporting this work.

25 *Note:* The authors declare no competing financial interest.

27 Appendix A. Supplementary data

28 Supplementary data to this article contain **Figure SI-1** and **Figure SI-2**.

References

- [1] Zaman, M. B. and D. F. Perepichka. "A new simple synthesis of poly(thiophene-methine)s." *Chem. Comm.* (2005) (33): 4187-4189. DOI: 10.1039/b506138e
- [2] Thomas, K. R. J., Hsu, Y.-C., Lin, J.T., Lee, K.-M., Ho, K.-C., Lai C.-H., Cheng, Y.-M., Chou, P.-T., "2,3-disubstituted thiophene-based organic dyes for solar cells." *Chem. Mater.* (2008), 20(5): 1830-1840. DOI: 10.1021/cm702631r
- [3] Sun, Y.M., Liu, Y.Q., Ma, Y.Q., Di, C.A., Wang, Y., Wu, W., Yu, G., Hu, W.P., Zhua, D.B., "Organic thin-film transistors with high mobilities and low operating voltages based on 5,5'-bis-biphenyl-dithieno[3,2-b : 2',3'-d]thiophene semiconductor and polymer gate dielectric." *Applied Physics Letters* (2006), 88(24). DOI: 10.1063/1.2209213
- [4] Sun, Y. M., Ma, Y.Q., Liu, Y.Q., Lin, Y.Y., Wang, Z.Y., Wang, Y., Di, C.A., Xiao, K., Chen, X.M., Qiu, W.F., Zhang, B., Yu, G., Hu, W.P., Zhu, D.B., "High-performance and stable organic thin-film transistors based on fused thiophenes." *Adv. Func. Mater.* (2006), 16(3): 426-432. DOI: 10.1002/adfm.200500547
- [5] Ahn, H. and J. E. Whitten. "Optical and electronic properties of electron polymerized thiophene films." Abstracts of Papers of the American Chemical Society (2001), 222: U288-U288.
- [6] Capobianco, M. L., Barbarella, G., Manetto, A., "Oligothiophenes as Fluorescent Markers for Biological Applications." *Molecules* (2012), 17(1): 910-933. DOI: 10.3390/molecules17010910
- [7] Åslund, A., Sigurdson, C.J., Klingstedt, T., Grathwohl, S., Bolmont, T., Dickstein, D.L., Glimsdal, E., Prokop, S., Lindgren, M., Konradsson, P., Holtzman, D.M., Hof, P.R., Heppner, F.L., Gandy, S., Jucker, M., Aguzzi, A., Hammarström, P., Nilsson, K.P.R., "Novel Pentameric Thiophene Derivatives for in Vitro and in Vivo Optical Imaging of a Plethora of Protein Aggregates in Cerebral Amyloidoses." *Acs Chemical Biology* (2009), 4(8): 673-684. DOI: 10.1021/cb900112v
- [8] Kok, D., Húngaro Duarte, M.A., Abreu Da Rosa, R., Wagner, M.H., Pereira, J.R., Reis Só, M.V., "Evaluation of epoxy resin sealer after three root canal filling techniques by confocal laser scanning microscopy." *Microsc. Res. Tech.* (2012), 75(9): 1277-1280. DOI: 10.1002/jemt.22061
- [9] Jando, T. and K. Mori. "Cross-Linking of Poly(Vinyl Chloride) Fibers with 2-Dibutylamino-4,6-Dimercapto-1,3,5-Triazine in Water." *Polymer J*; (1990), 22(9): 793-802. DOI: 10.1295/polymj.22.793
- [10] Saczewski, F., Bułakowska, A., Bednarski, P., Grunert, R., "Synthesis, structure and anticancer activity of novel 2,4-diamino-1,3,5-triazine derivatives." *Eur. J. Med. Chem.* (2006), 41(2): 219-225. DOI: 10.1016/j.ejmech.2005.10.013
- [11] Grossmann, K., Tresch, S., Plath, P., "Triaziflam and diaminotriazine derivatives affect enantioselectively multiple herbicide target sites." *Zeitschrift Fur Naturforschung C-a Journal of Biosciences* (2001), 56(7-8): 559-569.
- [12] Song, W.C., Xu, X.K., Chen, Q., Zhuang, Z.Z., Bu, X.H., "Nitrogen-rich diaminotriazine-based porous organic polymers for small gas storage and selective uptake" *Polym. Chem.* (2013), 4(17): 4690-4696. DOI: 10.1039/C3PY00590A
- [13] Mastalir, M., Stöger, B., Pittenauer, E., Allmaier, G., Kirchner, K., "Air-Stable Triazine-Based Ni(II) PNP Pincer Complexes As Catalysts for the Suzuki-Miyaura Cross-Coupling." *Org. Lett.* (2016), 18(13): 3186-3189. DOI: 10.1021/acs.orglett.6b01398
- [14] Imberdis, T., Ayrolles-Torro, A., Rodrigues, A.D., Torrent, J., Alvarez-Martinez, M.T., Kovacs, G.G., Verdier, J.-M., Robitzer, M., Perrier, V., "A Fluorescent Oligothiophene-Bis-Triazine ligand interacts with PrP fibrils and detects SDS-resistant oligomers in human prion diseases." *Molecular Neurodegeneration* (2016), 11, 1-19. DOI: 10.1186/s13024-016-0074-7
- [15] Raposo, M.M.M., Fonseca A.M.C., Kirsch, G., "Synthesis of donor-acceptor substituted oligothiophenes by Stille coupling." *Tetrahedron* (2004), 60(18): 4071-4078. DOI: 10.1016/j.tet.2004.03.022
- [16] Lapointe, D. and K. Fagnou. "Overview of the Mechanistic Work on the Concerted Metallation-Deprotonation Pathway." *Chem. Lett.* (2010), 39(11): 1119-1126. doi:10.1246/cl.2010.1118

