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Novel chromophores from alternated pyridine-ethylenedioxythiophene units oligomers: dramatic enhancement of photoluminescence properties in elongated derivatives

Floris Chevallier, Marina Charlot, Claudine Katan, Florence Mongin* and Mireille Blanchard-Desce*

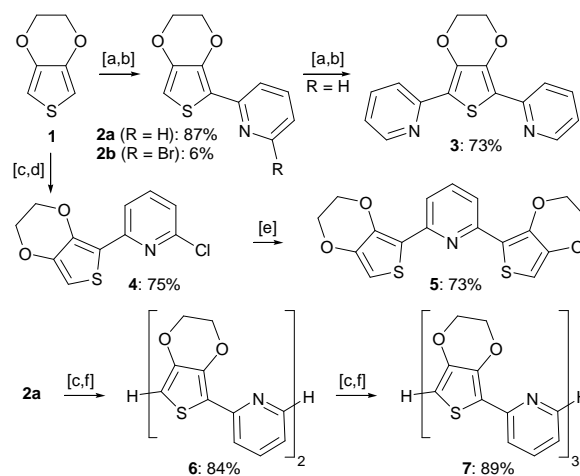
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Novel chromophores based on the alternation of electron-poor (pyridyl) and electron-rich (ethylenedioxythienyl) heterocycles were synthesized for the first time and shown to exhibit attractive optical properties in relation with their specific electronic and geometrical (coiled structure) features.

In the last decade, oligothiophenes¹ have received considerable attention in relation with their optical and electronic properties. 3,4-Ethylenedioxythiophene (EDOT, **1**) has been used as a building block in several conjugated systems due to its strong electron-donating ability which allows the tuning of the electronic properties of π -conjugated systems.² More generally oligomeric and polymeric conjugated derivatives³ can present conductive and electronic properties of major interest for the elaboration of optoelectronics devices such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs) or photovoltaic devices.⁴ Combining electron-rich (D) and electron-poor (A) (hetero)aromatic units in alternated (DA)_n polymeric systems (i.e. charge transfer (CT)-type polymers) has recently emerged as a popular strategy in the field of molecular-based electronics and photonics.⁵ Whereas oligomeric (DA)_n derivatives made of alternated thiophene and pyridine heterocyclic units have been reported,⁶ oligomers built from alternated electron-rich EDOT and electron-poor pyridine moieties have not been described up to now although electrochemical (including electrochromic) properties of poly(EDOTpyridine) have been reported.⁷ Only generic compound DA has been synthesized, with somewhat low yields (25-34%).⁸

With this aim in mind, we have implemented an efficient and stepwise route towards alternated ethylenedioxythiophene-pyridine oligomers of *defined and increasing length*. Firstly, we proceeded via deprotonation of the thiophene moiety followed by palladium-catalyzed cross-coupling⁹ with pyridine halides in a 'one-pot' procedure. We carried out the deprotonation of EDOT at the 2 position using 1/3 equivalent of lithium tributylmagnesate (Bu₃MgLi) in THF at room temperature.¹⁰ Subsequent cross-coupling of the lithium tri(aryl)magnesate intermediate with 2-bromopyridine afforded the DA dimeric species **2a** in 87% yield using a combination of PdCl₂ and 1,1'-bis(diphenylphosphino)ferrocene (dppf) ligand (3 mol% each) as the catalyst. Repeating the same deprotonation/cross-coupling sequence starting from heterodimer **2a** readily afforded heterotrimer **3** in 73% yield. The same procedure starting from **1** and using 2,6-dibromopyridine led to coupling product **2b** with only low yield. The synthetic strategy was accordingly modified and

switched to Negishi-like cross-couplings.^{9,11} Compound **1** was converted to the corresponding thienylzinc chloride by deprotonation with butyllithium at 0°C followed by transmetalation with ZnCl₂·TMEDA. Subsequent reaction with 2,6-dichloropyridine, catalytic amounts of PdCl₂ and dppf in refluxing THF afforded the mono-halogenated derivative **4**, which was isolated in 75% yield. The key building block **4** was then used as the starting material for the synthesis of heterotrimer **5** using the modified Negishi cross-coupling reaction after deprotonation/transmetalation of **1** (73% overall yield). This strategy can be extended to the preparation of elongated EDOT-pyridine alternating oligomers. Using the same cross-coupling method in an iterative synthetic approach and making use of selective deprotonation of the EDOT moiety, heterotetramer (DA)₂ **6** and heterohexamer (DA)₃ **7** were synthesized in high yields by coupling **4** with thiophene-deprotonated **2a** and **6** respectively (Scheme 1).



