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Synthesis and photophysical properties of α,ω-bis(terpyridine)oligothiophenes

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ABSTRACT

Four novel fully π-conjugated α,ω-bis(terpyridine)oligothiophenes characterized by NMR, IR, and HR-mass spectroscopy are presented and their electronic absorption/emission and redox properties are described based on both experiments and theoretical calculations. These compounds can be potentially utilized as building blocks for preparation of conjugated metallo-supramolecular polymers or dynamers and related functional materials.

1. Introduction

Ditopic compounds with terpyridine (*terpy*) end-groups are of scientific interest as suitable materials for preparation of metallo-supramolecular polymers[1,2] and dynamers (constitutional-dynamic polymers).[3] The specific configuration of nitrogen atoms allows easy tridentate facial or meridian coordination of a *terpy* group as a ligand to various metal atoms (ions), such as to atoms/ions of Ru, Os, Ir, Fe, Zn, and Co, giving rise to linear chains.[4–6] This feature, which is absent in many other modules,[7] allows metallo-supramolecular assemblies with well-defined stereochemistry, which is important for the reproducible preparation of functional materials.

The optical properties of *terpy* compounds are important for their applications as probes (sensors), active materials for light-emitting devices and dye-sensitized solar cells. The chemical structure of a *terpy* compound directly affects functionality of a metallo-supramolecular assembly comprising this compound, in particular the prevalence of the light-emitting or charge transporting properties. Therefore, the tailored synthesis of *terpy* compounds is a fundamental step in the preparation of high-performance metal-coordination functional materials. The main interest has been focused to mono-*terpy* compounds that are applied in dye-sensitized solar cells.[8–12] Among α,ω-bis(*terpy*)compounds, those in molecules of which conjugated oligomeric chains link two *terpy* end-units are of interest for optoelectronic applications because they can be used for preparation of conjugated dynamers, constitutional-dynamic counterparts of conjugated polymers.[3,13–27]

The choice of the linker between two *terpy* end-units has a strong influence on ligand properties. Low band-gap polythiophenes and oligothiophenes are one of the most important classes of conjugated compounds with a wide range of applications, such as conducting film, electrochromics, and field-effect transistors.[28–30] On the other hand, based to the best of our knowledge, bis-terpyridines containing only oligothiophene linker have not been reported to date.

In the present paper we describe the preparation and photophysical properties of four novel conjugated α,ω-bis(*terpy*)oligothiophenes that differ in the central-chain length and substitution of thiophene rings. The results of theoretical calculations on these molecules, which provide a useful tool for interpretation of photophysical measurements are also presented.

2. Results and discussion

2.1. Synthesis of α,ω-bis(*terpy*)oligothiophenes

Mono-terpyridines reported in this paper were prepared using the procedures based on the two-step Kröhnke methodology.[31] First thiophene-2-carbaldehyde (or its 3-methyl- derivative) reacted with 2-acetylpyridine to give the dicarbonyl precursor (Scheme 1). In the second step, the central pyridine ring was closed by treating the precursor with an excess of ammonium acetate. Preparation of 4′-(thiophen-2-yl)-2,2′;6′,2″-terpyridine has been described in the literature.[32] The derivative of this compound with a methyl-substituted thiophene ring, it was prepared with the aim to increase solubility of target bis(*terpy*) compounds. Brominations of both 4′-(thiophen-2-yl)terpyridines were carried out in the standard way using NBS[33] provided us monotopic precursors of α,ω-bis(*terpy*) compounds **1a** and **1b** (Scheme 1).

The desired α,ω-bis(*terpy*)oligothiophenes were prepared by Suzuki coupling of **1a** and **1b**, respectively, with: (i) bis(pinacolato) diborane—to obtain compounds **2a** and **2b** with dithiophene linkers between terminal *terpy* groups, and (ii) 2,5-thiophenediboronic acid—to obtain compounds **3a** and **3b** with terthiophene linkers (Scheme 2). Their low solubility in toluene enables easy isolation of **2a**, **2b**, and **3a** by simple filtration. On the other hand, **3b** had to be