- 1 [17] Lafrance, M. and K. Fagnou. "Palladium-catalyzed benzene arylation: Incorporation of catalytic pivalic acid
2 as a proton shuttle and a key element in catalyst design." *J.Am.Chem.Soc.* (2006), 128(51): 16496-16497.
3 DOI: 10.1021/ja067144j
- 4 [18] Rodrigues, A.D., Imberdis, T., Perrier, V., Robitzer, M., "Improved synthesis of a quaterthiophene-triazine-
5 diamine derivative, a promising molecule to study pathogenic prion proteins." *Tet. Lett.* (2015), 56(2): 368-
6 373. DOI: 0.1016/j.tetlet.2014.11.098
- 7 [19] Suzuki, K., Kobayashi, A., Kaneko, S., Takehira, K., Yoshihara, T., Ishida, H., Shiina, Y., Oishi, S., Tobita,
8 S., "Reevaluation of absolute luminescence quantum yields of standard solutions using a spectrometer with
9 an integrating sphere and a back-thinned CCD detector." *Phys. Chem. Chem. Phys* (2009), 11(42): 9850-9860. DOI:
10 10.1039/b912178a
- 11 [20] Zhou, Q. H., Zhou, M., Wei, Y., Zhou, X. Liu, S., Zhang, S., Zhang, B., "Solvent effects on the triplet-triplet
12 annihilation upconversion of diiodo-Bodipy and perylene." *Phys. Chem. Chem. Phys.* (2017) 19(2): 1516-1525. DOI:
13 10.1039/c6cp06897a
- 14 [21] Bhadwal A.S., Tripathi, R. M., Gupta R.K., Kumar N., Singh R.P., Shrivastav A., "Biogenic synthesis and
15 photocatalytic activity of CdS nanoparticles," *RSC Advances.*, 2014, 4, 9484-9490 DOI: 10.1039/c3ra46221
- 16 [22] Costa, J. C.S., Taveira, R. J. S., Lima, C.F.R.A.C., Mendes, A., Santos, L.M.N.B.F. "Optical band gaps of organic
17 semiconductor materials.". *Optical Materials* (2016), 58: 51-60, DOI: 10.1016/j.optmat.2016.03.041
- 18 [23] Sworakowski, J. "How accurate are energies of HOMO and LUMO levels in small-molecule organic semiconductors
19 determined from cyclic voltammetry or optical spectroscopy?," *Synthetic Metals* 235 (2018), 125-135.
20 DOI.org/10.1016.013
21

