# Synthesis, photophysics, and electrochemistry of thiophene-pyridine and thiophene-pyrimidine dyad comonomers

# Andréanne Bolduc, Stéphane Dufresne, Garry S. Hanan, and W.G. Skene

**Abstract:** A series of new  $\pi$ -conjugated donor (D) and acceptor (A) dyad comonomers were prepared using Suzuki coupling protocols. The D–A comonomers consisting of thiophene/bithiophene as donors and pyridine/pyrimidine as acceptors were prepared to investigate their photophysical and electrochemical properties. The dyads were spectroscopically confirmed to be highly conjugated. This was further supported by the X-ray crystal structure of the bithophene–pyridine dyad that showed all the heterocycles to be coplanar. It was further found that the fluorescence yields ( $\Phi_{fl}$ ) of the dyads were highly dependent on the number of thiophenes. The bithiophene derivatives exhibited  $\Phi_{fl}$  values  $\geq 0.3$  while the thiophene derivatives did not fluoresce. The suppressed fluorescence observed for the thiophene derivatives was due to their higher triplet energy resulting in efficient intersystem crossing (ISC) to the triplet state with  $\Phi_{ISC} \geq 0.8$ . This was confirmed both by time-resolved and steady-state measurements. The singlet excited state of both thiophene and bithiophene dyads was deactivated solely by either fluorescence and (or) ISC. Owing to their donor and acceptor character, the dyads could be oxidized and reduced both electrochemically and photochemically to afford the radical cation and anion, respectively.

Key words: comonomer, thiophene, pyridine, pyrimidine, photophysics, fluorescence.

**Résumé :** À l'aide d'un couplage de Suzuki, une série de comonomères conjugués contenant une fonction donneur d'électrons (D) et une fonction accepteur d'électrons (A) ont été préparés. Ces comonomères, dits D–A, qui utilisent le thiophène/bithiophène comme donneurs d'électrons et la pyridine/pyrimidine comme accepteurs d'électrons, ont été synthétisés dans le but d'analyser leurs propriétés photophysiques et électrochimiques. Il a été évalué spectroscopiquement que les dimères sont grandement conjugués. Ceci est d'ailleurs soutenu par la structure rayons-X du composé bithiophène–pyridine qui montre que tous les hétérocycles sont coplanaires. Il a été déterminé que les rendements quantiques de fluorescence ( $\Phi_{fl}$ ) des composés dépendent du nombre de thiophènes présents dans la molécule. En effet, les dérivés du bithiophène ont des  $\Phi_{fl} \ge 0,3$  tandis que les dérivés du thiophène ne fluorescent pas. Cette absence de fluorescence est causée par la formation d'un état triplet de haute énergie par croisement intersystème (ISC pour « intersystem crossing ») avec un  $\Phi_{ISC} \ge 0,8$ . L'état singulet excité des dimères de thiophène et de bithiophène est uniquement désactivé par la fluorescence ou le ISC. Grâce à leur caractéristique donneur/accepteur, les comonomères ont pu être oxydés et réduits électrochimiquement et chimiquement afin de former le radical cation et le radical anion.

Mots-clés : comonomère, thiophène, pyridine, pyrimidine, photophysique, fluorescence.

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# Introduction

Conjugated materials have attracted much attention because of their electrochemical and photophysical properties that are ideally suited for plastic electronics, including organic field effect transistor,<sup>1–4</sup> photovoltaics,<sup>5,6</sup> emitting devices,<sup>7,8</sup> and conducting materials,<sup>9,10</sup> to name but a few. Thiophenes have been widely used in these electronic applications owing to their low oxidation potential and their possibility of undergoing electropolymerization resulting in conjugated polymers possessing extremely low oxidation potentials. However, homopolymers of thiophene and its derivatives often have undesirably high HOMO–LUMO energy gaps ( $E_g$ ) and oxidation potentials ( $E_{pa}$ ) that are unsuitable for functional materials, as well as weak fluorescence.

The  $E_g$  and  $E_{pa}$  can be modulated by copolymerizing thiophene with different electron-donating and -accepting monomers. However, homopolymers are solely obtained if the oxidation potentials of both the monomer and thiophene are not closely matched. Although choosing monomers with  $E_{pa}$  that are closely matched to thiophene results in copolymers, the  $E_g$  and  $E_{pa}$  are similar to those of the homopolythiophene. This problem can be overcome with comonomers. The comonomer configuration consisting of a central aro-

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Scheme 1. Synthetic scheme for 1 and 3 (top) and 2 and 4 (bottom).



4 R = 2-thiophene

matic acceptor (A) core inserted between electron-rich donors (D) simplifies the electropolymerization process that would otherwise require two or three separate monomers to obtain analogous alternating copolymers via other coupling methods.<sup>11,12</sup> The same polymer can also be obtained by cathodic polymerization of a D–A–D comonomer.

Comonomers consisting of electron-deficient heterocycles, such as pyridine, pyrazine, and pyrimidines, are also interesting because they can coordinate with metals. This can be done either prior to- or post-polymerization, affording metalcontaining polymers. Property tailoring for a given application is possible by coordinating different metals. *n*-Doping of the electron-deficient-containing compounds is further possible resulting in the both *p*- and *n*-type polymers.

