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Novel donor—acceptor type thiophene pyridine conjugates: synthesis and ion recognition features

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1. Introduction

The design and syntheses of organic π -conjugated materials has been intensively pursued over the last few decades, due to their great potential in a variety of advanced technological applications. Generally, the intrinsic properties (electronic, optical, conductivity, stability) of these materials should be tailored with respect to the desired application. One of the best ways of tailoring the electronic structure and properties of organic materials is combining an appropriate electron-rich (donor, D) moiety with an electron-poor (acceptor, A) unit.¹ This D–A strategy in the design of organic π conjugated materials does not only allow fine tuning of the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy levels and the band gap (E_{g}) of the system, 2^{-5} but also provides perfectly controlled architectures with compatibility and tunable intrinsic properties offered by the structural design. Thus, the D-A approach has so far allowed the creation of excellent molecular systems, which hold promise for the applications in the field of organic light emitting diodes.^{6–8} photovoltaics,9-11 transistors, molecular electronics and

ABSTRACT

In order to reveal the effect of the donor units on the structure–property relationship, three novel directly linked donor–acceptor type systems, **1–3**, which are based on thiophene and pyridine conjugates, are designed, synthesized and characterized by spectroscopic methods. It is noteworthy that these D–A systems exhibit distinct electrochemical and optical features depending on the strength of the D-unit or the conjugation length. Furthermore, it is found that two of these novel systems, **2** and **3**, can be used in both chromogenic and fluorogenic detection of Cu²⁺ among other ions.

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electrochromic devices.^{12–14} However, only a few directly linked D–A systems with pyridine as the A-unit have been reported to date,^{15–18} in spite of the fact that much literature concerning the design of other electron deficient units as the A-part of the D–A type materials^{19,20} exists (e.g., quinoxaline,²¹ 2,1,3-benzoxadiazole²² and 2,1,3-benzoselenodiazole^{23,24}). Furthermore, it is important to note that most of the reports concerning the directly linked D–A type thiophene pyridine conjugates have just focused on the design and synthesis, but not on the systematic comparison of the structure–property relationship.¹⁵ In this context, it is a challenging task to attain novel directly linked D–A type thiophene pyridine conjugates and elucidate the structure–property relationships in a systematical manner.

On the other hand, the development of functional organic compounds that allow selective and sensitive detection of target metal ions have recently attracted considerable attention due to the fact that these ions play essential and/or deleterious roles in biological and environmental processes.^{25–29} Among these metal ions, Cu^{2+} is an important trace element, which plays crucial roles in various biological processes. In addition to these crucial roles, however, Cu^{2+} is a significant environmental pollutant, and has toxic effects to organisms especially at high concentration levels, since it can displace other metal ions that act as cofactors in





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enzyme-catalyzed reactions,³⁰ thus causing Alzheimer's, Parkinson's and Wilson diseases, hypoglycemia, dyslexia and infant liver damage.^{31–34} Consequently, significant efforts have been devoted to the design and syntheses of novel Cu^{2+} ion sensors.^{35–45} None-theless, the number of selective and sensitive chemosensors that give dual channel (fluorogenic and chromogenic) response to Cu^{2+} ions are limited,^{46–52} thus the newer ones are welcome.

2. Results and discussion

2.1. Design and synthesis

In order to reveal the effect of the D-units on the structure-property relationship, three different D-A systems, **1**–**3**, were taken into account (Fig. 1). At this stage, it was envisaged that each combination would result in the formation of a different D-A system with distinct electrochemical and photophysical properties (redox potential, absorption, emission etc.), which is not unexpected, since each D-unit had a different electronic nature. It is also noteworthy that these systems **1**–**3** would give the opportunity to understand the effect of the D-units on both the electrochemical and the photophysical properties of the corresponding D-A systems in a systematic manner. Convinced by the above strategy, the synthesis of the target compounds **1–3** was started with the construction of the A-unit. Initial efforts, which were directed towards the synthesis of the A-part, involved the bromination of 1,10-phenanthroline (**4**) according to a published method (Scheme 1).⁵³ The bromination reaction was carried out in the presence of sulfur monochloride and pyridine in chlorobutane to give 3,8-dibromo-1,10-phenanthroline (**5**) albeit in low (ca. 35%) yield. Then, the oxidation of dibromide **5** with KMnO₄ under basic conditions provided **6** after treatment with HCl. Compound **6** was characterized on the basis of ¹H, ¹³C NMR and FTIR spectroscopy and elemental analysis, which firmly established the structure (see Supplementary data for ¹H and ¹³C NMR spectra, Fig. S1 and 2).