Scheme 1 Reagents and conditions: [a] Bu₃MgLi (1/3 eq), THF, rt, 2 h; [b] 2-bromopyridine (R = H) or 2,6-dibromopyridine (R = Br) (1 eq), PdCl₂ (3 mol%), dppf (3 mol%), reflux, 18 h; [c] BuLi (1 eq) then ZnCl₂·TMEDA (1 eq), THF, 0°C, 1 h; [d] 2,6-dichloropyridine (1 eq), PdCl₂ (2 mol%), dppf (2 mol%), reflux, 48 h; [e] 3,4-ethylenedioxythienylzinc chloride (1 eq), PdCl₂ (2 mol%), dppf (2 mol%), reflux, 48 h; [f] **4** (1 eq), PdCl₂ (2 mol%), dppf (2 mol%), reflux, 48 h.

The X-ray diffraction analysis of single crystals of compounds **3** (ADA), **5** (DAD) and **6** ((DA)₂) reveals that alternated (EDOT-pyridine) oligomers tend to adopt a *coiled* structure in the solid state.† Interestingly HF/6-31G optimized geometry calculations† indicate that this structural conformation is also favoured in the case of *isolated* molecules (Table 1). This particular structural feature can be

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related to the repulsion between N and O atoms of successive rings in linear conformation while coiled conformations favour intramolecular hydrogen bonds.

All oligomeric compounds are readily soluble in chloroform and dichloromethane, and soluble in medium to high polarity solvents such as ethyl acetate, THF, acetone, DMSO... Although the coiled structure demonstrated in the solid state and supported by isolated molecules calculations cannot be directly transposed to molecules in solution, the common observation for boundary conditions provides a strong hint that the molecules adopt similar conformations in solution. This should be the case as long as strong interactions (such as H-bonds, π -interactions...) with solvent molecules can be ruled out via suitable choice of solvents. The photophysical properties of the series of derivatives **2a** (DA), **3** (ADA), **5** (DAD), **6** ((DA)₂) and **7** ((DA)₃) in CHCl₃ are collected in Table 2. All chromophores present an intense absorption band in the near UV region as well as additional absorption bands at higher energy which gain relative intensity in comparison to the lower energy absorption band whose intensity levels off with increasing length.^{†‡} This low energy band bathochromically shifts towards the visible with increasing length indicating that electronic conjugation extends beyond the DA pair. Indeed, natural transition orbitals (NTO)¹² calculations indicate that significant electronic redistribution involving the whole structure takes place upon excitation (Table 1). Dimeric chromophore DA (**2a**) clearly shows a directional intramolecular CT from the EDOT unit to the pyridine moiety with an increase in dipole moment upon excitation (from 4.5 to 7 D based on TD-B3LYP calculations). In contrast, trimers **3** (ADA) and **5** (DAD) show a *quadrupolar*

charge redistribution from the core to the periphery (**3**) or from the periphery to the core (**5**) with only small dipole moment changes upon excitation. The charge redistribution in tetramer **6** and hexamer **7** is somewhat of a combination of both processes and results in lower electronic density on the peripheral EDOT moiety as compared to the inner EDOT moieties (Table 1). In both cases, excitation leads to an increase of the dipole moment (from 5 to 9 D for **6**, and 2 to 6 D for **7**). These calculations are supported by the solvatochromic behaviour of compounds **2a**, **3**, **5**, **6** and **7** in solution: whereas the lowest energy absorption band of chromophores **2a**, **6** and **7** shows a slight red-shift with increasing polarity, chromophores **3** and **5** absorption spectra are almost insensitive to solvent polarity.[†]

All chromophores show photoluminescence (PL) properties whose characteristics strongly depend on their length. The emission band progressively shifts from near UV to visible blue region with increasing length (Fig. 1). Dimeric chromophore **2a** shows an unstructured emission band with a significant Stokes shift (4800 cm⁻¹) indicative of a CT excited state. Chromophores **2a**, **6** and **7** show a slight positive solvatochromic behaviour,[†] in agreement with an increase of dipole moment upon excitation as expected from NTO calculations. In contrast, the emission of trimers **3** and **5** is almost insensitive to solvent polarity, consistent with a mainly quadrupolar charge redistribution.[†]

Interestingly, increasing length induces a marked *increase*

Table 1 ORTEP diagrams of ADA **3**, DAD **5** heterotrimers and (DA)₂ **6** heterotetramer (thermal ellipsoids at 50% probabilities), and HF/6-31G optimized geometries for DA **2a** and (DA)₃ **7**, and TD-B3LYP/6-31G/HF/6-31G natural transition orbitals¹² for all derivatives.