Unlike the polymerization of D–A–D or A–D–A comonomers that can be done in one step, the polymerization of D–A comonomers requires two steps. This can either be done by anodic dimerization followed by cathodic polymerization or the reverse. The added advantage of the stepwise polymerization of D–A comonomers is that the anodically and cathodically coupled dimers can be characterized, and the metal complexes can be isolated and characterized as well. Structure–property relationships are therefore possible in addition to tailoring the properties for a given application. This is in contrast to their triad cousins that are insoluble when polymerized, precluding their spectroscopic and molecular-weight characterization.

Our ongoing investigation of conjugated polymers<sup>13–19</sup> and our previous endeavors in comonomer synthesis<sup>11,20</sup> prompted us to prepare a series of  $\pi$ -rich and  $\pi$ -poor dyad comonomers consisting of thiophenes and both pyridine and pyrimidine. These compounds are of particular interest because they are expected to exhibit mutual *p*- and *n*-doping properties allowing for selective stepwise anodic and cathodic coupling potentially leading to D–A–A–D and A–D–D–A comonomer products, respectively. These can then subsequently be electropolymerized. Furthermore, the  $\pi$ -donor/acceptor arrangement provides the means to tune the HOMO–LUMO energy levels and to tailor the spectroscopic and electrochemical properties.<sup>21–24</sup>

Herein, we present the preparation of new  $\pi$ -donor/acceptor

Chart 1. Comonomers synthesized.



dyad comonomers along with their steady-state and timeresolved photophysics and electrochemical characterization. The combined effect of thiophene and bithiophene  $\pi$ -donors coupled with pyridine and pyrimidine  $\pi$ -acceptors for comonomers is presented. Although such compounds are of interest for their electrochemical properties, little work has examined the photophysics for such dyads. Their structure-property relationships and the understanding of their fluorescence deactivation mechanisms are of interest for the design and property tuning of new compounds. For these reasons, the photophysical properties, including the emission yields and excited-state deactivation pathways, of these new comonomers are studied. The investigation of such properties provides valuable information for determining the suitability of such precursors for functional materials and for the design of future compounds.

# **Synthesis**

The comonomers **2** and **4** (Chart 1) were prepared by standard Suzuki coupling.<sup>25,26</sup> The 2-thiophene boronic acid and 2-bithiophene boronic acid precursors required for Suzuki coupling were obtained by standard aryl anion formation with *n*-BuLi followed by nucleophilic addition to triethylboronate ester starting from inexpensive thiophene and bithiophene, respectively.<sup>27</sup> The boronic acids were

Table 1. Details of crystal structure determination for 4.

Formula	C. H.NS.
$M_{\rm w}$ (g/mol); $F(000)$	243.33 g/mol; 504
Crystal color and form	Yellow plate
Crystal size (mm)	$0.15\times0.07\times0.05$
$T$ (K); $d_{\text{calcd.}}$ (g/cm <sup>3</sup> )	150 (2); 1.407
Crystal System	Orthorhombic
Space group	$Pna2_1$
a (Å)	19.5336 (19)
<i>b</i> (Å)	10.1891 (10)
c (Å)	5.7716 (6)
$\alpha$ (°)	90.000
$\beta$ (°)	90.000
γ (°)	90.000
V (Å <sup>3</sup> ); Z	1148.7 (2); 4
$\theta$ range (°); completeness	4.53-72.47; 0.852
Reflections: collected/independent; $R_{int}$	8286/1783; 0.093
$\mu (mm^{-1})$	3.930
Abs. Corr.	Semi-empirical
$R1(F); wR(F^2) [I > 2\sigma (I)]$	0.0581; 0.1260
$R1(F)$ ; $wR(F^2)$ (all data)	0.0725; 0.1321
$GoF(F^2)$	1.065
Max. residual e <sup>-</sup> density	0.284 e <sup>-</sup> Å <sup>-3</sup>

coupled with a chloropyridine by Suzuki coupling in aqueous isopropanol, and this solvent led to homogenous reaction mixtures resulting in higher yields.<sup>11</sup> The reaction proceeded cleanly at 50 °C with only 1 mol% of catalyst. Conversely, **1** and **3** (Chart 1) were less straightforward to prepare, since the required 4-halogenopyrimidine commercially precursor is unavailable and the 2- and the 5-substituted derivatives are expensive. The required pyrimidine precursors for the synthesis of **1** and **3** were therefore prepared by a Michael reaction according to Scheme 1. This route unfortunately required a slow ring-closing step requiring 7 days for completion.<sup>28–30</sup>

# Crystallography

Confirmation of the formation of **4** was obtained by X-ray diffraction (Table 1). Suitable crystals for analysis were obtained from the slow evaporation of **4** in dichloromethane. The resolved structure is shown in Fig. 1. The resolved structure shows disorder of the terminal thiophene consisting of in inversion of the thiophene. The thiophene (S1–C1–C2–C3–C4) weights are 76% for the structural representation with the two thiophene adopting an anti conformation. The remaining 24% is attributed to the minor isomer in which the two thiophenes are syn. It should be noted that the heterocycles are nearly coplanar, contributing in part to its high degree of conjugation (vide infra). The torsion angle between the pyridine and the central thiophene is  $5.38^{\circ}$  while that of two thiophenes is  $9.75^{\circ}$ , and is consistent with similar structures.<sup>11</sup>