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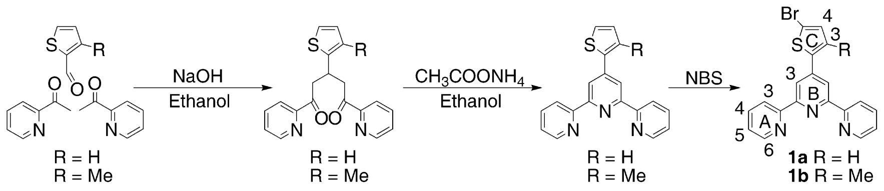
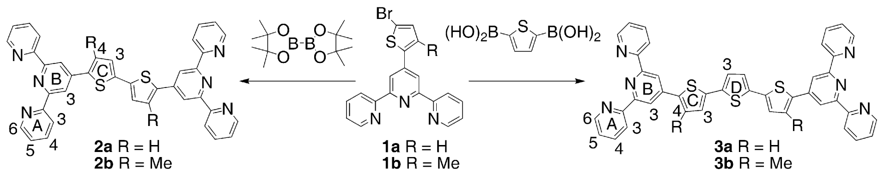


Scheme 1. Preparation of 4′-(thiophen-2-yl)terpyridines.



Scheme 2. Preparation of α,ω-bis(terpyridine)oligothiophenes.

purified using column chromatography as it was significantly soluble in toluene. All ligands were prepared in quite good yields (45–85%) except for **3b** (mainly owing to a loss of the product during the liquid-phase purification). Couplings of **1a** and **1b** were carried out using the Stille method gave lower yields of all bis(*terpy*) compounds.

The successful transformation of **1a** and **1b** to corresponding bis (*terpy*) compounds was confirmed by NMR and HRMS analyses (see Experimental section). Occurrence of bands pertaining to π–π* transitions in conjugated oligothiophene linkers in the optical spectra of **2a** to **3b** (Fig. 1) provides additional evidence since a similar band is absent in spectra of **1a** and **1b**.

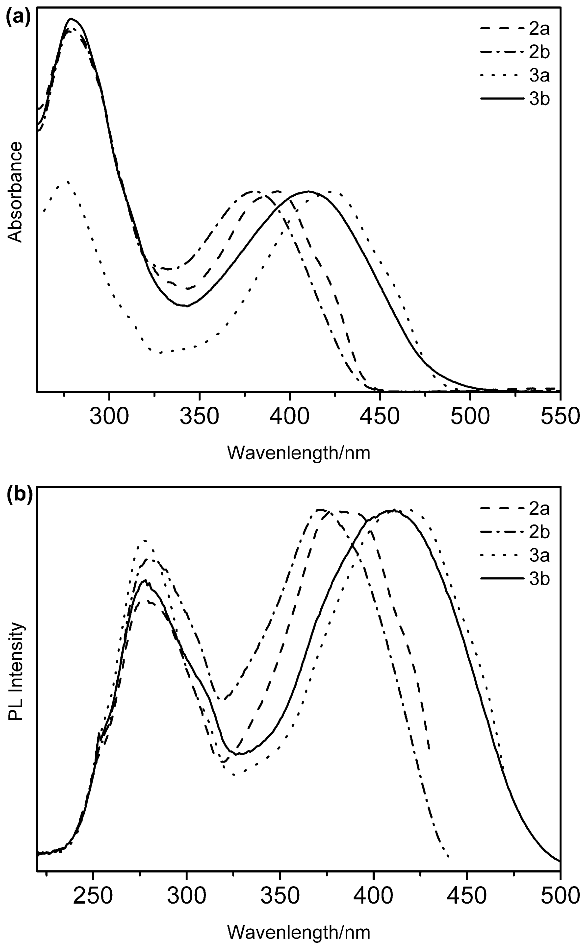


Fig. 1. UV/vis (a) and excitation photoluminescence (b) spectra of prepared bis(terpyridine)s; THF, room temperature.

A comparison of the IR spectra of all α,ω-bis(*terpy*)oligothiophenes with the spectrum of 2,2′;6′,2″-terpyridine shows that the bands of vibrational modes in the *terpy* end-groups unambiguously predominate in the spectra of bis(*terpy*) compounds (see Experimental section). Bands pertaining to vibrations in the oligothiophene chains are mostly reduced to shoulders. Similar features show IR spectra of polythiophene carrying 6-(1-methylimidazolium-3-yl)hexyl side groups,[34] in which bands of imidazolium groups predominate. The much higher transition dipole moments of nitrogen heterocycles compared to that of sulfur heterocycles is the reason for it. Ordinary FT Raman spectra (λ_{ex}=1064 nm) of bis(*terpy*) compounds are not accessible due to high-intensity fluorescence of the samples.