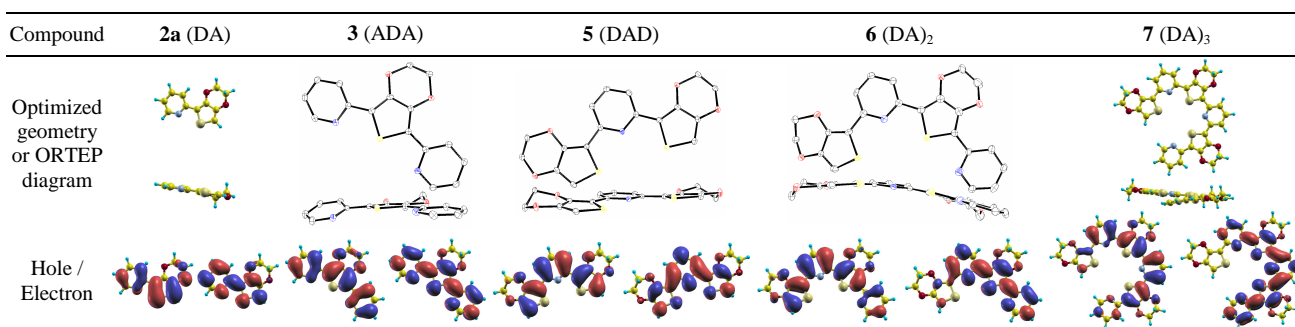


Table 2. Photophysical data of alternated oligomeric EDOT-pyridine derivatives in chloroform.

Compound	$\lambda_{\max}^{\text{abs } a}$ (nm)	$10^{-4} \epsilon_{\max}^{\text{abs } b}$ (cm ⁻¹ M ⁻¹)	$\lambda_{\max 2}^{\text{abs } a}$ (nm)	$10^{-4} \epsilon_{\max 2}^{\text{abs } b}$ (cm ⁻¹ M ⁻¹)	$\lambda_{\max 1}^{\text{abs } a}$ (nm)	$10^{-4} \epsilon_{\max 1}^{\text{abs } b}$ (cm ⁻¹ M ⁻¹)	$\lambda_{\max}^{\text{em } c}$ (nm)	Φ^d %	τ^e (ns)	k_r^f (10 ⁹ s ⁻¹)	k_{nr}^f (10 ⁹ s ⁻¹)	$E_{0.0}^g$ (eV)
2a (DA)	-	-	286 (sh)	1.22	315.5	1.71	372	1.3	0.36	0.04	2.74	3.64
3 (ADA)	-	-	-	-	339 (sh), 356, 373 (sh)	3.26	391 (sh), 411, 437 (sh)	4.4	0.18	0.24	5.31	3.25
5 (DAD)	-	-	287	3.65	348	2.07	399	19	1.39	0.14	0.58	3.33
6 ((DA) ₂)	299	2.49	297	2.23	373, 389 (sh)	3.12	408, 429 (sh), 459 (sh)	15	0.51	0.29	1.67	3.11
7 ((DA) ₃)	310	3.47	353	3.62	390	3.11	426, 450 (sh), 485 (sh)	41	1.95	0.21	0.30	2.97

^a Experimental absorption maximum. ^b Molar extinction coefficient. ^c Experimental emission maximum. ^d Fluorescence quantum yield determined in chloroform relative to quinine in 0.5 M H₂SO₄. ^e Experimental fluorescence lifetime. ^f Radiative (k_r) and non-radiative (k_{nr}) decay rates. ^g Electronic gap (0-0 transition energy) estimated from the intersection of normalized absorption and emission spectra.

in the fluorescence quantum yield of (DA)_n oligomers although the electronic gap concomitantly *decreases* (Table 2). Whereas the shorter compound **2a** shows only weak fluorescence,§ the longest derivative **7** is a strong blue emitter. This striking length effect can be related predominantly to a marked decrease of the non-radiative decay rate (Table 2). Such unusual behaviour can be related to a reduction of the torsional degrees of freedom in the excited state of chromophores **6** and **7** in relation with the shortening of the intercycles connecting bonds in the excited state (as suggested by excited-state optimized geometry calculations)† and steric constriction in the coiled structures. The well-defined emission spectra of chromophores **6** and **7** are indeed consistent with rigid structures in the excited state.