The molecules of **4** in the crystal lattice align along the a-b axis in a zig-zag fashion as shown in Fig. 2. This arrangement is in part a result of non-conventional H-bonding occurring between C11–H and N1. The distance between C11 and N1 is 3.443 Å, which is within a suitable distance for such a weak interaction. Face-edge  $\pi$ -stacking also oc-

Fig. 1. X-ray structure of 4 and the numbering scheme adopted.



curs between S2–C5–C6–C7–C8 and the pyridine through C12 with the two being separated by 3.665 Å. C1 is also directed towards the N1–C9–C10–C11–C12–C13 ring, and they are separated by a distance of 3.427 Å (Fig. 3).

## Spectroscopy

The effect of the number of heterounits in the comonomer on the spectroscopic properties can be seen from the spectroscopic data in Table 2. Both the absorption and fluorescence maxima of **3** and **4** are bathochromically shifted relative to **1** and **2**. The bathochromic shifts imply an increased degree of conjugation resulting from the bithiophene unit relative to thiophene. The increased degree of conjugation of the bithiophene dyad relative to the thiophene is also evident from the  $E_g$ , which is lower for **3** and **4** than for **1** and **2**. It is noteworthy that the  $E_g$  is larger for pyridinecontaining dyads compared with their pyrimidine analogues, owing to the more electron deficient nature of diazines, which perturbs the LUMO level.

Functional materials with high fluorescence yields are of interest for emitting devices. High fluorescence yields are also desired for efficient ligand-to-metal energy transfer. For these reasons, we examined the fluorescence quantum yields for the comonomer dyads. Both the bithiophene dyads are highly fluorescent relative to their thiophene analogues. High fluorescence yields were confirmed by measuring the absolute emissions with an integrating sphere. The advantage of the integrating sphere is that references with similar absorption, emissions, and emission yields to the compounds of study are not required. Even though the fluorescence values measured for 1 and 2 are below the detection limit of the integrating sphere, accurate fluorescence measurements of 3 and 4 are possible. It can be concluded that 1 and 2 are nonfluorescent. The difference in fluorescence between the two sets of dyads implies two different deactivation pathways of the singlet excited state are present. Although both the thiophene and bithiophene dyads exhibit unimolecular fluorescence decays of approximately < 2 ns, an efficient deactivation mode competes with fluorescence for 1 and 2, resulting in suppressed fluorescence.

Deactivation of the excited state by intramolecular charge transfer (ICT) can lead to suppressed fluorescence. ICT often results from charge separation occurring on separate donor–acceptor moieties. Charge separation can be visualized from the molecular orbitals, which can be accurately calculated by theoretical means. The HOMO and LUMOs of the comonomers were therefore investigated to afford insight into the different excited-state deactivation modes. As





**Fig. 3.** The interactions involved in the lattice of **4**. The disorder is omitted for clarity. (i) 0.5 + x, 0.5 + y, z; (ii) 1.5 - x, 0.5 + y, 0.5 + z; (iii) 1.5 - x, -0.5 + y, 0.5 + z.



Compound	$\lambda_{abs} (nm)$	$\Delta E$ (eV)	$E_{\rm g}~({\rm eV})$	λ <sub>em</sub> (nm)	$\Phi_{\mathrm{fl}}{}^a$	$\tau_{fl}$ (ns)	$\Delta G_{\text{et}}$ (kJ/mol) <i>N</i> , <i>N</i> -Dimethylaniline <sup>b</sup>	$\Delta G_{\text{et}}$ (kJ/mol) Benzoquinone <sup>b</sup>
1	306	3.7	3.3	380	< 0.01 (0)	2.6	-79	-223
2	320	3.8	3.7	356	0.04 (0.08)	5.3	-69	-213
3	365	3.1	2.9	433	0.66 (0.86)	1.9	-2	-175
4	354	3.2	3.1	420	0.15 (0.30)	6.2	-11	-174

Table 2. Comonomer spectroscopic properties measured in anhydrous and deaerated dichloromethane.

<sup>a</sup>Values in parentheses were measured using a calibrated integrating sphere.

<sup>b</sup>Calculated energetics of photoinduced electron transfer ( $\Delta G_{el}$ ) between the different comonomers and electron donors and acceptors.

Fig. 4. HOMO (left) and LUMO (right) energy levels calculated via DFT of 4 (A), 3 (B), and 2 (C).



seen in Fig. 4, the HOMO and LUMO orbitals calculated from DFT single-point energies from the X-ray crystal coordinates are not isolated on one heterocycles and they are evenly distributed across the heterocycles regardless of the dyad. ICT is therefore not responsible for the different fluorescence yields despite the  $\pi$ -donor/acceptor character.