2.2. Spectroscopic and redox characterizations

The absorption UV/vis spectra and the excitation photoluminescence spectra of prepared bis(*terpy*) compounds **2a** to **3b** are compared in Fig. 1 and the absorption spectra obtained from DFT calculations in Fig. 2. Each spectrum exhibits a band at 280 nm due to π–π* and *n*–π* transitions within pyridine and thiophene rings and a strong broad band with weak shoulders and a flat maximum occurring in the region from 370 nm to 425 nm (see Table 1). The latter band shifts to longer wavelengths when going from the dithiophene (compounds **2**) to the terthiophene (compounds **3**) linker. This proves that this band is associated with π–π* (HOMO–LUMO) transitions in the molecule's backbone. DFT calculations have shown that both HOMO and LUMO are of π-nature typical of conjugated systems and

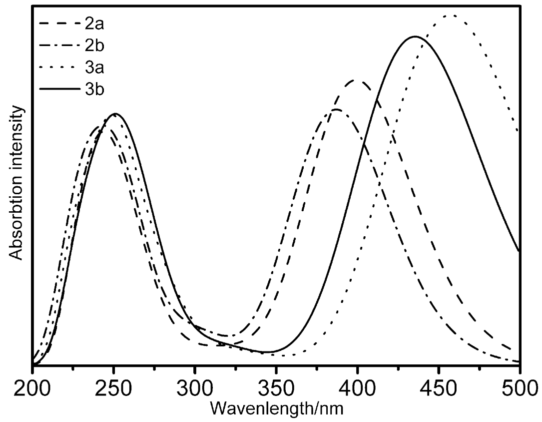


Fig. 2. Absorption spectra obtained using DFT calculation.

Table 1
Spectroscopic and redox data for prepared α,ω-bis(*terpy*) compounds at room temperature

Compound	λ_{abs}[a] [nm]	λ_{ex}[b] [nm]	λ_F[c] [nm]	φ_F[d] [%]	τ_F[e] [ns]	E_{ox}[f] [V]	E_{red}[f] [V]
2a	393	379	441	33	0.57	1.55	−1.57
2b	382	370	445	14	0.77	1.48	−1.65
3a	425	420	481	43	0.53	1.51	−1.57
3b	411	411	507	12	0.54	1.53	−1.66

[a] λ_{abs}, the absorption maximum from the UV/vis spectra in THF solution.
[b] λ_{ex}, the maximum in photoluminescence excitation spectra in THF solution.
[c] λ_F, the photoluminescence emission maximum in THF solution.
[d] φ_F, photoluminescence quantum yield in THF solution relative to quinine sulfate in 0.5 M H_2SO_4. Excitation wavelength was 380 nm for all samples.
[e] τ_F, the lifetime of excited states in THF solution. Excitation wavelength was 370 nm for all samples.
[f] Potentials E_{oxy} and E_{red} determined by cyclic voltammetry of thin film on disc graphite electrode. Potentials referred versus Ag/AgCl reference electrode.

localized mainly over the thiophene central chain and adjacent pyridine rings (see Fig. 3). As for the HOMO, the C=C bonds are π-bonding and have an alternating phase with respect to their adjacent C=C bonds, whereas for the LUMO, the C=C bonds are π-antibonding and the inter-ring C^{β}–$C^{\beta'}$ bonds are bonding. This means that the excited oligomeric chain acquires the quinoid-like electronic configuration.

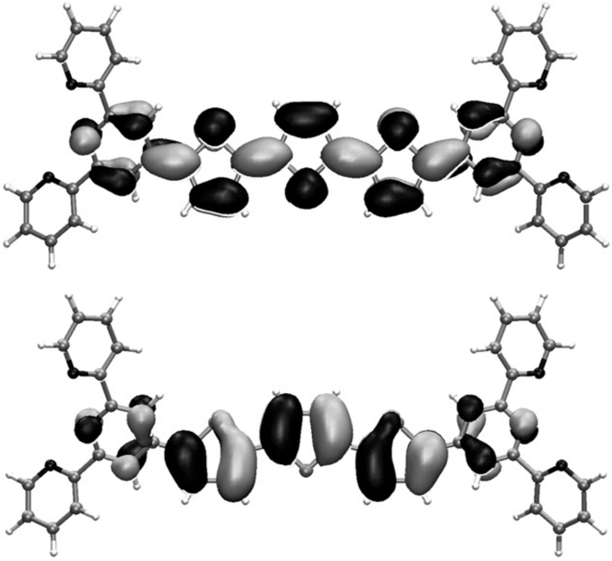


Fig. 3. Electronic density contours for LUMO (up) and HOMO (down) of **3a** obtained using DFT calculations.