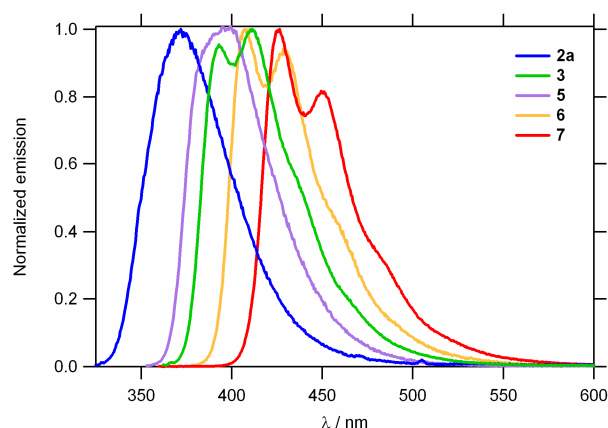


Fig. 1 Normalized emission spectra of chromophores **2a**, **3**, **5**, **6** and **7** in chloroform.

The odd-numbered derivatives (i.e. compounds **3** and **5**) show distinct behavior. The DAD derivative (**5**) shows a higher energy gap and much higher fluorescence quantum yield as well as longer experimental lifetime than its ADA counterpart (**3**) or its longer even-numbered analogue **6**. This results from the combination of reduced radiative (in relation with lower transition dipole) and non-radiative decay rates. This suggests that odd-numbered elongated derivatives of the (DA)_nD type might be complementary emitters as compared to even-numbered (DA)_n derivatives. Such derivatives would however require excitation at shorter wavelengths thus taking advantage of the intense higher energy band (Table 2) which is not present in the ADA analogue.

In conclusion, we have implemented an efficient synthetic route towards alternated (DA)_n oligomers built from EDOT and pyridine moieties that show *coiled* structures. These novel chromophores exhibit intense and broad absorption in the UV region. Increasing their length results in decreasing electronic gap and broader (multibands) absorption as well as bathochromic shift of the lowest energy absorption band. A dramatic enhancement of their PL properties is also obtained as a consequence of the increased rigidity in the excited state which reduces non-radiative processes. The present work has thus opened a new route towards coiled DA oligomers with intense absorption in the UV region and whose PL characteristics can be tuned from near UV to visible blue by

playing on the length or symmetry.

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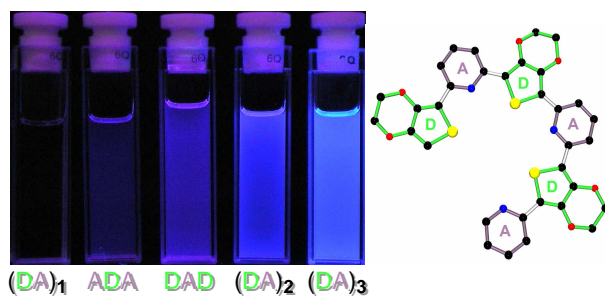
Notes and references

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- 55 † Electronic Supplementary Information (ESI) available: General methods, procedures and characterization of products, ¹H and ¹³C NMR spectra, crystal data, solvent effect on absorption and emission spectra, computational methods, optimized geometries, CIF files of **3**, **5** and **6** (CCDC 699627, 699628 and 707007). See DOI: 10.1039/b000000x/
- 60 ‡ With the exception of heterotrimer **3** (ADA) which shows only a weak higher energy absorption band.
- § Chromophore **2a** (DA) shows a much lower radiative decay rate than elongated oligomers (DA)_n although its extinction coefficient is roughly twice smaller. This suggests that emission originates from a different excited state with lower transition dipole than the vertical excited state.
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Graphical abstract:

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