The singlet excited state deactivation pathways of the comonomers were further investigated using various quenchers. In all cases, the comonomers were self-quenched with diffusion-controlled kinetics in acetonitrile  $(2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}).^{31}$ All spectroscopic measurements were subsequently done at extremely low concentrations  $(10^{-6} \text{ mol/L})$  to avoid selfquenching. An electron acceptor (benzoquinone) and donor (N,N'-dimethylaniline) were added to determine whether the comonomers could undergo photoinduced electron transfer. Interestingly, all the comonomers studied were quenched at diffusion-controlled limits by both benzoquinone and N,N'dimethylaniline (Fig. 5). This implies that the comonomers are capable of generating both radical cations and radicals. This is in contrast to thiophene derivatives that can generate only radical cations while pyridine and pyridimine afford uniquely radical anions. The photoinduced electron-transfer mechanism leading to radical ion intermediates is further supported by the exergonic  $\Delta G_{\text{et}}$  values calculated from the Rehm–Weller equation, shown in Table 2.<sup>31</sup> The dual quenching confirms that the comonomers can potentially be both oxidized and reduced while their increased degree of conjugation relative to their discrete monomers afford the means to tailor the spectroscopic and electrochemical properties.

# Laser flash photolysis

The donor-acceptor character of the comonomers can lead to radical ions upon photoirradiation, as observed by the fluorescence quenching with the electron donor and ac**Fig. 5.** Static Stern–Volmer analysis of **3** as a function of benzoquinone. Inset: Decrease in fluorescence intensity of **3** with benzoquinone addition in deaerated acetonitrile.



ceptor. Laser flash photolysis (LFP) was used for spectroscopically detecting these intermediates in addition to any triplets, either of which could be responsible for the reduced fluorescence of 1 and 2. The transient absorption spectra for the dyads studied are found in the inset of Fig. 6. Both the thiophene and bithiophene comonomers exhibited transient spectra whose absorption maxima are dependent on the number of thiophenes. The unimolecular decay (Fig. 6) implies that the observed transients are triplets. Triplet assignment was further confirmed by the fast quenching of the transients with known triplet quenchers; oxygen, 1,3-cyclohexadiene,  $\beta$ -carotene, and 2-methylnaphthalene (Table 3). The unimolecular decay precludes the formation of radical ions that can be produced by intramolecular photoinduced electron transfer. The observed transients were further assigned to triplets, since they were not quenched by radical ion generators, benzoquinone, or N,N-dimethylaminopyridine.

Quantification of the triplet state is possible by LFP according to eq. [1]

[1] 
$$\Phi_x = \frac{\Delta Abs_x \cdot \Phi_{ref} \cdot \varepsilon_x}{\Delta Abs_{ref} \cdot \varepsilon_{ref}}$$

where  $\Phi_{TT}$  is the quantum yield of triplet formation,  $\varepsilon_{TT}$  is the triplet-triplet molar absorption coefficient,  $\Delta Abs$  is the signal intensity monitored at the maximum triplet absorption as a function of laser power, ref refers to the actinometer, and *x* refers to the corresponding comonomer. Either  $\Phi_{TT}$  or  $\varepsilon_{TT}$  can be derived by direct comparison of the comonomer triplet signal to the reference, xanthone. Equation [1] can be simplified to eq. [2] for calculating the triplet comonomer yield without knowing  $\varepsilon_{TT}$ , which is not normally precisely known.

$$[2] \qquad \Phi_x = \frac{\Delta Abs_x \cdot \Phi_{ref}}{\Delta Abs_{ref} \cdot \Phi_x}$$

Equation [2] is valid if both the reference and the comonomer produce a common triplet. This is the case when 2-



methylnaphthalene (MN) is added to both the reference and comonomer samples. In this case, MN quenches the comonomer and xanthone triplet by energy transfer to produce triplet MN that is observed at 420 nm. MN is the quencher of choice because its triplet cannot be produced by direct excitation. More importantly, its triplet can be detected by LFP and its absorption does not overlap with any of the comonomers or with xanthone. Equation [2] is valid if all the triplets produced within the laser pulse are rapidly quenched by energy transfer to produce the triplet methylnaphthalene. The amount of MN required for deactivating at least 95% of the comonomer and xanthone triplets can be calculated by the quenching rate constant derived from Fig. 7.

The  $\Phi_{TT}$  of the comonomers can be derived from the slope of the maximum triplet signal as a function of laser power relative to xanthone ( $\Phi_{TT} = 1$ ; Fig. 8) according to the simplified eq. [2] by observing the common triplet MN. The comonomer  $\varepsilon_{TT}$  can similarly be calculated from the slope of the maximum signal observed at the comonomer absorption maximum as a function of laser power versus xanthone in the absence of MN. The calculated triplet values found in Table 4 show that the  $\varepsilon_{TT}$  are larger for the bithiophene dyads than for the thiophene comonomers. The larger  $\varepsilon_{TT}$  implies the bithiophene triplets exhibit a higher degree of conjugation than 1 and 2.