The spectra presented in Fig. 1 show that the position of the band of π–π* transitions in the molecule backbone shifts to lower wavelengths when going from compounds **a** (without CH_3 groups on thiophene rings) to compounds **b** (with CH_3 groups on thiophene rings). This proves the decreased extent of delocalization of π-electrons upon substitution of thiophene rings with CH_3 groups, which can be ascribed to increased chain distortion caused by substitution of thiophene rings. The effect of CH_3 substituents is also seen on the shape of the π–π* band. More distinct shoulders and flatter maxima are seen on the bands of **2a** and **3a** (without CH_3) compared to those of **2b** and **3b** (with CH_3). This indicates a higher conformational disorder of oligomeric chains with methyl-substituted rings stemming from the decreased symmetry of the rings, which makes rotation of the rings caused by interactions with solvent molecules faster.

The effect of the linker length on the photoluminescence of α,ω-bis(*terpy*)oligothiophenes is seen visually: dithiophene compounds **2** show blue-light emission while the terthiophene ones (**3**) emit green light. Unlike the absorption spectra, the photoluminescence emission spectra of α,ω-bis(*terpy*)oligothiophenes (Fig. 4) show certain vibrational structure, that is better seen in the spectra of unsubstituted compounds **a** than in those of the substituted ones (**b**). In addition, the photoluminescence emission maxima, λ_F, of samples **b** occur at longer wavelengths than the maxima of corresponding samples **a**. Decreased vibrational structure of and longer wavelength of emission bands of compounds **b** reflects can be explained by faster rotational dynamics of **b**-type molecules. This explanation is supported by the results of measurements of the photoluminescence emission quantum yields, φ_F, which were found to be 33% and 43% for **2a** and **3a** (without CH_3), respectively, and 12–14% for **2b** and **3b** (with CH_3). This drop in φ_F when going from **a** to **b** molecules can be also ascribed to a lowered torsion robustness of the S_1 excited state of type **b** chains (with CH_3 groups), which enhances (facilitates) a non-radiative decay of excited states. The mean lifetimes of excited states found for α,ω-bis(*terpy*) compounds prepared are rather short but comparable (0.53–0.77 ns; Table 1).

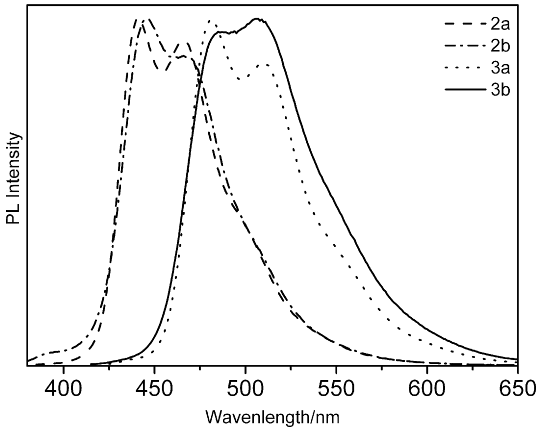


Fig. 4. Emission photoluminescence spectra of prepared α,ω-bis(terpyridine) oligothiophenes.

The cyclic voltammetry spectra of the ligands (Fig. 5) exhibit band-gap energy values from 3.07 to 3.19 eV (Table 1), which relatively is in a good agreement with data obtained from optical measurements.