In the next step, diacid **6** was converted to diester **7** by treatment with SOCl₂ in ethanol. In the ¹H NMR spectrum of **7**, two aromatic protons resonated as two sets of doublets at 8.81 (d, J=2.5 Hz, 1H) and 8.50 (d, J=2.5 Hz, 1H) ppm, whereas the methyl and methylene protons resonated at 4.17 (q, J=8 Hz, 2H) and 1.15 (t, J=8 Hz, 3H) ppm, respectively (Fig. S3). An eight-line ¹³C NMR spectrum was also consistent with the structure (Fig. S4).

At this stage, tributylstannyl derivatives of the D-units, $\mathbf{8}$, 16 $\mathbf{9}^{54}$ and $\mathbf{10}^{16}$ were prepared. Finally, Stille coupling reaction of **7** with **8** afforded the D–A system **1** in 55% yield (Scheme 2). In a similar





vein, compounds **2** and **3** were synthesized from the coupling reactions of **7** with **9** and **10** in 60% yields, respectively (Scheme 2). Note that compounds **1–3** were comprised of a 2,2'-bipyridine scaffold as the A-part that was linked with 3,4-ethylene-dioxythiophene (EDOT), thiophene and 2,2'-bithiophene, respectively, as different D-units. This allows the investigation of the effect of the D-units in a systematic manner.

Initial characterization of **1–3** was based on NMR and FTIR spectroscopic data along with the elemental and HRMS analysis (see Supplementary data), which confirmed the structures.

2.2. Electrochemical properties

In order to determine the role of the D-units on the redox behaviour of pyridine based D-A systems 1-3, cyclic voltammetry studies were carried out in 0.1 M Bu₄NPF₆, which was dissolved in acetonitrile. During anodic scans, irreversible oxidation waves were observed at (E_a^{ox}) 0.82 V, 1.72 V and 1.24 V (vs Ag/AgCl) for 1–3, respectively (Fig. S11). It was found that the voltammograms nicely reflected the electronic nature of the D units: **3** had an oxidation potential of 1.24 V, which was between those of 1 and 2, as depicted in Fig. 2. It is well established that EDOT is electron rich compared to thiophene, due to the presence of electron donating alkoxy substituents. For that reason, compound 1, which has the EDOT ring as a D-unit, gave rise to the lowest oxidation potential when compared to 2 and 3. However, compound 3 had a lower oxidation potential when compared to 2. This could be attributed to the increased conjugation in **3**, which provided strong coupling between the π systems of the thiophene and pyridine rings. The electron density of systems 1–3 probably followed an increasing order as 2, 3 and 1, as well as with the ease of oxidation in the same order (Fig. S11).

2.3. Photophysical properties

The absorption profiles of the compounds **1–3** were examined in CH₃CN solution. The UV–vis spectra of **1** and **2** were characterized by broad bands between 280 and 350 nm (λ_{max} =315 and 310 nm) with molar extinction coefficients (ε_m) of 9633 and 96,011 M⁻¹ cm⁻¹, respectively. The low energy absorption band in compound **1** exhibited a slight hypsochromic shift in the electronic spectra of compound **2**. This is not surprising since the electron density of **1** is higher than **2**. However, the UV–vis spectrum of **3** exhibited a bathochromic shift with respect to **2** probably due to the increased conjugation, as expected, with a λ_{max} =370 nm (ε_m =196,724 M⁻¹ cm⁻¹).

Next, the metal cation complexing properties of 1-3 were investigated by spectrophotometric titrations with different metal ions. First of all, it was found that the absorption of 1 was quite sensitive to the presence of metal ions (e.g., \hat{Fe}^{3+} , Cu^{2+} , Ni^{2+} , Zn^{2+} and Co^{2+}), although did not exhibit any selectivity (Fig. 2A). This behaviour of **1** was attributed to the presence of extra oxygen atoms on the EDOT units, which donate a greater amount of electron density into the bipyridine, increasing the basicity of nitrogens and consequently increasing their ion binding strength but reducing selectivity, when compared to the thiophenes on 2 and 3. In contrast, the absorption spectra of **2** and **3** were not influenced upon addition of Hg^{2+} , Ag^+ , Cd^{2+} , Co^{2+} , Cu^+ , Fe^{2+} , Fe^{3+} , Li^+ , Mn^{2+} , Pb^{2+} , Pt^{2+} and $Zn^{2+}(1 \text{ equiv})$ ions, all of which gave no significant change as shown in Fig. 2B and C. On the other hand, it was noted that Cu^{2} ions revealed dramatic changes in both the shape and the maxima of the original absorption bands of 2 and 3 (Fig. 2B and C). As an aside, it was also noted that Ni²⁺ ions caused slight changes in the absorption spectra of 2 and 3.