Supplementary Information

Original Synthesis and Spectroscopic Study of Thiophene Triazine Derivatives with Enhanced Luminescence Properties

Alysson Duarte Rodrigues^{a,c}, Nathalie Marcotte^{a,c}, Françoise Quignard^a, Stefano Deabate^{b,c}, Mike Robitzer^{a,c,*} and Dan A. Lerner^{a,c,*}

^a ICGM, Univ Montpellier, ENSCM, CNRS, Montpellier, France

^b Institut Européen des Membranes, IEM – UMR 5635, ENSCM, CNRS, Univ Montpellier, Montpellier, France

^c Ecole National Supérieure de Chimie de Montpellier, 240 Avenue du Professeur E. Jeanbrau, 34296 Montpellier Cedex 5, France

mike.robitzer@enscm.fr and dan.lerner@enscm.fr

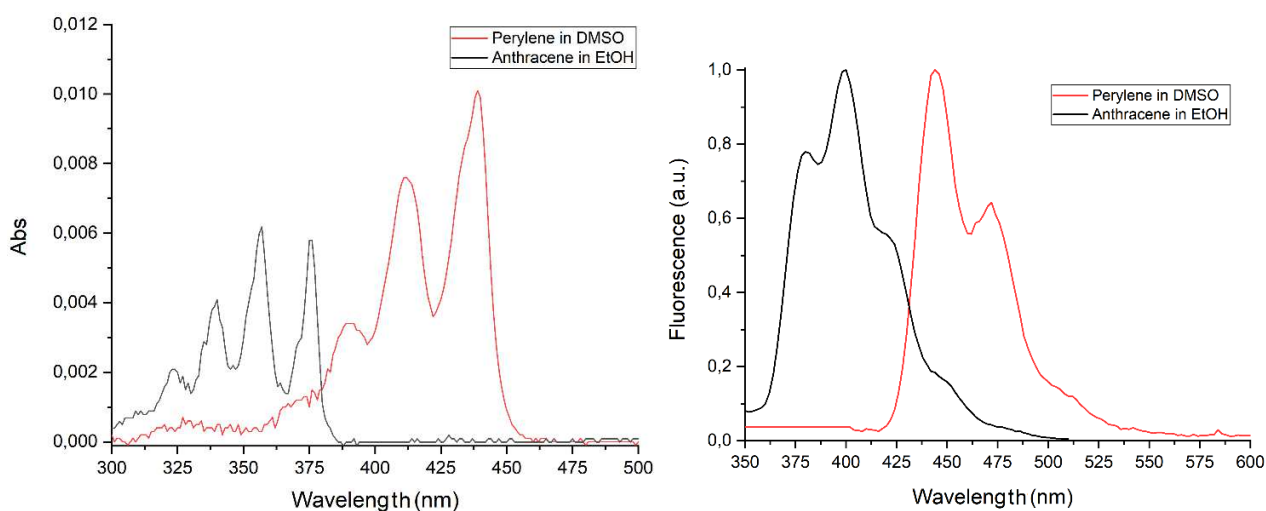
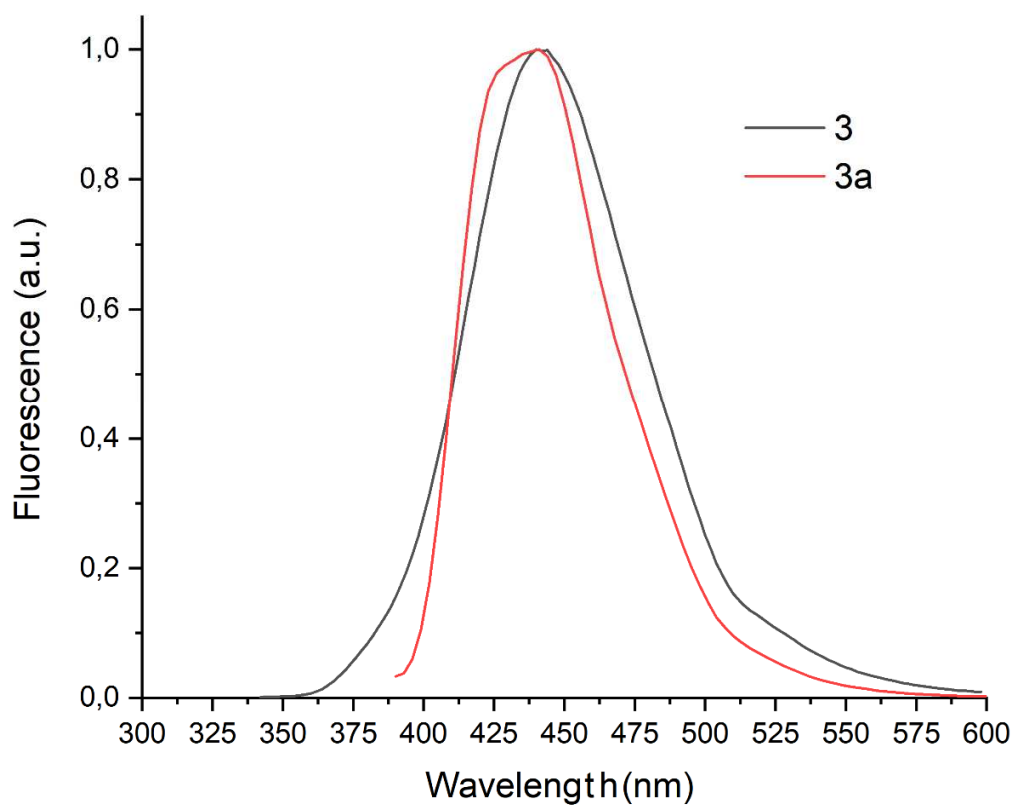