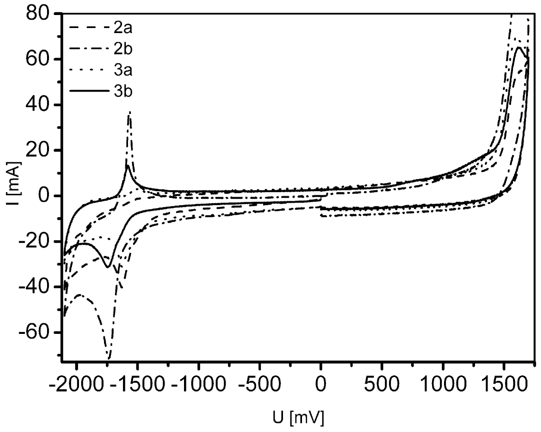


Fig. 5. Cyclic voltammogram of a thin film of prepared bis(terpyridine)s on a 1 mm diameter graphite disc electrode at 50 mV s^{-1} in CH_3CN containing 0.1 M [n-Bu_4N][PF_6] as supporting electrolyte.

3. Experimental section

3.1. Measurements

^{1}H and ^{13}C NMR spectra were measured on a Varian $^{\text{UNITY}}$INOVA 400 or Varian SYSTEM 300 spectrometer in d_8-THF or $CDCl_3$. Chemical shifts δ are reported in parts per million relative to the solvent peak (for ^{1}H 7.25 ppm ($CDCl_3$) or 3.58 ppm (d_8-THF); for ^{13}C 77.0 ppm ($CDCl_3$) or 67.57 ppm (d_8-THF)). Coupling constants, J (in Hz), were obtained by first-order analysis. Infrared spectra were recorded on a Nicolet Magna 760 IR instrument equipped with an Inspector IR module using KBr-diluted samples and diffuse reflectance technique (DRIFT) (128 or more scans at resolution 4 cm^{-1}). UV/vis spectra were measured using a Shimadzu UV-2401PC and solutions of prepared compounds in THF. Photoluminescence spectra were measured on a Fluorolog 4 Jobin Yvon Spex instrument (Jobin Yvon Instruments S. A., Inc., USA) using four-window quartz cuvette (1 cm) and THF solutions of the samples. The photoluminescence emission spectra were recorded using excitation wavelength, λ_{ex} equal to the position of absorption maximum of particular compound. Quantum yields, φ_F, of photoluminescence were determined by means of a comparison of the integrated spectrum of the compound in question with that of quinine sulfate diluted solution in 0.5 M H_2SO_4 used as the standard with $\varphi_F=0.54$; $\lambda_{ex}=380$ nm was used for all measured samples. Time-resolved fluorescence decays were monitored on an Edinburgh Instruments ED 299 T fluorometer equipped with a laser diode with excitation wavelength 370 nm by means of the time-correlated single-photon-counting technique. Cyclic voltammograms (CV) were measured on a potentiostat UMμE Eco-Trend using films of compounds deposited on a carbon disc electrode (diameter 1 mm) by the drop-casting technique $(Bu_4N)(PF_6)$ solution (0.1 M) in acetonitrile as the supporting electrolyte, Ag/AgCl reference electrode and the scanning rate of 380 mV s^{-1}.

3.2. Materials

Thiophene-2-carbaldehyde, 3-methylthiophene-2-carbaldehyde, 2-acetylpyridine, ammonium acetate, *N*-bromosuccinimide (NBS), bis-(pinacolato)-diboran, thiophene-2,5-diboronic acid and PEPPSI-Ipr catalyst (all Aldrich) as well as K_2CO_3 (Lachner) were used as received. 4′-(Thiophen-2-yl)-2,2′;6′,2″-terpyridine was prepared using the two-step synthesis described in literature[32] and then brominated with NBS to obtain 4′-(5-bromothiophen-2-yl)-2,2′;6′,2″-terpyridine **1a**.[33]

3.3. Calculations

Theoretical calculations were done using the density functional theory (DFT), namely the Becke's three parameter functional with the non-local Lee-Yang-Parr correlation functional (B3LYP) with the standard 6-31G(d) basis set as implemented in Ref. 35 After optimization of the geometry and ensuring that the found stationary point is a local minimum we calculated excited states up to corresponding photon wavelength of 250 nm. After convolution with a Gaussian kernel with width of 0.25eV we obtained theoretical electronic spectra of studied molecules.