Fig. 3 shows the absorption spectral changes of **2** and **3** as a function of Cu^{2+} concentration in CH_3CN solution at room temperature. Notably, during the addition of Cu^{2+} ions, a progressive decrease in absorbance at the λ_{max} was observed with simultaneous formation of a new red shifted absorption band, which increased in intensity, at 392 nm and 460 nm for **2** and **3**, respectively. Similarly, Ni²⁺ ions also caused bathochromic shifts in the absorption spectra of **2** and **3**, but in these cases the changes were not so distinct when compared to Cu^{2+} ions (see Fig. S12).

Furthermore, the red shift of the absorption bands of **2** and **3** were around 80 and 90 nm for Cu^{2+} ions, respectively. Fortunately,



Fig. 2. UV-vis spectra of (A) 1 (6×10^{-5} M), (B) 2 (5.7×10^{-6} M) and (C) 3 (2.85×10^{-6} M) in the presence of various metal ions (1 equiv) in CH₃CN.

such red-shifts were enough to make the colour of the solution of **2** change from a colourless state to a yellow colour, thus allowing the naked-eye (colorimetric) detection of Cu^{2+} and/or Ni²⁺ ions among the others (Fig. S13a). On the other hand, the yellow colour of the

solution of **3** turned red with Cu^{2+} and orange with Ni^{2+} ions (Fig. S14a). It is important to note that colour change is one of the most convenient visual detection methods used in classical chemical analysis, which is straightforward without the need for



Fig. 3. UV–vis spectra of (A) **2** (8.57×10⁻⁶ M) in the presence of various amounts of Cu²⁺ ions (0, 0.08, 0.16, 0.25, 0.33, 0.42, 0.50, 0.58, 0.66, 0.75, 0.83, 0.92, 1.0, 1.5, 2.0, 3.0 equiv) in CH₃CN and (B) **3** (3.35×10⁻⁶ M) in the presence of various amounts of Cu²⁺ ions (0, 0.08, 0.16, 0.25, 0.33, 0.42, 0.50, 0.58, 0.66, 0.75, 0.83, 0.92, 1.0, 1.5, 2.0, 3.0 equiv) in CH₃CN.

any instrument. It was reasonable to assume that the colorimetric responses of **2** and **3** to metal ions were probably based on the mechanism of internal charge transfer (ICT). The metal cation interacting with the acceptor group enhances the electron-withdrawing character of this group; thus, the absorption spectrum is, red-shifted.

On the other hand, the fluorescence spectra of **2** and **3** in CH₃CN exhibited broad emission peaks with $\lambda_{max(emis)}$ at 423 nm and 505 nm, respectively. Increased conjugation length in **3** provided a dramatic enhancement of fluorescence properties. This was probably a consequence of the increased rigidity of the system in the excited state, which could reduce the non-radiative processes. It was found that the emissions of **2** and **3** were not influenced at all upon addition of Ag⁺, Cd²⁺, Co²⁺, Cu⁺, Fe²⁺, Fe³⁺, Hg²⁺, Li⁺, Mn²⁺, Pb²⁺, Pt²⁺ and Zn²⁺ ions, all of which gave no significant change in the emission profiles of **2** and **3** as shown in Fig. 4.

(365 nm) (Figs. S13B and S14B). Upon binding of Cu^{2+} ions to compounds **2** and **3**, the fluorescence emissions were totally quenched. The quenching mechanism was presumably based on the electron transfer between **2**/**3** and the metal cation, which might provide an efficient non-radiative decay of the excited state. Similarly, Ni²⁺ ions also quenched the emissions of **2** and **3** to an extent, but the changes in these cases were not so distinct when compared to Cu²⁺ ions (Fig. S17), thus the emission was not turned off.