It is also evident from Table 3 that the comonomers produce appreciable amounts of triplet. From the energy conservation ( $1 = \Sigma \Phi_x = \Phi_{fl} + \Phi_{ISC} + \Phi_{IC}$ ) and the spectroscopic data, it can be concluded that the comonomers deactivate their singlet excited state predominately by two pathways: either fluorescence or intersystem crossing (ISC) to form their triplet state. In the case of the thiophene comonomers, the singlet excited manifold is deactivated predominately by ISC, supported by the fluorescence and LFP data. This is most likely a result of their higher triplet level favoring ISC. The higher triplet energy of 1 and 2 is confirmed by the phosphorescence emissions that are significantly hypsochromically shifted relative to 3 and 4 (Table 4 and

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Quencher	$1 (10^9 \text{ M}^{-1} \text{ s}^{-1})$	$2 (10^9 \text{ M}^{-1} \text{ s}^{-1})$	$3 (10^9 \text{ M}^{-1} \text{ s}^{-1})$	$4 (10^9 \text{ M}^{-1} \text{ s}^{-1})$
1.3-Cyclohexadiene	4.5	0.2	0.4	0.3
β-Carotene	4.8	5.5	2.2	4.3
2-Methylnaphthalene	4.5	0.004	0.003	0.001
Self-quenching	3.8	8.4	19.9	16.4

 Table 3. Triplet-quenching rate constants for the different comonomers with various quenchers measured in anhydrous and deaerated acetonitrile.

**Fig. 7.** Variation of triplet rate constant of **1** with the addition of 2methylnaphthalene measured at 390 nm. Inset: Effect of triplet transient of **1** monitored at 390 nm with 0 (black), 26 mmol/L (red), and 53 mmol/L (green) 2-methylnaphthalene.



**Fig. 8.** Maximum absorption of triplet 2-methylnaphthalene as a function of laser power produced upon energy transfer from xanthone ( $\blacksquare$ ), 1 ( $\bigcirc$ ), 2 ( $\bigcirc$ ), 3 ( $\square$ ), and 4 ( $\blacktriangle$ ) monitored at 420 nm in anhydrous and deaerated acetonitrile.



Fig. 9). The increased degree of conjugation resulting in splitting of the singlet-triplet energy levels is consistent with previous reports and further confirms that deactivation does not occur from intramolecular photoinduced electron transfer or other radiative means, such as internal conver-

sion.<sup>32,33</sup> The steady-state and time-resolved data collectively confirm that the fluorescence can be tuned as a function of comonomer structure and that the excited-state energy can be channeled to the emitting manifolds. Tuning of the spectroscopic properties as a function of structure is therefore possible.

# Electrochemistry

Cyclic voltammetry of each comonomer was done to determine their redox potentials. All the comonomers exhibited both oxidation and reduction potentials corresponding to the radical cation and anion, respectively. The electrochemical data also demonstrate the inherent dual n- and p-type character of the comonomers. This behaviour is corroborated by the fluorescence quenching data. The HOMO and LUMO values, and the corresponding energy gaps can be calculated from the measured redox potentials by standard methods leading to the values reported in Table 5.23 It is evident from the calculated values that the  $\pi$ -donating thiophene group affects the LUMO of the  $\pi$ -accepting nitrogen-containing heterocycles. This is supported by the less-negative reductive potentials  $(E_{pc})$  of 1-4 compared with pyridine  $(E_{pc} = -2.6 \text{ V})$  and pyrimidine  $(E_{pc} = -2.4 \text{ V}).^{34,35}$  Conversely, the oxidation potentials  $(E_{pa})$  of the comonomers are unchanged compared to their thiophene  $(E_{pa} = 1.6 \text{ V})^{36}$ and bithiophene ( $E_{pa} = 1.3$  V) monomers.<sup>37</sup> This is a result of the  $\pi$ -accepting character of the adjacent nitrogen heterocycle, further confirming that the comonomers are conjugated.

Both the reduction and oxidation processes of the comonomers are not reversible, as seen in Fig. 10. This is expected, since the radical ions are highly reactive and can cross-couple to form their corresponding dimers.<sup>38</sup> Electrochemical dimerization using a large-surface-area mesh electrode was used to afford sufficient quantities of dimers for characterization. Unfortunately, only products insoluble in standard organic solvents were obtained. This is most likely a result of multiple radical ion coupling on the same comonomer. This nonetheless confirms that the donor–acceptor dyads are electrochemically active and that D–A–A–D and A–D–D–A products are possible.

# Conclusion

A series of new donor-acceptor dyad comonomers were prepared. The spectroscopic and electrochemical properties can be modulated as a function of structure. The comonomers can both be photochemically and electrochemically oxidized and reduced resulting in radical ions. This dual active behaviour is a result of incorporating both  $\pi$ -donors and  $\pi$ -acceptors to form the comonomers. The singlet excited state was found to deactivate exclusively by either fluores-

Table 4.	Triplet	properties	of the	different	comonomers	measured	in	anhydrous	and	deaerated	acetonitrile.
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Compound	$\lambda_{TT}$ (nm)	$\tau_{TT}$ (µs)	$k_0 (s^{-1}) (10^{-5})$	$\epsilon_{TT}~(M^{-1}~cm^{-1})$	$\Phi_{TT}$	$\lambda_{\text{phos}} (\text{nm})^a$	$\tau_{phos} \ (ms)^a$
1	390	4.8	2.1	4000	0.79	522	190
2	380	7.9	1.3	8000	0.83	534	71
3	490	12.3	0.8	15 000	0.30	700	6
4	490	11.2	0.9	20 000	0.86	703	5

<sup>a</sup>Measured in a 4:1 ethanol/methanol matrix at 77 K.