3.4. Synthesis of monoterpyridine compounds

3.4.1. 4′-[3-Methylthiophen-2-yl]-2,2′;6′,2″-terpyridine. A solution of 3-methyl-2-thiophenecarbaldehyde (5.56 mL; 6.80 g; 60 mmol) in ethanol (1000 mL) was mixed with a solution of NaOH (16.0 g; 400 mmol) in deionized water (100 mL) in a three-neck round-bottomed flask and a solution of 2-acetylpyridine (13.36 mL; 14.44 g; 120 mmol) in ethanol (800 mL) was added dropwise under stirring during 30 min. The resultant reaction mixture was stirred for 20 h at room temperature, then ethanol and was removed on a rotary evaporator and the crude intermediate was extracted into CH_2Cl_2 (1000 mL). The obtained organic phase was successively washed with deionized water (3×800 mL) and brine (100 mL), dried over magnesium sulfate and CH_2Cl_2 was evaporated to obtain oil intermediate to which ethanol (400 mL) and stoichiometric excess of ammonium acetate (120 g;) was added. The resulting mixture was kept under reflux for 18 h, then cooled down to room temperature, ethanol was evaporated, the residue was taken up in toluene (1000 mL) and the organic phase was washed with distilled water (3×400 mL), dried over magnesium sulfate, and concentrated. The obtained crude product was dissolved in aqueous HCl (0.5 M; 300 mL) and washed with CH_2Cl_2 (3×280 mL). Then the aqueous layer was neutralized using aqueous NaOH, which gave a brown oil product that was extracted into CH_2Cl_2 and isolated by evaporating the solvent. Purified using column chromatography (silica gel, 10% methanol/$CHCl_3$). Isolated yield: 1.67 g; 8.5%. R_f (10% methanol/$CHCl_3$) 0.34. δ_H (400 MHz, $CDCl_3$) 8.71 (ddd, $^3J=4.8$ Hz, $^4J=1.6$ Hz, $^5J=0.8$ Hz, 2H, A^6), 8.62–8.66(m, 2H, A^3), 8.58 (s, 2H, B^3), 7.86 (ddd, $^3J\approx7.8$ Hz, $^4J=1.7$ Hz, 2H, A^4), 7.33 (ddd, $^3J=7.5$ and 4.7 Hz, $^4J=1.2$ Hz, 2H, A^5), 7.32 (d, $^3J=5.1$ Hz, 1H, C^5), 6.98 (d, $^3J=5.1$ Hz, 1H, C^4), 2.51 (s, 3H, CH_3). δ_C (100.6 MHz, $CDCl_3$) 156.1 (A^2), 155.8 (B^2), 149.2 (A^6), 144.5 (B^4), 136.8 (A^4), 136.3 (C^3), 135.7 (C^2), 131.6 (C^4), 125.0 (C^5), 123.8 (A^5), 121.3 (A^3), 120.3 (B^3), 15.5 ($-CH_3$). HRMS found m/z: 330.1056 $[M+H]^+$; $C_{20}H_{16}N_3S$ requires: 330.1059. IR (DRIFT), cm^{-1}: 3054 and 3009 (merged ν_{CH} pyridine and thiophene rings); 2949, 2920, and 2866 (ν_{CH} methyl); 1600, 1583, 1568, 1469, 1447, and 1398 (ν_{CC} pyridine rings); 1548 (ν_{CC} thiophene rings, weak); 1266 (s), 1215 (s), 1130 (s), 994 (s), 890 (s), 793 (vs), 743 (s), 660 (s), 621 (s).