On the basis of the above spectrophotometric titrations, the detection limit⁵⁵ of compounds **2** and **3** was calculated to be 3.09×10^{-6} M and 1.44×10^{-6} M, respectively. Considering the fact that the limit of copper in drinking water determined by the U.S. Environmental Protection Agency (EPA) is around 2×10^{-5} M (20 μ M),⁵⁶ these compounds serve as promising dual channel (colorimetric and fluorometric) responsive probes for the detection of Cu²⁺ ions. Furthermore, the binding constants (K_a) of **2** and **3**



Fig. 4. Fluorescence spectra of (A) 2 (1.42×10^{-6} M) (λ_{exc} =310 nm) and (B) 3 (0.4×10^{-6} M) (λ_{exc} =370 nm) in the presence of various metal ions in CH₃CN.

However, the blue emission of **2** and green emission of **3** were totally quenched upon addition of Cu^{2+} ions (*turn off*). Clearly, the changes in the emission profiles of **2** and **3** upon addition of Cu^{2+} indicated the formations of well-defined complexes between these compounds and the metal ions. Evaluation of Job plots for the determination of the stoichiometry of the complexes of **2** and **3** with Cu^{2+} ions revealed `1 ratios (Fig. S15). NMR titrations of compound **3** with Cu(II) indicated that there is no significant change (ca. 0.1 ppm) in the protons of the ester groups, whereas significant up field shifts (ca. 0.5 ppm) in the protons of the pyridine ring were observed in the ¹H NMR spectrum (Fig. S16). This mainly suggested that metal ion is coordinated to the pyridine nitrogens rather than the ester units.

Fig. 5 shows the fluorescence spectral changes of **2** and **3** as a function of the Cu²⁺ concentration in CH₃CN at room temperature. Note that a progressive decrease in emissions at $\lambda_{max(emis)}$ was observed.

The changes in the fluorescence spectra of 2 and 3 upon addition of Cu²⁺ could also be observed by the naked eye when the solutions of compounds with metal ions were illuminated under UV light

with Cu²⁺ were determined from the emission intensity data following the steady-state fluorometric method,⁵⁷ in which I_0 referred to the fluorescence intensities of solutions of **2** or **3**. When $I_0/(I-I_0)$ is plotted against $[M]^{-1}$, K_a was calculated to be 1.08×10^5 and 2.75×10^6 for **2** and **3**, respectively, from the ratio of intercept/slope with good correlation coefficients (*R*=0.9777 and 0.9896 for **2** and **3**, respectively).

3. Conclusion

In summary, the design, synthesis, electrochemical and photophysical properties of three novel directly linked D–A type compounds **1–3** has been described. EDOT, thiophene and 2,2'bithiophene were chosen as D-units while 2,2'-bipyridine with ester subunits was taken as the A-unit in these systems. It was noteworthy that these D–A systems **1–3** exhibited distinct electrochemical and optical features depending on the strength of the D-unit and the conjugation length. Moreover, it was found that two of these novel systems, **2** and **3**, could be used as molecular probes for both chromogenic and fluorogenic^{58,59} detection of Cu²⁺ among



Fig. 5. Fluorescence spectra of (A) **2** (1.42×10^{-6} M) ($\lambda_{exc}=310$ nm) in the presence of various amounts (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.5, 2.0, 3.0, 4.0, 5.0 equiv) of Cu²⁺ ions in CH₃CN and (B) **3** (0.44×10^{-6} M) ($\lambda_{exc}=370$ nm) in the presence of various amounts (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 2.0, 3.0, 4.0, 5.0 equiv) of Cu²⁺ ions in CH₃CN.

other ions. Further work to elucidate the versatility of these novel compounds is currently underway in our laboratory, and the results will be reported in due time.

4. Experimental

4.1. General methods

All chemicals were purchased from Sigma-Aldrich or Merck and used as received unless otherwise noted. FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 model FTIR with an attenuated total reflectance (ATR). ¹H (400 or 300 MHz) and ¹³C (100 or 75 MHz) NMR spectra were recorded on a Bruker DPX-400 or Ultrashield 300 NMR Spectrometers. Combustion analysis was carried out by using an LECO CHNS-932 analyzer. High resolution mass spectra (HRMS ESI⁺) were recorded on a Waters SYNAPT MS system. UV-vis and fluorescence measurements were recorded on Varian Cary 50 and Varian Cary Eclipse spectrophotometers, respectively. 0.1 M Bu₄NPF₆, dissolved in acetonitrile was used as electrolyte solution. A platinum button (0.02 cm²) and a platinum wire were used as working and counter electrodes, respectively, as well as an Ag/AgCl reference electrode (calibrated externally using 10 mM solution of ferrocene/ferrocenium couple, which is an internal standard calibrated to be 0.44 V in acetonitrile solution vs Ag/AgCl). Melting points were determined on a Schorrp MPM-H2 model apparatus and are uncorrected. Column chromatography was performed on silica gel (60-200 mesh) from Merck Company. TLC was carried out on Merck 0.2 mm silica gel 60 F₂₅₄ analytical aluminium plates. For spectrophotometric titrations, metal ions were freshly prepared from perchlorate salts. The syntheses of compounds 5,⁵³ 8,¹⁶ 9⁵⁴ and 10¹⁶ were carried out according to previously published procedures.