**Fig. 9.** Normalized absorbance ( $\blacktriangle$ ) and fluorescence ( $\bigcirc$ ) of **1** measured in dichloromethane at room temperature and phosphorescence ( $\blacksquare$ ) measured at 77 K in 4:1 ethanol/methanol glass matrix.



cence or intersystem crossing. The deactivation pathway can be tailored by adjusting the triplet energy level, which in turn, is controlled by the degree of conjugation and the number of thiophenes. These novel comonomers are ideal candidates for emitting applications owing to their high fluorescence yields.

# **Experimental**

# Analyses

## Spectroscopic measurements

Absorbance measurements were recorded on a Cary-500 spectrometer, while fluorescence measurements were performed with an Edinburgh Instruments FLS-920 fluorimeter after deaerating the sample for 20 min with nitrogen. Fluorescence quantum yields were measured at low sample concentration in dichloromethane by exciting the compounds close to their maximum absorption wavelength and by comparing the emission to bithiophene ( $\Phi_{\rm fl} = 0.013$ ) at the same wavelength. Phosphorescence measurements were done on a Cary Eclipse at 77 K in a 4:1 ethanol/methanol solvent.

# Laser flash photolysis (LFP) measurements

Laser flash photolysis experiments were done on a Luzchem mini-LFP system excited at 355 nm with the third harmonic of a Nd-YAG laser. The solutions were prepared with absorbances between 0.3 and 0.5 at the excitation wavelength. Triplet-state quantum yield and triplet-triplet molar absorption coefficients were measured against xanthone in dichloromethane ( $\Phi_{TT} = 1$ ,  $\varepsilon_{TT} = 28\ 000\ mol/L^{-1}\ s^{-1}$ ) and were determined using standard techniques.<sup>39–42</sup>

#### Crystal structure determination

Diffraction data for **4** was collected on a Bruker Smart 6000 diffractometer using graphite-monochromatized Cu K $\alpha$  radiation with 1.54178 Å. The structures were solved by direct methods (SHELXS97). Disorder was found in the terminal thiophene and consisted of a flip of this heterounit. The weight of each isomer was optimized. All non-hydrogen atoms were refined based on Fobs2 (SHELXS97), while hydrogen atoms were refined on calculated positions with fixed isotropic U, using riding model techniques.

#### Electrochemical measurements

Cyclic voltammetry measurements were recorded with a Bio Analytical Systems Ec Epsilon potentiostat. The compounds of study were dissolved in anhydrous and deaerated dichloromethane with 0.1 mol/L TBAPF<sub>6</sub>. A platinum electrode was employed as the working electrode, while a platinum wire was used as the auxiliary electrode. The reference electrode was a saturated Ag/AgCl electrode.

#### Syntheses

# Thiophen-2-ylboronic acid

Thiophene (998 mg, 11 mmol) and butyl lithium 2.5 mol/L (5 mL, 12 mmol) were added to anhydrous THF (25 mL) at 0 °C under nitrogen. Trimethylborate (4.05 mL, 36 mmol) was added dropwise to the solution at -78 °C. The temperature was raised to room temperature, and the solution was stirred for 1 h before 10% H<sub>2</sub>SO<sub>4</sub> (20 mL) was added. The product was extracted with dichloromethane (20 mL), and the organic layer was then washed with 3 mol/L NaOH (50 mL). The pH of the aqueous layer was adjusted to 1 using 3.2 mol/L HCl, then it was washed with dichloromethane (60 mL). The product was isolated as a yellow-orange solid (840 mg, 55%) and was used without additional purification. Mp 137-139 °C. <sup>1</sup>H NMR (acetone $d_6$ ):  $\delta = 7.71$  (d, 1H,  ${}^{3}J = 4.4$  Hz), 7.31 (s, 1H), 7.18 (t, 1H,  ${}^{3}J = 4.1$  Hz), 5.79 (s, 2H).  ${}^{13}C$  NMR (acetone- $d_{6}$ ):  $\delta = 136.1$ , 131.7, 128.4, 128.3.

## 1-(2,2'-Bithiophen-5-yl)ethanone (5)

To anhydrous THF (20 mL) was added 2,2'-bithiophene (1.72 g, 10 mmol), and the resolution solution was cooled to -78 °C. *n*-Butyl lithium (10 mol/L, 1 mL, 10 mmol) was added under nitrogen, then the temperature was raised to room temperature and the mixture was allowed to stir for 1 h. *N*,*N*-Dimethylacetamide (0.93 mL, 10 mmol) was added, and the reaction was stirred for an additional 2 h at room temperature. The reaction was quenched with water

Compound	$E_{\rm pa}$ (V)	$E_{\rm pc}$ (V)	HOMO (eV)	LUMO (eV)	$E_{\rm g}~({\rm eV})$
1	1.5	-1.4	5.9	3.0	2.9
2	1.7	-1.6	6.1	2.8	3.3
3	1.4	-1.6	5.8	3.1	2.7
4	1.5	-1.6	5.9	3.2	2.7

**Table 5.** Cyclic voltammetry data obtained in 1 mol/L TBAPF<sub>6</sub> in anhydrous and deaerated dichloromethane.

**Fig. 10.** Cyclic voltammogram of **4** measured in anhydrous and deaerated dichloromethane with TBAPF<sub>6</sub> at 100 mV/s.