*3.4.2. 4′-(5-Bromo-3-methylthiophen-2-yl)-2,2′;6′,2″-terpyridine **1b**.* 4′-(3-Methylthiophen-2-yl)-2,2′;6′,2″-terpyridine (0.835 g; 0.7 mmol), acetic acid (10 mL), NBS (0.146 g; 0.8 mmol), and CH_2Cl_2 (10 mL) were placed into a round-bottomed flask and the resulting mixture was stirred at room temperature overnight. Then the reaction mixture was cautiously neutralized with a saturated solution of $NaHCO_3$, the aqueous phase was extracted with CH_2Cl_2 (3×50 mL) and both organic phases were combined, washed with brine (50 mL), dried over magnesium sulfate and concentrated by evaporating CH_2Cl_2. Isolated yield: 0.53 g; 52%. δ_H (400 MHz, $CDCl_3$) 8.68 (ddd, $^3J=4.8$ Hz, $^4J=1.7$ Hz, $^5J=0.8$ Hz, 2H, A^6), 8.61 (ddd, $^3J=7.9$ Hz, $^4J\approx{}^5J\approx1.0$ Hz, 2H, A^3), 8.50 (s, 2H, B^3), 7.84 (ddd, $^3J=7.7$ Hz, $^4J=1.8$ Hz, 2H, A^4), 7.31 (ddd, $^3J=7.5$, 4.8 Hz, $^4J=1.1$ Hz, 2H, A^5), 6.92 (s, 1H, C^4), 2.42 (s, 3H, CH_3). δ_C (100.6 MHz, $CDCl_3$) 155.8 (A^2+B^2), 149.2 (A^6), 143.3 (B^4), 137.0 (C^2), 136.9 (A^4), 136.3 (C^3), 134.2 (C^4), 123.9 (A^5), 121.3 (A^3), 120.0 (B^3), 112.2 (C^5), 15.4 (-CH_3). HRMS found m/z: 408.0161 $[M+H]^+$; $C_{20}H_{15}N_3BrS$ requires: 408.0165. IR (DRIFT), cm^{-1}: 3053 and 3007 (merged ν_{CH} pyridine and thiophene rings); 2952, 2924 and 2866 (ν_{CH} methyl); 1599, 1584, 1567, 1467, 1450, and 1397 (ν_{CC} pyridine rings); 1553, 1535 (ν_{CC} thiophene rings, weak); 1265 (s), 991 (s), 879 (s), 790 (vs), 746 (s), 734 (s), 675 (s), 660 (s), 622 (s).

3.5. Synthesis of α,ω-bis(*terpy*) compounds

3.5.1. General procedure for the synthesis by Suzuki–Miyaura coupling. Monoterpyridine compound (0.656 mmol), diboronic compound (0.328 mmol); bis-(pinacolato)-diboran (synthesis of type **2** compounds) or 2,5-thiophenediboronic acid (synthesis of type **3** compounds) and K_2CO_3 (120 mg, 0.868 mmol) were dissolved in a degassed toluene/methanol mixture (5 mL, 1:1), argon was bubbled through the solution for 10 min, then PEPPSI-IPr catalyst (6 mg) was added and the reaction mixture kept under stirring for 18 h at 100°C. The mixture was diluted with toluene (20 mL), water was added (20 mL) and the formed two-phase system was filtered.

The obtained greenish or brownish sediment was dissolved in a large amount of hot THF, filtered and solvent was evaporated to obtain the desired product.

3.5.2. 5,5′-Bis(terpy)-2,2′-dithiophene ***2a***. Greenish powder prepared from **1a**; isolated yield: 143 mg; 69%. δ_H (400 MHz, d_8-THF) 8.85 (s, 4H, B^3), 8.74–8.67 (m, 8H, A^6+A^3), 7.94–7.88 (m, 4H, A^4), 7.88 (d, J=3.9, 2H, C^3), 7.53 (d, J=3.9, 2H, C^4), 7.39 (ddd, J=1.2, 4.7, 7.4, 4H, A^5). HRMS found m/z: 629.1568 [M+H]$^+$; $C_{38}H_{25}N_6S_2$ requires: 629.1577. IR (DRIFT), cm^{-1}: 3085 and 3050 (ν_{CH} thiophene rings); 3064 and 3015 (ν_{CH} pyridine rings); 1601, 1584, 1567, 1480, 1467, 1448, and 1398 (ν_{CC} pyridine rings); 1547, 1516 (ν_{CC} thiophene rings, weak); 1268 (s), 1010 (s), 879 (s), 783 (vs), 743 (s), 737 (s), 728 (s), 681 (s), 658 (s), 624 (s).

3.5.3. 5,5′-Bis(terpy)-(4,4′-dimethyl-2,2′-dithiophene) ***2b***. Greenish powder prepared from **1b**; isolated yield: 72 mg; 45%. δ_H (400 MHz, d_8-THF) 8.77 (s, 4H, B^3), 8.75–8.66 (m, 8H, A^6+A^3), 7.95–7.87 (m, 4H, A^4), 7.42–7.36 (m, 4H, A^5), 7.33 (s, 2H, C^3), 2.58 (s, 6H, CH_3). HRMS found m/z: 657.1880 [M+H]$^+$; $C_{40}H_{29}N_6S_2$ requires: 657.1890. IR (DRIFT), cm^{-1}: 3087 and 3049 (ν_{CH} thiophene rings); 3062 and 3012 (ν_{CH} pyridine rings); 2955, 2923, and 2853 (ν_{CH} methyl); 1601, 1585, 1567, 1478, 1467, 1446, and 1397 (ν_{CC} pyridine rings); 1549 (ν_{CC} thiophene rings, weak); 1376 (ν_{CC} methyl-thiophene); 1267 (s), 880 (s), 789 (vs), 731 (s), 686 (s), 666 (s), 658 (s), 643 (s), 623 (s), 493 (s).