4.2. Synthesis

4.2.1. 5,5'-Dibromo-2,2'-bipyridine-3,3'-dicarboxylic acid (**6**). A mixture of dibromide 5^{53} (3.38 g, 0.01 mol), sodium hydroxide

(0.8 g, 0.02 mol) and potassium permanganate (4.74 g, 0.03 mol) in distilled water (200 mL) was heated under reflux for 6 h with vigorous stirring. The brown precipitate of MnO₂ was filtered while hot and the volume of the filtrate was reduced to 70 mL on a rotary evaporator. Concentrated HCl was added dropwise to the filtrate to give needle shaped crystals when the pH reached 2–3. The solid was filtered off, washed with water, ethanol and dried in air to give **6**; 2.82 g, 70% yield, white solid, mp 252–254 °C (with decomposition); ¹H NMR (400 MHz, DMSO-*d*₆) δ /ppm: 8.82 (br s, 2H), 8.34 (br s, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ /ppm: 160.7, 155.3, 150.3, 139.0, 131.0, 119.1; FTIR (cm⁻¹): 3079, 2806, 2601, 2444, 2324, 1848, 1738, 1684, 1570, 1560, 1428, 1284, 1196, 1105, 1085, 1036, 916, 843, 738, 711. Anal. Calcd for C₁₂H₆Br₂N₂O₄: C, 35.85; H, 1.50; N, 6.97; Found: C, 35.83; H, 1.48; N, 6.95. HRMS Calcd for C₁₂H₇Br₂N₂O₄: 400.8773; Found: 400.8788 [M+H]⁺.

4.2.2. Diethyl 5,5'-dibromo-2,2'-bipyridine-3,3'-dicarboxylate (**7**). SO-Cl₂ (0.28 mL, 4 mmol) was dropwise added to a solution of diacid **6** (402 mg, 1 mmol) in ethanol (30 mL) at room temperature. Then the solution was heated under reflux until the starting material was totally consumed. The solvent was removed and the residue was chromatographed on silica gel by eluting with CH₂Cl₂ to give the product; 435 mg, 95% yield, white solid, mp 90–92 °C; ¹H NMR (400 MHz, CDCl₃) δ /ppm: 8.81 (d, *J*=2.5 Hz, 2H), 8.50 (d, *J*=2.5 Hz, 2H), 4.17 (q, *J*=8 Hz, 4H), 1.15 (t, *J*=8 Hz, 6H); ¹³C NMR (400 MHz, CDCl₃) δ /ppm: 164.1, 156.8, 152.6, 140.5, 126.9, 119.8, 61.8, 13.8; FTIR (cm⁻¹): 3057, 2983, 2935, 1723, 1699, 1420, 1274, 1207, 799; Anal. Calcd for C₁₆H₁₄Br₂N₂O₄: C, 41.95; H, 3.08; N, 6.12; Found: C, 41.80; H, 3.16; N, 6.22. HRMS Calcd for NaC₁₆H₁₄Br₂N₂O₄: 478.9218; Found: 478.9209/480.9192/482.9198 [M+Na]⁺.

4.2.3. Representative procedure for the synthesis of D–A conjugates **1–3**. To an argon degassed solution of **7** (92 mg, 0.20 mmol) and **8/9** or **10** (0.44 mmol) in dry toluene (25 mL) was added Pd(PPh₃)₄ (5 mg) and the mixture was heated under reflux until all the starting materials were consumed. After cooling to room temperature, the solvent was removed under reduced pressure. The crude

mixture was chromatographed on silica gel by eluting with chloroform to give 1/2 or 3.