(50 mL), and the organic layer was extracted with dichloromethane (60 mL). The product was purified by flash chromatography eluted with hexanes/ethyl acetate (90:10, v/v) to give a yellow powder (451 mg, 21%). <sup>1</sup>H NMR (acetone $d_6$ ):  $\delta = 7.80$  (d, 1H, <sup>3</sup>J = 4), 7.56 (dd, 1H, <sup>3</sup>J = 5.2, <sup>5</sup>J =1.2), 7.46 (dd, 1H, <sup>3</sup>J = 3.6, <sup>5</sup>J = 0.8), 7.34 (d, 1H, <sup>3</sup>J = 4), 7.14 (dd, 1H, <sup>3</sup>J = 5.2 and 4), 2.52 (s, 3H).

# (2,2'-Bithiophen-5-yl)-3-(dimethylamino)prop-2-en-1-one (6)

To a 2:1 ethanol/dichloromethane solution (3 mL) was added **5** (110 mg, 0.5 mmol), and the solution was then refluxed for 1 h. *N*,*N*-Dimethylformamide dimethyl acetal (225 mg, 1.9 mmol) was added, and the reaction was refluxed for 17 h. The reaction was cooled to room temperature, and then hexanes were added and the solution was left to cool in the freezer overnight. The precipitate was filtered to afford the product as an orange solid (102 mg, 75%). The compound was used without any further purification. <sup>1</sup>H NMR (acetone- $d_6$ ):  $\delta = 7.68$  (d, 1H,  ${}^{3}J = 12.4$ ), 7.65 (d, 1H,  ${}^{3}J = 3.6$ ), 7.49 (dd, 1H,  ${}^{3}J = 5.2$ ,  ${}^{5}J = 1.2$ ), 7.39 (dd, 1H,  ${}^{3}J = 3.6$ , 5.79 (d, 1H,  ${}^{3}J = 12$ ), 3.21 (s, 3H), 2.98 (s, 3H).

#### 4-(Thiophen-2-yl)pyrimidine (1)

To absolute ethanol (25 mL) was added **6** (2.00 g, 11 mmol). The solution was brought to reflux after which time formamidine acetate (3.45 g, 33 mmol) was added, and the solution was refluxed for an additional 10 min. So-dium (0.77 g, 33 mmol) in absolute ethanol (2 mL) was then

added. The mixture was then refluxed for 16 h. The solvent was then evaporated, the solid washed with dichloromethane, and then filtered. The filtrate was purified by flash chromatography using hexanes/ethyl acetate (70:30, v/v) to afford the product as a yellow powder (541 mg, 31%). Mp 54–56 °C. <sup>1</sup>H NMR (acetone- $d_6$ ):  $\delta = 9.05$  (s, 1H), 8.74 (d, 1H,  ${}^{3}J = 5.2$  Hz), 7.99 (dd, 1H,  ${}^{3}J = 4$  Hz,  ${}^{5}J = 1.2$  Hz), 7.88 (dd, 1H,  ${}^{3}J = 5.2$  Hz), 7.23 (dd, 1H,  ${}^{3}J = 3.6$  Hz and 1.2 Hz). <sup>13</sup>C NMR (acetone- $d_6$ ):  $\delta = 160.8$ , 160.5, 159.4, 144.1, 132.5, 130.5, 130.0 117.1. HR-MS(+) calculated for [C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>S + H]<sup>+</sup>: 163.03245; found: 163.03303.

# 2-Thiophene-2-yl-pyridine (2)

To isopropanol (40 mL) was added a 2 mol/L Na<sub>2</sub>CO<sub>3</sub> solution in water (5 mL). Thiophene-2-yl-2-boronic acid (459 mg, 36 mmol) and 2-chloropyridine (408 mg, 36 mmol) were then added. Tetrakis (triphenylphosphine) palladium (101 mg, 0.36 mmol) was added under nitrogen under the cover of light. The temperature was raised to 50 °C, and the reaction was stirred at this temperature for 17 h. The product was extracted with dichloromethane and then purified by flash chromatography using hexanes/ethyl acetate (95:5, v/v) followed by 10% ethyl acetate. The product was isolated as a yellow solid (268 mg, 46%). Mp 56-58 °C. <sup>1</sup>H NMR (acetone- $d_6$ ):  $\delta = 8.52$  (d, 1H, <sup>3</sup>J = 4.8), 7.85 (dd, 1H,  ${}^{3}J = 6.8$ ,  ${}^{5}J = 0.8$ ), 7.79 (td, 1H,  ${}^{3}J = 7.2$ ,  ${}^{5}J = 1.6$ ), 7.74 (dd, 1H,  ${}^{3}J = 4$ ,  ${}^{5}J = 1.2$ ), 7.54 (dd, 1H,  ${}^{3}J =$ 5.2,  ${}^{5}J = 1.2$ ), 7.24 (dd, 1H,  ${}^{3}J = 4.8$ ,  ${}^{5}J = 1.2$ ), 7.14 (dd, 1H,  ${}^{3}J = 4$  and 1.2).  ${}^{13}C$  NMR (acetone- $d_6$ ):  $\delta = 154.4$ , 151.3, 147.0, 138.7, 129.9, 126.5, 123.9, 120.3. HR-MS(+) calculated for  $[C_9H_7NS + H]^+$ : 162.03719; found: 162.03711.