Figure S11. (Left) UV absorption spectra of anthracene (black line - C: $8.24 \times 10^{-7} \text{M}$ in ethanol; λ_{max} Absorption = 357 nm; absorbance = 0.0062) and perylene (red line - C: $3.41 \times 10^{-9} \text{M}$ in DMSO, λ_{max} Absorption = 439 nm; absorbance = 0.0101) used in the quantum yield determinations. (Right) Normalized fluorescence emission of anthracene (black line; fluorescence emission $\lambda_{\text{max}} = 398 \text{ nm}$) and perylene (red line; fluorescence emission $\lambda_{\text{max}} = 442 \text{ nm}$).



1

2

Figure SI2. Normalized emission spectra of compounds **3** (black line) and **3a** (red line) showing a very strong overlap and nearly identical λ_{max} at 442 nm.

3

4

Original Synthesis and Spectroscopic Study of Thiophene Triazine Derivatives with Enhanced Luminescence Properties

Alysson Duarte Rodrigues^{a,c}, Nathalie Marcotte^{a,c}, Françoise Quignard^a, Stefano Deabate^{b,c}, Mike Robitzer^{a,c,*} and Dan A. Lerner^{a,c,*}

^a ICGM, Univ Montpellier, ENSCM, CNRS, Montpellier, France

^b Institut Européen des Membranes, IEM – UMR 5635, ENSCM, CNRS, Univ Montpellier, Montpellier, France

^c Ecole National Supérieure de Chimie de Montpellier, 240 Avenue du Professeur E. Jeanbrau, 34296 Montpellier Cedex 5, France

mike.robitzer@enscm.fr and dan.lerner@enscm.fr