4.2.4. Diethyl 5,5'-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,2'-bipyridine-3,3'-dicarboxylate (**1**). Viscous liquid, 63 mg, 55% yield; ¹H NMR (400 MHz, CDCl₃) δ /ppm: 9.07 (d, *J*=2.5 Hz, 2H), 8.57 (d, *J*=2.5 Hz, 2H), 6.43 (s, 2H), 4.36–4.34 (m, 4H), 4.28–4.26 (m, 4H), 4.17 (q, *J*=8 Hz, 4H), 1.08 (t, *J*=8 Hz, 6H); ¹³C NMR (400 MHz, CDCl₃) δ /ppm: 166.2, 155.7, 147.8, 142.3, 140.1, 134.3, 132.0, 128.7, 126.2, 99.7, 64.9, 64.4, 61.3, 13.8; FTIR (cm⁻¹): 3058, 2955, 2922, 2870, 1722, 1590, 1501, 1454, 1437, 1363, 1306, 1272, 1251, 1242, 1169, 1118, 1070, 1039, 1029, 998, 959, 910, 876, 866, 789, 721, 693. Anal. Calcd for C₂₈H₂₄N₂O₈S₂: C, 57.92; H, 4.17; N, 4.82; S, 11.04; Found: C, 57.70; H, 4.30; N, 4.96; S, 10.90. HRMS Calcd for C₂₈H₂₅N₂O₈S₂: 581.1052; Found: 581.1056 [M+H]⁺.

4.2.5. Diethyl 5,5'-di(thiophen-2-yl)-2,2'-bipyridine-3,3'-dicarboxylate (**2**). Yellow solid, 55 mg, 60% yield; mp 125–127 °C; ¹H NMR (400 MHz, CDCl₃) δ /ppm: 9.00 (d, *J*=2.5 Hz, 2H), 8.50 (d, *J*=2.5 Hz, 2H), 7.49 (dd, *J*=4, 2 Hz, 2H), 7.43 (dd, *J*=5, 2 Hz, 2H), 7.17 (dd, *J*=5, 4 Hz, 2H), 4.19 (q, *J*=8 Hz, 4H), 1.12 (t, *J*=8 Hz, 6H); ¹³C NMR (400 MHz, CDCl₃) δ /ppm: 165.6, 157.2, 148, 139.1, 134.8, 129.8, 128.5, 126.8, 126.2, 125, 61.5, 13.8; FTIR (cm⁻¹): 3122, 2983, 2927, 1724, 1713, 1445, 1291, 1237, 1199, 1093, 1025, 793, 712. Anal. Calcd for C₂₄H₂₀N₂O₄S₂: C, 62.05; H, 4.34; N, 6.03; S, 13.80; Found: C, 62.15; H, 4.45; N, 6.20; S, 14.10. HRMS Calcd for C₂₄H₂₁N₂O₄S₂: 465.0943; Found: 465.0927 [M+H]⁺.

4.2.6. Diethyl 5,5'-di(2,2'-bithiophen-5-yl)-2,2'-bipyridine-3,3'-dicarboxylate (**3**). Yellow solid, 75 mg, 60% yield; mp 168–170 °C; ¹H NMR (400 MHz, CDCl₃) δ /ppm: 9.00 (d, *J*=2.5 Hz, 2H), 8.50 (d, *J*=2.5 Hz, 2H), 7.42 (d, *J*=4 Hz, 2H), 7.29–7.27 (m, 4H), 7.23 (d, *J*=4 Hz, 2H), 7.07 (dd, *J*=4, 4 Hz, 2H), 4.21 (q, *J*=8 Hz, 4H), 1.14 (t, *J*=8 Hz, 6H); ¹³C NMR (400 MHz, CDCl₃) δ /ppm: 165.5, 157.0, 147.7, 138.9, 137.4, 136.7, 134.3, 129.5, 128.0, 126.2, 125.8, 125.1, 124.8, 124.3, 61.5, 13.9; FTIR (ATR, cm⁻¹): 3096, 3059, 2982, 2966, 1729, 1707, 1547, 1463, 1288, 1251, 1216, 1079, 803; Anal. Calcd for C₃₂H₂₄N₂O₄S₄: C, 61.12; H, 3.85; N, 4.46; S, 20.40; Found: C, 61.08; H, 3.83; N, 4.49; S, 20.30. HRMS Calcd for C₃₂H₂₅N₂O₄S₄: 629.0697; Found: 629.0696 [M+H]⁺.

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Supplementary data

Copies of ¹H, ¹³C NMR and HRMS spectra for all new compounds. Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.tet.2013.03.008.

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