## 4-(2,2') Bithiophenyl-5-yl-pyrimidine (3)

In ethanol (25 mL) was added 1-(2,2') bithophenyl-5-yl-3dimethylamino-propenone (178 mg, 0.67 mmol), and the solution was refluxed for 1 h. Formamidine acetate was then added (227 mg, 2 mmol), and the reaction was stirred for 10 min followed by the addition of sodium (57 mg, 2.5 mmol) in ethanol (2 mL). The slurry was then refluxed for 7 days. The solvent was evaporated, the product was taken up in dichloromethane, and the remaining inorganic salts were filtered. The product was purified by flash chromatography using hexanes/ethyl acetate (95:5, v/v) to afford the product as a bright yellow solid (144 mg, 87%). Mp 113–115 °C. <sup>1</sup>H NMR (acetone- $d_6$ ):  $\delta = 9.06$  (d, 1H,  ${}^{3}J = 1.6$ ), 8.74 (d, 1H,  ${}^{3}J = 5.2$ ), 7.96 (d, 1H,  ${}^{3}J = 4$ ), 7.90 (dd, 1H,  ${}^{3}J$ = 5.6,  ${}^{5}J$  = 1.6), 7.53 (dd, 1H,  ${}^{3}J$  = 5.2,  ${}^{5}J$  = 1.2), 7.45 (dd, 1H,  ${}^{3}J = 3.6$ ,  ${}^{5}J = 0.8$ ), 7.39 (d, 1H,  ${}^{3}J = 4$ ), 7.15 (dd, 1H,  ${}^{3}J$  = 3.6 and 1.6).  ${}^{13}C$  NMR (acetone- $d_6$ ):  $\delta$  = 160.8, 160.1, 159.3, 143.7, 142.4, 131.0, 130.3, 128.0, 126.9, 126.8, 116.8. HR-MS(+) calculated for  $[C_{12}H_8N_2S_2 + H]^+$ : 245.02017; found: 245.02088.

#### 2-(2,2') Bithiophenyl-5-yl-pyridine (4)

To ethanol (25 mL) was added 2 mol/L Na<sub>2</sub>CO<sub>3</sub> (5 mL) followed by (2,2') bithiophenyl boronic dimethyl ester (1.5 g, 7.27 mmol) and 2-chloropyridine (1.65 g, 14.54 mmol) under nitrogen. Tetrakis (triphenylphosphine) palladium (822 mg, 72.7 mmol) was then added under nitrogen and in the absence of light. The reaction mixture was heated to 50 °C for 16 h. The product was extracted with dichloromethane and was purified by flash chromatography using hexanes and increasing the polarity with hexanes/ethyl acetate (90:10, v/v). The product was isolated as a pale orange solid (656 mg, 40%). Mp 124-126 °C. <sup>1</sup>H NMR (acetone- $d_6$ ):  $\delta = 8.53$  (d, 1H,  ${}^{3}J = 4.8$ ), 7.83 (d, 1H,  ${}^{3}J = 8$ ), 7.81 (td, 1H,  ${}^{3}J = 7.6$ ,  ${}^{5}J = 2$ ), 7.68 (d, 1H,  ${}^{3}J = 3.6$ ), 7.46 (dd, 1H,  ${}^{3}J = 5.2$ ,  ${}^{5}J = 1.2$ ), 7.37 (dd, 1H,  ${}^{3}J = 3.6$ ,  ${}^{5}J = 1.2$ ), 7.29 (d, 1H,  ${}^{3}J = 3.6$ ), 7.25 (dd, 1H,  ${}^{3}J = 4.8$ ,  ${}^{5}J = 0.8$ ), 7.11 (dd, 1H,  ${}^{3}J$  = 3.6 and 1.2).  ${}^{13}C$  NMR (acetone- $d_6$ ):  $\delta$  = 154.0, 151.3, 145.8, 140.9, 139.1, 138.7, 130.1, 127.4, 127.0, 126.428, 126.0, 124.0, 120.2. HR-MS(+) calculated for  $[C_{13}H_9NS_2 + H]^+$ : 244.02492; found: 244.02546.

#### Anodic dimerization

The comonomer **2** (20 mg, 0.12 mmol) was dissolved in anhydrous dichloromethane (12 mL) under nitrogen. FeCl<sub>3</sub>·6H<sub>2</sub>0 (166 mg, 0.61 mmol) was added, and the mixture was refluxed for 24 h. After refluxing, an insoluble precipitate formed. The soluble product was extracted with dichloromethane, the solvent evaporated, and taken up into THF for MS analysis.

# Supplementary data

Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5336. For more information on obtaining material, refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub\_e.shtml. CCDC 753448 contains the X-ray data in CIF format for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving. html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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