3.5.4. 5,5″-Bis(terpy)-2,2′;5′,2″-terthiophene ***3a***. Brown powder prepared from **1a**; isolated yield: 196 mg; 85%. δ_H (400 MHz, d_8-THF) 8.83 (s, 4H, B^3), 8.73–8.69 (m, 8H, A^6+A^3), 7.95–7.88 (m, 4H, A^4), 7.87 (d, J=3.9, 2H, C^3), 7.43 (d, J=3.9, 2H, C^4), 7.41 (s, 2H, D^3), 7.39 (ddd, J=1.0, 4.4, 6.1, 4H, A^5). δ_C (100.6 MHz, d_8-THF) 157.5, 156.9, 152.8, 150.2, 138.3, 137.7, 129.0, 128.1, 126.5, 126.1, 125.0, 121.8, 117.2, 111.8. HRMS found m/z: 711.1451 [M+H]$^+$; $C_{42}H_{27}N_6S_3$ requires: 711.1454. IR (DRIFT), cm^{-1}: 3061 and 3010 (merged ν_{CH} pyridine and thiophene rings); 1600, 1584, 1568, 1467, 1456, and 1400 (ν_{CC} pyridine rings); ν_{CC} of thiophene rings are not resolved; 1267 (w), 1010 (s), 879 (m), 782 (vs), 740 (m), 728 (m), 685 (m), 659 (s), 623 (s).

3.5.5. 5,5″-Bis(terpy)-(4,4″-dimethyl-2,2′;5′,2″-terthiophene) ***3b***. Brown powder prepared from **1b**; isolated yield: 25 mg; 14%. δ_H (400 MHz, d_8-THF) 8.74 (s, 4H, B^3), 8.73–8.68 (m, 8H, A^6+A^3), 7.94–7.87 (m, 4H, A^4), 7.38 (ddd, J=1.4, 5.0, 5.9 4H, A^5), 7.31 (s, 2H), 7.26 (s, 2H), 2.56 (s, 6H, CH_3). δ_C (100.6 MHz, d_8-THF) 157.2, 156.9, 150.3, 144.6, 138.3, 137.7, 137.3, 135.6, 129.7, 126.2, 125.0, 121.8, 120.7, 120.2, 16.2. HRMS found m/z: 739.1755 [M+H]$^+$; $C_{44}H_{31}N_6S_2$ requires: 739.1767. IR (DRIFT), cm^{-1}: 3065 and 3010 (merged ν_{CH} pyridine and thiophene rings); 2955, 2920, and 2853 (ν_{CH} methyl); 1600, 1583, 1568, 1467, 1447, and 1398 (ν_{CC} pyridine rings); ν_{CC} of thiophene rings are not resolved; 1264 (s), 879 (s), 789 (vs), 740 (s), 730 (s), 677 (s), 660 (s), 622 (s).

4. Conclusions

In summary, novel π-conjugated bis-terpyridines with oligothiophene linker were synthesized using a Suzuki-type cross-coupling strategy. The photophysical properties of the obtained compounds are presented. On the basis of our results, we can draw several principal conclusions: (i) the wavelength of the longer-wavelength maximum of the ligand absorption increases with oligothiophene linker prolongation and (ii) decreases with introduction of methyl group onto thiophene ring, (iii) the emission maximum in photoluminescence spectra increases with conjugated chain prolongation. The lifetimes of excited states are relatively short (0.55–0.77 ns) and the photoluminescence emission quantum yields are 33–43% for bis-terpyridines with non-substituted thiophene rings and 12–14% for compounds with methyl-substituted thiophene rings. Thus, these novel compounds are promising candidates for the construction of metallo-supramolecular polymers. Further work concerning the photophysical properties of the polymer material is currently underway in our laboratory.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.11.039.

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